**Characterization of the electronic
properties of LaIrIn_5 :
calculations, transport-, heat capacity-
and de Haas-van Alphen-experiments**

Dissertation
zur Erlangung des Doktorgrades
der Mathematisch-Naturwissenschaftlichen Fakultäten
der Georg-August-Universität zu Göttingen

vorgelegt von
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aus Milano - Italien

Göttingen, 2006

D7

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Tag der mündlichen Prüfung: 12.01.2007

Characterization of the electronic properties of LaIrIn_5 : calculations, transport-, heat capacity- and de Haas-van Alphen-experiments

Eugenio Angelo Forzani

Figure
Fermi sheets from the 131 and 133 bands of the band structure of LaIrIn_5

... the reliable measurement ... required not only careful control of experimental variables ... but also a high degree of control over the physical perfection of crystals.

R. J. HIGGINS and D. H. LOWNDES

Preface

During the experimental work

Research on the electronic properties of diborides and relative intermetallic compounds ¹,

major interest was devoted to the determination and the possible complete characterization of reference systems, which the anomalous properties of relative compounds could be referred to. Inside the class of the **diborides**, the transition metal diboride ZrB_2 was chosen as a convenient model of their normal state properties, which was studied down to 40 mK. The isostructural compound MgB_2 [70] departs from the normal state and is discovered to be superconducting at 39 K. Superconductivity responsible factors are thus established on the basis of ZrB_2 and the results are extensively described by the author in the works [29, 31, 22].

Another class of interesting intermetallic compounds are the **heavy-fermion systems**. They show, besides superconductivity and magnetism, anomalous conduction electron masses [28, 61]. The present work is addressed to one of their sub-classes: the 1 1 5-systems, with heavy rare-earth and/or magnetic elements. These new materials are composed of three different elements in the ratio 1 : 1 : 5. The system LaIrIn_5 is at the top of the rare-earth compounds and constitutes the very convenient reference model for the compounds of its class.

Only the study of the electronic system in an ordered crystal structure was considered. The theoretical and experimental results thus gave the intrinsic properties of this material. Moreover they constitute the reference parameters for the future theoretical and experimental works on related compounds and a closing view to past researches [91, 60, 61]. A full relativistic band structure calculation was performed in collaboration with Dr. Saad Elgazzar and Dr. Ingo Opahle from the theoretical group of the IFW Institute Dresden ². High quality single crystals were prepared in the 1. Institute of Physics, Göttingen. The single crystal characterization was executed in collaboration with Dr. Heidrun Sowa at the Center for Geoscience Göttingen ³. The measurements of electrical transport, heat capacity, de Haas-van Alphen effect and crystal orientation were performed at the 1. Institute of Physics, Göttingen. Among these, the de Haas-van Alphen effect constitutes the most intriguing source of information about the electronic system, which is only observable under extreme conditions of very low temperatures and high magnetic fields of typically 500 mK and 10 T respectively.

This dissertation also describes the development and use of high-sensitive detection techniques for use in the low-temperature environment. The complexity of the effects studied imposes many efforts in data analysis and interpretation. The way of explanation used in this thesis was then conceived to describe the steps of the research, which can be read as the modern methodology for the research on the electronic structure of intermetallic compounds in general.

¹Title of the Project: "Untersuchung der elektronischen Eigenschaften von Diboriden und verwandten intermetallischen Verbindungen", Göttinger Graduate School of Physics.

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Acknowledgements

My thanks to

Prof. Dr. Klaus Winzer

and

Dr. Saad Elgazzar and Dr. Ingo Opahle
Dr. Heidrun Sowa and Dipl. Chem. André Gand

also

Prof. Dr. Gustav Beuermann
Dr. Marianna Biadene
Prof. Dr. Herbert C. Freyhardt
Elmar Gatzemaier
Dipl. Ang. Jacoba Kanne
Dr. Jörg Malindretos
Prof. Dr. Konrad Samwer
Dipl. Phys. Alexander Weismann.

Dedicated to my parents
Livia and Armando Forzani

and with profound gratitude to my girlfriend
Ana Liz Ojeda.

For the financial support I acknowledge the
Georg-Christoph-Lichtenberg-Fellowship of the Land Niedersachsen
and the 1. Institute of Physics Göttingen.

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Conventions

Fundamental constants

e	$1.602\,177 \cdot 10^{-19} \text{ C}$	elementary charge
h	$6.626\,075\,5 \cdot 10^{-34} \text{ J s}$	Planck constant
$\hbar$	$1.054\,572\,66 \cdot 10^{-34} \text{ J s}$	Planck constant ($h/2\pi$)
k_B	$1.380\,658 \cdot 10^{-23} \text{ J K}^{-1}$	Boltzmann constant
R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	gas constant
N_A	$6.022\,14 \cdot 10^{23} \text{ mol}^{-1}$	Avogadro constant
m_e	$9.109\,39 \cdot 10^{-31} \text{ kg}$	mass of electron
ϵ_0	$8.854\,187\,816 \cdot 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$	vacuum permittivity
μ_0	$4\pi \cdot 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$	vacuum permeability
μ_B	$9.274\,015\,4 \cdot 10^{-24} \text{ J T}^{-1}$	Bohr magneton
eV	$1.602\,177 \cdot 10^{-19} \text{ J}$	unit of energy

Definitions

$\mathbf{A}$	vector quantity
$\hat{\mathbf{A}}$	unity vector, direction
A	vector modulus, scalar quantity
$\mathcal{A}$	scalar quantity
$\mathbf{A}$	tensor

Abbreviations

RE	rare-earth element
TM	transition metal element
AREDOS	Angle-Resolved Electron-Diamagnetic-Oscillation Spectrometry
FPLO	Full-Potential Local-Orbital Minimum-Basis Scheme
MEMS	Micro-Electro-Mechanical-System

The International System of Units (SI) is used.

Source code and implementation symbols are written in LaTeX.

Typewriter-style: `usepackage palatino`.

Chapter 1

Introduction

1.1 Heavy-fermion materials

Heavy-fermion intermetallic compounds comprise a unique class of materials that display interesting physical properties because of the screening of the magnetic moment by the conduction electrons, as described in [61]. The magnetic moment typically originates from a Ce or U atom with partially-filled $4f$ - or $5f$ -shells. At room temperature, heavy-fermion materials behave as normal metals where the f -electrons interact weakly with conduction electrons and display local-moment magnetic properties. The conduction electrons progressively screen the magnetic moment as temperature decreases, resulting in effective masses as large as 10^2 times that of a free electron, hence the term, "heavy-fermion". Because of the effective mass enhancing factor is proportional to the electronic specific heat, unusually large values in electronic specific heat can be observed in heavy-fermion compounds, where the parameter γ is typically larger than $400 \text{ mJ mol}^{-1}\text{K}^{-2}$, while in the reference non heavy-fermion compounds only about $5 \text{ mJ mol}^{-1}\text{K}^{-2}$. As a consequence of the screening of magnetic moments, magnetic ordering can also be observed in these materials, although at low temperatures [28]. Heavy-fermion compounds show a variety of behaviours. Most order antiferromagnetically or do not order at all, although a few heavy-fermion compounds even become superconducting. In the U-based heavy-fermion compounds UBe_{13} [72], URu_2Si_2 [73, 62], UPt_3 [99], UNi_2Al_3 [34] and UPd_2Al_3 [35, 36] there are antiferromagnetic transitions followed by superconducting transitions ranging between 0.5 K and 4.6 K. Ce compounds are also superconductors - CeCu_2Si_2 [98] and the more recently discovered, $\text{Ce}_n\text{TMIn}_{3n+2}$ ($\text{TM} = \text{Co, Rh, Ir}$; $n = 1, 2$) [50, 69].

Superconducting heavy-fermion intermetallic compounds typically contain a magnetic moment. Local magnetic moments provide unpaired spins, thus destroying the formation of electron pairs, or Cooper pairs, that are usually responsible for superconductivity [10]. Thus, the fact that some heavy-fermion compounds simultaneously display superconductivity and magnetism is intriguing [61]. In addition, the competition between superconducting

and magnetic states makes heavy-fermion compounds a promising realm of materials in which to find quantum critical points. Quantum criticality refers to a temperature region in a magnetic phase diagram of a material where the system can be tuned chemically or through some external parameters, such as pressure or magnetic field, so that the transition temperature (of say, magnetic ordering) is driven towards absolute zero [86]. The discovery of new heavy-fermion materials, therefore, will provide more opportunities to enhance our understanding of how quantum fluctuations influence resistivity, magnetic susceptibility, and specific heat of materials [18], refer to [61].

1.2 The $RETMIn_5$ systems

The rare-earth and transition-metal $RETMIn_5$ compounds have been subjected to recent interest because of their analogy to $CeTMIn_5$. The Ce-compounds, with $TM = Co, Rh$ and Ir , are heavy-fermion materials. They were found to have various interesting magnetic properties and display heavy-fermion superconductivity. The ground-state properties of the electronic system were only approximately studied in comparison to the non-4*f* reference compound $LaRhIn_5$ [91]. Experimental results are thus summarized from [61].

Of the three $CeTMIn_5$ ($TM = Co, Rh, Ir$) compounds, $CeCoIn_5$ has the highest T_c (2.3 K) [75]. Superconductivity in two dimensions is thought to be common in copper-oxide-based high T_c materials, and the upper critical field of $CeCoIn_5$ below 0.5 K is found to be highly anisotropic. Furthermore, the transition exhibits hysteresis for an external magnetic field directed in the basis plane of the tetragonal structure. The hysteresis disappears at temperatures above 1.4 K, relative to the zero field transition temperature of 2.3 K.

$CeRhIn_5$ is antiferromagnetic at ambient pressure and superconducting at high pressures [42]. It has a 3.8 K Néel temperature at ambient pressure and a 2 K superconducting transition for pressures above 16 kbar. A Fermi surface determination of a continuous series of alloys, $La_{1-x}Ce_xRhIn_5$, showed conclusively that the Ce 4*f*-electrons are localized. The band structure of $CeRhIn_5$ is best represented by the band structure of $LaRhIn_5$, rather than a delocalized 4*f* Ce band structure [7].

$CeIrIn_5$ is an ambient pressure superconductor at 0.4 K [42], and T_c increases with applied pressure reaching a maximum value of 1 K at approximately 15 kbar. Also, there is preliminary de Haas-van Alphen evidence that the Ce 4*f*-electrons in superconducting $CeIrIn_5$ and $CeCoIn_5$ interact more strongly with the conduction electrons, leading to a delocalized 4*f*-electron picture for the band structure in these cases [45, 41].

The role of 4*f*-electrons was recently studied [43] by extending the investigations to the compounds with the next rare-earth element Pr. The only difference between the Ce and Pr atoms being the addition of one 4*f*-electron. The Pr compounds reveal no magnetic ordering and a low specific heat, almost the same as in $LaRhIn_5$. They are not heavy-fermion systems.

Both the Ce- and Pr-series showed anomalies in the experimental Fermi surface. Thus some parts of the electronic band structure could not be detected and the results concerning the electronic correlations in the ground state remained incomplete. In fact the non-4*f* reference $LaRhIn_5$ is anomalous too.

As another non-4*f* compound in the class of the rare-earth $RETMIn_5$ systems, we introduce $LaIrIn_5$. The study of its ground-state electronic structure implied many efforts in theory and experiments in order to furnish a possibly complete reference for the isostructural heavy-fermion compounds and to resolve the question of the anomalies in the Fermi surface.

Chapter 2

Theory

SUMMARY

The analysis of the electron system is based on the concept of the electronic structure in the quantum mechanical formalism presented in Section 2.1. The most striking result is the definition of Fermi surface and its electron properties, which are actually involved in the measurable phenomena. The solution of the electronic structure model of LaIrIn_5 in the RFPLO scheme is illustrated in the last Section 2.2, which constitutes the theoretical reference for the experiments on the electronic system of LaIrIn_5 that follow in the next chapters.

2.1 The electronic structure of single crystals

2.1.1 The band structure

In periodic crystals the atoms are arranged on the points of a lattice, which is defined by three linearly independent axis vectors with

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 , \quad (2.1)$$

where n_1, n_2 and n_3 are integer numbers. The volume of the unit cell is

$$V_c = |\det(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)| = |(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3|. \quad (2.2)$$

Since the lattice points are arranged periodically, the atoms potential, which acts on the electrons at the place $\mathbf{r}$, is also periodic for every $\mathbf{R}_n$

$$V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r}). \quad (2.3)$$

For the determination of a periodic function like (2.3) it is sufficient to state its values in an elemental volume, from which the whole space can be covered by vector translations $\mathbf{r} + \mathbf{R}_n$. A convenient elemental cell, that also reproduces the lattice symmetry, is the Wigner-Seitz cell. It is delimited by symmetry planes between nearest neighbour points to the lattice origin. In this way the space is reduced into a unit cell where all points have a distance from the center, which is smaller than the distance from all other lattice points

$$W.S. = \left\{ \mathbf{r} : (\mathbf{r} \cdot \mathbf{R}_n) \leq \frac{1}{2} |\mathbf{R}_n|^2, \forall \mathbf{R}_n \right\}. \quad (2.4)$$

The volume of *W.S.* is the volume pro lattice point V_c , centered at that point.

For every lattice a reciprocal lattice is defined by basis vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$, which satisfy the relation

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad (2.5)$$

and can be calculated by

$$\mathbf{b}_i = \frac{2\pi}{V_c} (\mathbf{a}_j \times \mathbf{a}_k) \quad (i, j, k = 1, 2, 3 \text{ cyclic}). \quad (2.6)$$

The corresponding reciprocal-lattice vectors are given by

$$\mathbf{K}_h = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3 \quad (2.7)$$

with integer numbers h_1, h_2 and h_3 . The Wigner-Seitz cell of the reciprocal lattice is the Brillouin zone

$$BZ = \left\{ \mathbf{q} : (\mathbf{q} \cdot \mathbf{K}_h) \leq \frac{1}{2} |\mathbf{K}_h|^2, \forall \mathbf{K}_h \right\}. \quad (2.8)$$

The volumes satisfy relation $V_{BZ} \cdot V_c = (2\pi)^3$.

The potential (2.3) with the lattice periodicity can thus be written as a Fourier series of the reciprocal lattice

$$V(\mathbf{r}) = \sum_{\mathbf{K}_h} V_h e^{i\mathbf{K}_h \cdot \mathbf{r}} \quad (2.9)$$

with Fourier coefficients

$$V_h = \frac{1}{V_c} \int_{W.S} d\mathbf{r}' e^{i\mathbf{K}_h \cdot \mathbf{r}'} V(\mathbf{r}'), \quad (2.10)$$

thus the description of a lattice potential reduces to its value inside the unit cell, while the reciprocal lattice reproduces the periodicity.

The general time-independent wave-function of the electron is eigenfunction of the fundamental dynamics equation in the Schrödinger formalism

$$\left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E \Psi(\mathbf{r}) \quad (2.11)$$

and can be chosen such that it satisfies the Bloch theorem

$$\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2.12)$$

with $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n)$ and $\mathbf{k}$ the reciprocal-space wave-vector. Function (2.12) is also eigenfunction of the translation operator of lattice vectors $\mathbf{R}_n$ ¹

$$T(\mathbf{R}_n) = e^{i \mathbf{R}_n \cdot (\frac{\hbar}{i} \nabla)} \quad (2.13)$$

and consequently the Fourier expansion of $\Psi_{\mathbf{k}}(\mathbf{r})$ contains only plane waves, which differ from $\mathbf{k}$ by reciprocal-lattice vectors $\mathbf{K}_h$

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{h}} c_{\mathbf{h}}(\mathbf{k}) e^{i(\mathbf{k} + \mathbf{K}_h) \cdot \mathbf{r}}. \quad (2.14)$$

If this expression is taken as an ansatz for the wave-function $\Psi_{\mathbf{k}}(\mathbf{r})$ and inserted into the Schrödinger equation (2.11), the following homogeneous system of equations for the expansion coefficients $c_{\mathbf{h}}(\mathbf{k})$ is obtained

$$\left[-\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K}_h)^2 - E \right] c_{\mathbf{h}}(\mathbf{k}) + \sum_{\mathbf{h}'} V_{\mathbf{h}-\mathbf{h}'} c_{\mathbf{h}'}(\mathbf{k}) = 0. \quad (2.15)$$

For a given $\mathbf{k}$, solutions of (2.15) only exist for a discrete set of energies $E = E_{\nu}(\mathbf{k})$, $\nu = 1, 2, \dots$, which can be ordered according to their size as $E_1(\mathbf{k}) \leq E_2(\mathbf{k}) \leq \dots E_{\nu}(\mathbf{k})$. They are continuous functions of $\mathbf{k}$ and delimitate the allowed energies in **bands** forming the band structure of the crystal. The band energies are periodic functions of $\mathbf{k}$, where the periodicity

$$E_{\nu}(\mathbf{k}) = E_{\nu}(\mathbf{k} + \mathbf{K}_h) \quad (2.16)$$

is determined by the reciprocal lattice, which means that the problem can be restricted to the wave-vectors $\mathbf{q}$ in the Brillouin zone. In fact, after Eq. (2.16), for every Bloch vector $\mathbf{k}$

$$\forall \mathbf{k}, \exists \mathbf{q} \in BZ \ / \ \mathbf{q} = \mathbf{k} - \mathbf{K}_h \wedge E_{\nu}(\mathbf{q}) = E_{\nu}(\mathbf{k}). \quad (2.17)$$

Band gaps are energy regions, where no eigenvalues $E_{\nu}(\mathbf{k})$ exist, and **band overlap** occurs for regions, where several eigenvalues exist.

Important quantities, which can be derived from the band structure, are the surfaces of constant energy $E = E_{\nu}(\mathbf{q})$ and density of states

$$n(E) = \frac{2}{V_{BZ}} \sum_{\nu} \int_{BZ} \delta(E - E_{\nu}(\mathbf{q})) d\mathbf{q}, \quad (2.18)$$

the factor 2 considers the electron spin degeneracy ($\pm \frac{1}{2}$). The δ function can be interpreted as follows: if the energy is scanned for a particular $\mathbf{q}$ vector in the Brillouin zone, only discrete values of $E - E_{\nu}(\mathbf{q})$ can contribute to the density of states and give unit contribution². The integrated density of states

$$N(E) = \int_0^E n(E') dE' \quad (2.19)$$

counts the number of electronic states below energy E . Charge neutrality determines the Fermi energy E_F through the condition that the charge of the electrons given by $N(E_F) \cdot e$ must be compensated by the positive charge of the atomic nuclei. The resulting Fermi surface in the reciprocal space, defined by $E_F = E_{\nu}(\mathbf{q})$, is determined in general by several bands ν and thus consists of several sheets³. Band overlaps sometimes cause band character mixing on a Fermi sheet, like in ZrB_2 [30].

The problem of band structure calculation becomes the definition of an electronic model. With which an ansatz for the wave-functions $\Psi_{\mathbf{k}}(\mathbf{r})$ and the crystal potential $V(\mathbf{r})$ can be made. Then the calculation reduces into a self-consistent determination of their coefficients.

¹ The wave-function $\Psi_{\mathbf{k}}(\mathbf{r})$ translated to $\mathbf{R}_n$

$$T(\mathbf{R}_n) \Psi_{\mathbf{k}}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{R}_n} \Psi_{\mathbf{k}}(\mathbf{r})$$

is the same and only phase shifted. Phase shift is zero *i.e.* $2\pi(h_1 n_1 + h_2 n_2 + h_3 n_3)$ when $\mathbf{k} = \mathbf{K}_h$.

² Experimentally, due to electron-phonon interactions and finite temperature smearing, the δ -function peaks become broadened peaks.

³ Experimentally, comparable to the factors that broaden the δ -function of Eq. (2.18), finite temperature and dissipative interactions cause a smearing of the occupied states at E_F and consequently of the actual Fermi sheets.→

One-electron-model: nearly-free-electron, LCAO, APW

Each electron is treated as an independent particle moving in a defined potential, and the interactions between conduction electrons are ignored. As first approximation, the electrons can be considered as plane waves

$$\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2.22)$$

satisfying the Bloch theorem, and of energy

$$E(\mathbf{k}) = \frac{\hbar^2}{2m} |\mathbf{k}|^2. \quad (2.23)$$

Electrons in states of wavelength comparable with the lattice spacing undergo strong diffraction effects. In quantum mechanical terms the potential $V(\mathbf{r})$ is treated as an energy perturbation on free-electron states. Thus, considering the behaviour of $E(\mathbf{k})$ along a particular direction in $\mathbf{k}$ -space, it follows a free-electron parabola, with jump discontinuities when it crosses a Brillouin zone boundary. In particular for $\mathbf{k} = \frac{1}{2}\mathbf{K}_h$ and in general when $(\mathbf{k} - \mathbf{K}_h) \cdot \mathbf{K}_h = \frac{1}{2}\mathbf{K}_h$. The magnitude of each discontinuity depends on the strength of the particular Fourier component V_h of the potential $V(\mathbf{r})$.

The nearly-free-electron method considers wave-functions like plane waves in the atomic potential lattice. The consideration that, next to the cores, they look like atomic orbitals, suggests a different scheme for the construction of electron wave-functions. The wave-function becomes a linear combination of atomic orbitals (LCAO) in the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot\mathbf{R}_n} \psi(\mathbf{r} - \mathbf{R}_n), \quad (2.24)$$

where

$$\psi(\mathbf{r} - \mathbf{R}_n) = \sum_j b_j \Psi_j(\mathbf{r} - \mathbf{R}_n), \quad (2.25)$$

is the expansion in a set of localized atomic wave-functions on the atom at $\mathbf{R}_n$. Eq. (2.24) works as a trial wave-function, for an estimate of the energy, to be minimized by suitable choice of the coefficients b_j .

The objection to the LCAO method is the assumption of an abruptly constant potential between the atoms. It rather suggests a muffin-tin potential, spherically symmetrical within some radius R_s about each site and constant in the interstitial regions, so that the spheres do not intersect. Thus the Schrödinger equation can be solved exactly: the wave-functions are spherical harmonics within each sphere and plane waves in the volume between the spheres. The solution in the spherical potential is of the form

$$\psi(\mathbf{r}) = \sum_{lm} C_{lm} R_l(r, E) Y_{lm}(\theta, \phi), \quad (2.26)$$

where $Y_{lm}(\theta, \phi)$ is a spherical harmonic for the direction (θ, ϕ) of the vector $\mathbf{r}$ and $R_l(r, E)$ is the solution of the radial atomic Schrödinger equation of energy E . The coefficients C_{lm} are chosen

← Moreover, a probability function $0 \leq f(E) \leq 1$ describes the occupancy of states with energy E for vanishing temperature T

$$f(E, T) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad (\text{Fermi-Dirac statistics}), \quad (2.20)$$

being a step function, which switches from value 1 (occupied state energy) to 0 (non occupied) at the Fermi energy E_F . At finite temperatures, electrons below E_F can be excited to empty states above E_F . Therefore $f(E)$ exhibits a smeared step near E_F . In general, the integrated density of occupied states becomes

$$N(E, T) = \int_0^E f(E', T) n(E') dE'. \quad (2.21)$$

so that $\psi(\mathbf{r})$ exactly matches at the surface $r = R_s$ to a single plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. Eq. (2.26) becomes an augmented plane wave (APW) $\psi_{\mathbf{k}}(\mathbf{r})$ which satisfies

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}_n} \psi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_n), \quad (2.27)$$

inside the sphere centered on $\mathbf{R}_n$. This is the first attempt to construct a solution for the Schrödinger equation throughout the crystal. Indeed, no result for a relationship between the energy of the state E and the wave-vector $\mathbf{k}$ exists. But the final wave-function is easily constructed out of APW's by the Bloch formulation

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}_h} a_{\mathbf{k}-\mathbf{K}_h} \psi_{\mathbf{k}-\mathbf{K}_h}(\mathbf{r}), \quad (2.28)$$

where the coefficients $a_{\mathbf{k}-\mathbf{K}_h}$ have to be determined in a variational estimate of the energy.

Hartree and Hartree-Fock methods

The interactions between conduction electrons are here considered, being the *Coulomb force* between the charges and the so-called *exchange force* associated with the antisymmetry of the wave-functions. These interactions can be taken care of by a Hartree or Hartree-Fock self-consistent calculation that adjusts the atomic potentials for the charge distribution of the valence electrons, as well as the electrons in the closed shells of the ion cores. A many-electron wave-function can be written as a product of one-electron functions $\Psi(\mathbf{r}_i)$

$$\Psi(\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_N) = \prod_i \Psi(\mathbf{r}_i) \quad (2.29)$$

for which the Schrödinger equation (2.11) becomes

$$\sum_i \left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}_i) + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \prod_i \Psi(\mathbf{r}_i) = E \prod_i \Psi(\mathbf{r}_i). \quad (2.30)$$

The ground-state of the system is the eigenstate at which the minimum of E is obtained, where the single-particle wave-functions are the variational parameters to be chosen. This is satisfied and the product solution is minimum in energy by solving the single-particle **Hartree equations**

$$\left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) + V_H(\mathbf{r}) \right] \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}), \quad \forall i \quad (2.31)$$

with the Hartree potential of the direct interaction

$$V_H(\mathbf{r}_i) = \sum_{j \neq i} \int \Psi_j^*(\mathbf{r}_j) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi_j(\mathbf{r}_j) d\mathbf{r}_j. \quad (2.32)$$

Adding the requirement that the total wave-function be antisymmetric, with respect to interchange of any two electrons, so that $\Psi(\dots \mathbf{r}_i \mathbf{r}_j \dots) = -\Psi(\dots \mathbf{r}_j \mathbf{r}_i \dots)$, it gives an additional term in the energy

$$E_{XC} = \frac{1}{2} \sum_{j \neq i} \int \Psi_i^*(\mathbf{r}_i) \Psi_j^*(\mathbf{r}_j) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi_i(\mathbf{r}_j) \Psi_j(\mathbf{r}_i) d\mathbf{r}_i d\mathbf{r}_j. \quad (2.33)$$

This is the exchange energy and its addition in Eq. (2.31) leads to the **Hartree-Fock equation**.

Density functional method

Contrary to the Hartree and Hartree-Fock methods, which approximate the ground-state energy of the many-electron system by a functional of single-electron wave-functions, density-functional theory describes the ground-state energy by a functional of the electron density. Its fundamental justification is found in the Hohenberg-Kohn theorems. Hohenberg and Kohn [44, 56] could show that the ground-state energy E_0 is given by a unique functional $E[\rho_0(\mathbf{r})]$ of the ground state of the electron density $\rho_0(\mathbf{r})$ and that in analogy to Rayleigh-Ritz method a variational principle exists with the property

$$E[\rho(\mathbf{r})] \geq E_0 = E[\rho_0(\mathbf{r})] . \quad (2.34)$$

This means that the ground-state energy E_0 is determined by inserting the ground-state density $\rho_0(\mathbf{r})$ into the functional $E[\rho(\mathbf{r})]$ and that any other density leads to a larger value for $E[\rho(\mathbf{r})]$. This variational principle can be used to determine $\rho_0(\mathbf{r})$ provided that the functional $E[\rho(\mathbf{r})]$ can be defined explicitly in the form

$$\sum_i \int \Psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 \right) \Psi_i(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_{XC}[\rho(\mathbf{r})] \quad (2.35)$$

with

$$\rho(\mathbf{r}) = \sum_i \rho_i |\Psi_i(\mathbf{r})|^2 , \quad (2.36)$$

where the sum is over all occupied states. The variation of $E[\rho(\mathbf{r})]$ with respect to the single-particle wave-functions leads to the Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC} \right] \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}) , \quad \forall i \quad (2.37)$$

for N -interacting electrons, with the Hartree and exchange-correlation terms

$$V_H(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad V_{XC} = \frac{\partial E_{XC}}{\partial \rho(\mathbf{r})} . \quad (2.38)$$

The Kohn-Sham equations have the structure of single-particle equations and are exact, if the exchange-correlation potential as well as the exchange-correlation energy are known. Thus all complications of many-particle problems are hidden in V_{XC} and E_{XC} . In the Local (Spin-) Density Approximation (LSDA) the exchange-correlation potential is approximated by the homogeneous electron gas model with constant density and magnetization. The LDA has proved to be very efficient for the extended systems, such as large molecules and solids [49], but problematic for strongly correlated materials, like the heavy-fermion systems. Such systems usually contain transition-metal or rare-earth metal ions with partially filled d - (or f -) shells. The most successful approximation is the LDA+U, that considers a statically screened Coulomb interaction.

Relativistic density functional method

The influence of relativistic effects refers to the quality of valence electrons from s - and p -orbitals which possess next to the cores a finite probability density and a higher velocity, thus being energetically stabilized and strongly localized. It follows that the d - and f -electrons are disturbed from the core potential and so energetically destabilized [19]. Another effect, the spin-orbit interaction, which for the $4f$ -states causes an energy splitting of about 1 eV, causes the coupling of spin and spatial degrees of freedom responsible for magnetic anisotropy.

In the relativistic formulation, relativistic quantities of Eq.(2.37) are substituted using their four-current analogon [27]. The current density functional theory [26] leads to the Kohn-Sham-Dirac equation

$$\left[-i c \boldsymbol{\alpha} \cdot \nabla_{\mathbf{r}} + \beta m c^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC} + \frac{e \mu_0}{2 m} \beta \boldsymbol{\Sigma} \cdot \mathbf{B}_{XC} \right] \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}), \quad \forall i, \quad (2.39)$$

where, additionally to the traditional quantities of Eq.(2.37), the spin density $\boldsymbol{\Sigma}$, the exchange-correlation field $\mathbf{B}_{XC}$, and c the velocity of light appear. α and Σ , built from the Pauli matrices, and β are all 4×4 matrices.

2.1.2 The Fermi surface

Electronic states below the Fermi energy are occupied for $T \approx 0$ K and constitute in the $\mathbf{k}$ -space the Fermi body. But the states at the Fermi energy level are actually involved in all electronic equilibrium thermodynamic and transport properties of the material, as only the electrons closed to the Fermi level can be excited by small amounts of energy. It follows that a direct determination of both dimension and topology of the Fermi surface is very important. Locally, complex Fermi surfaces can be reduced to highly anisotropic nearly-free-electron Fermi surface sheets [83], thus a general description of Fermi surface by this model is here made. From the nearly-free-electron approximation the constant energy surfaces are described as Eq. (2.23), with a constant, isotropic mass. Three unit vectors $\hat{\mathbf{k}}_1$, $\hat{\mathbf{k}}_2$ and $\hat{\mathbf{k}}_3$ span the general orthogonal coordinate system for the arbitrary wave-vector $\mathbf{k}$. Considering the existence of anisotropies due to interactions with the crystal lattice or dissipative effects, it is convenient and straightforward to replace the mass by a tensor, thus

$$E(\mathbf{k}) = \frac{\hbar^2}{2 m_e} \mathbf{k}^T \mathbf{M}^{-1} \mathbf{k} \quad (2.40)$$

with $\mathbf{k}^T = [k_1 \ k_2 \ k_3]$, while $\mathbf{M}^{-1}$ is a full 3×3 symmetric matrix with elements $\frac{1}{m_{ij}}$ defined

$$\frac{1}{m_{ij}} = \frac{m_e}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}. \quad (2.41)$$

The effective masses m_{ij} are thus written as enhancing factors of the free electron mass m_e , describing the effects of interactions on the electrons at $\mathbf{k}$.

Eq. (2.40) can be written in compact form as

$$E(k_1 \ k_2 \ k_3) = \frac{\hbar^2}{2 m_e} \sum_{i,j=1}^3 \frac{k_i k_j}{m_{ij}}. \quad (2.42)$$

In the case $E(\mathbf{k})$ is at a conduction band minimum $\mathbf{k}_0$, thus the wave-vectors $\mathbf{k}$ can be referred to the center of the minimum by

$$\mathbf{k} = \mathbf{k}_0 + \Delta \mathbf{k}, \quad (2.43)$$

with in general $\mathbf{k}_0 \neq \mathbf{0}$. When $\mathbf{k}_0 = \mathbf{0}$, then the wave-vectors $\mathbf{k} = \Delta \mathbf{k}$ refer to the center of the $\mathbf{k}$ -space. The energy function reduces to an expression

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2}{2 m_e} \Delta \mathbf{k}^T \mathbf{M}^{-1} \Delta \mathbf{k}. \quad (2.44)$$

For a Fermi energy next to the band minimum, constant energy surfaces can be described by local simple ellipsoidal surfaces. The basis for the ellipsoid coordinate system consists of the unit vectors $\hat{\Delta \mathbf{k}}_a$, $\hat{\Delta \mathbf{k}}_b$ and $\hat{\Delta \mathbf{k}}_c$, chosen along the principal axes a , b and c of each ellipsoid of energy E . An arbitrary vector of the ellipsoid being $\Delta \mathbf{k}_{abc} = [k_a \ k_b \ k_c]^T$. In general the ellipsoid

Figure 2.1: Fermi surface of the anisotropic nearly-free-electron system.

principle axes are not alligned with the general coordinate system $\hat{\mathbf{k}}_1$, $\hat{\mathbf{k}}_2$ and $\hat{\mathbf{k}}_3$ or the crystal reciprocal lattice $\hat{\mathbf{b}}_1$, $\hat{\mathbf{b}}_2$ and $\hat{\mathbf{b}}_3$. This allows the introduction of 3×3 projection matrices $\mathbf{P}_{\mathbf{k} \leftarrow \mathbf{b}}$ and $\mathbf{P}_{\mathbf{b} \leftarrow abc}$, which transform an arbitrary vector $\Delta \mathbf{k}$ to its vector in the ellipsoid coordinate system

$$\Delta \mathbf{k} = \mathbf{P}_{\mathbf{k} \leftarrow \mathbf{b}} \mathbf{P}_{\mathbf{b} \leftarrow abc} \Delta \mathbf{k}_{abc} . \quad (2.45)$$

Inserting (2.45) into (2.44)

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2}{2 m_e} \Delta \mathbf{k}_{abc}^T \mathbf{M}_{abc}^{-1} \Delta \mathbf{k}_{abc} , \quad (2.46)$$

the inverse effective mass tensor in the ellipsoid coordinate system becomes

$$\mathbf{M}_{abc}^{-1} = \mathbf{P}_{\mathbf{k} \leftarrow \mathbf{b}}^T \mathbf{P}_{\mathbf{b} \leftarrow abc}^T \mathbf{M}^{-1} \mathbf{P}_{\mathbf{k} \leftarrow \mathbf{b}} \mathbf{P}_{\mathbf{b} \leftarrow abc} , \quad (2.47)$$

a 3×3 diagonal matrix of elements m_a , m_b and m_c along the diagonal. This is actually the intrinsic result of the projection referred to the ellipsoid principle axes a , b and c , which reduces expression (2.42) into an expansion of the energy about its minimum, for which the mixed terms disappear. Equation (2.44) can be rewritten as

$$E(\mathbf{k}) = E(k_a k_b k_c) = E_0 + \frac{\hbar^2}{2 m_e} \left[\frac{k_a^2}{m_a} + \frac{k_b^2}{m_b} + \frac{k_c^2}{m_c} \right] \quad (2.48)$$

referred to the band minimum.

An analogous form is used to describe constant energy surfaces where $E(\mathbf{k})$ has a maximum for $\mathbf{k}_0$ at the origin $\mathbf{0}$ or on a boundary of the Brillouin zone. Equation (2.48) applies from the top of the band, which is to be thought of as containing holes, since the effective masses of the expansion from the maximum are negative. The solution of Eq. (2.48) for an anisotropical electronic system of masses $m_a = 1$, $m_b = 2$ and $m_c = 3$ (in units of the free electron mass m_e) for the constant energy $E(\mathbf{k}) = 1$ eV, say the Fermi energy, is represented in Fig. 2.1.

In this description the electrons are no longer simple plane waves, even in the free-particle model. It is more appropriate to speak about wave packets whose motion then corresponds to particle motion. Thus, in a dispersive medium, the velocity is the group velocity of the wave packet with energy $E(\mathbf{k})$, the vector

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}) \quad (2.49)$$

Figure 2.2: Fermi surface and Fermi velocity. Detail of the Fermi velocity vectors at the Fermi surface.

centered at the wave-vector $\mathbf{k}$. The velocity of one electron is just the gradient of $E(\mathbf{k})$ in $\mathbf{k}$ -space. In general the velocity vector is not parallel to the wave-vector but locally perpendicular to the surface of constant energy, as it is to see in figure 2.2 for the ellipsoidal Fermi surface of Fig. 2.1.

Experimentally, in order to reduce equation (2.40) into (2.48), one chooses the general coordinate system $\hat{\mathbf{k}}_1 \hat{\mathbf{k}}_2 \hat{\mathbf{k}}_3$ to be equivalent to the reciprocal lattice $\hat{\mathbf{b}}_1 \hat{\mathbf{b}}_2 \hat{\mathbf{b}}_3$, for which

$$\mathbf{P}_{\mathbf{k} \leftarrow \mathbf{b}} = \mathbf{I}, \quad (2.50)$$

by cutting the crystal along the required directions for transport measurements. The coordinate system $\hat{\mathbf{k}}_1 \hat{\mathbf{k}}_2 \hat{\mathbf{k}}_3$ becomes directly equivalent to the coordinate system $\hat{\Delta}\mathbf{k}_a \hat{\Delta}\mathbf{k}_b \hat{\Delta}\mathbf{k}_c$ of a local Fermi surface sheet, for which

$$\mathbf{P}_{\mathbf{k} \leftarrow \mathbf{b}} \mathbf{P}_{\mathbf{b} \leftarrow abc} = \mathbf{I}, \quad (2.51)$$

by orienting the crystal in angular dependent de Haas-van Alphen measurements.

Electronic properties at the Fermi surface

Electrons properties at the Fermi surface are band structure quantities calculated at the wave-vectors $\mathbf{k}_F$ of the Fermi surface. Due to the usual presence of different bands ν passing the Fermi level, the Fermi surface is composed of different sheets. This implies that in a single wave-vector direction $[h_1 h_2 h_3]$, electrons with different point properties can coexist.

The electron mass

$$\frac{1}{m_\nu(\mathbf{k}_F)} = \frac{m_e}{\hbar^2} \frac{\partial^2 E_\nu(\mathbf{k})}{\partial \mathbf{k}^2} \Big|_{\mathbf{k}_F} \quad (2.52)$$

is a point property describing the inertia in the direction of $\mathbf{k}_F$. The Fermi velocity

$$v_\nu(\mathbf{k}_F) = \frac{1}{\hbar} \frac{\partial E_\nu(\mathbf{k})}{\partial \mathbf{k}} \Big|_{\mathbf{k}_F} \quad (2.53)$$

is strictly a point property, which value in the direction of $\mathbf{k}_F$ becoming the projection

$$\mathbf{v}_\nu(\mathbf{k}_F) \cdot \frac{\mathbf{k}_F}{k_F}. \quad (2.54)$$

Thus the total Fermi velocity is more properly the average of band velocities projected on the direction $[h_1 \ h_2 \ h_3]$

$$\mathbf{v}_{[h_1 \ h_2 \ h_3]} = \left\langle \mathbf{v}_v(\mathbf{k}_F) \cdot \frac{\mathbf{k}_F}{k_F} \right\rangle_{[h_1 \ h_2 \ h_3]} . \quad (2.55)$$

Perpendicular to a direction $[h_1 \ h_2 \ h_3]$ arbitrary planes $k(h_1 \ h_2 \ h_3)$ of the $\mathbf{k}$ -space for $k \in \mathbb{R}$ exist. Orbits of different bands v are the result of the intersection of the Fermi surface and one plane. Fig. 2.3 shows an orbit of the ellipsoidal Fermi surface for an arbitrary direction. The area enclosed by an orbit Ω (cut-section)

$$\mathcal{A} = \oint_{\Omega} \mathbf{k}_{\perp} \cdot d\mathbf{k} \quad (2.56)$$

considers the Fermi vector projection on the plane and gives the size of the Fermi body in the chosen plane, as represented in Fig. 2.3.

From the relation between velocity and wave-vector $m(\mathbf{k}) \mathbf{v}_{\mathbf{k}} = \hbar \mathbf{k}$, known from quantum mechanics one can introduce an average orbit mass

$$\langle m \rangle_{\Omega} = \frac{\hbar}{m_e} \cdot \left\langle \frac{\mathbf{k}}{v(\mathbf{k})} \right\rangle_{\Omega} = \frac{\hbar}{2 \pi m_o} \oint_{\Omega} \frac{d\mathbf{k}}{v_{\perp}(\mathbf{k})} = m_{\Omega} . \quad (2.57)$$

$v_{\perp}(\mathbf{k})$ denotes the projection of the Fermi velocity in the plane of the orbit, which is always locally perpendicular to the Fermi surface. Introducing relations (2.53) and (2.56), equation (2.57) becomes dependent from the Fermi surface topology

$$\langle m \rangle_{\Omega} = \frac{\hbar^2}{2 \pi m_e} \frac{\partial \mathcal{A}}{\partial E} . \quad (2.58)$$

Consistently with the orbit formula (2.57) for the mass m_{Ω} , the orbit velocity

$$\langle v \rangle_{\Omega} = \frac{\hbar}{m_o} \cdot \left\langle \frac{k}{m(\mathbf{k})} \right\rangle_{\Omega} = \frac{\hbar}{\langle m \rangle_{\Omega} \cdot m_o} \sqrt{\frac{\mathcal{A}}{\pi}} = v_{\Omega} \quad (2.59)$$

expresses the average of the point properties of the Fermi surface on the orbit Ω in terms of the Fermi surface size. v_{Ω} corresponds to the point Fermi velocity only for a circular orbit with constant point velocity $v_{\mathbf{k}}$ and with orbit-averaged wave-vector equal to the circumference radius $\mathbf{k}_{\Omega}$.

Figure 2.3: Orbit and area of a cut-section for the ellipsoidal Fermi surface.

2.2 Calculated electronic structure of LaIrIn₅

The calculation of the electronic structure in solids using density functional theory within the framework of the Kohn-Sham theory as illustrated in Section 2.1.1 was enabled by development of a number of self-consistent band-structure schemes. They differ essentially in their representation of basis functions, such as with LCAO, (L)APW (their basical formulation was introduced in Section 2.1.1 for the tight-binding models) or liner muffin-tin orbitals (LMTO) and many others [54]. A common feature of all these approaches is an approximate representation of the crystal potential with basically the muffin-tin construction. Additionally, there exist LDA implementations for the exchange-correlation potential. Further improvements take into account the real potential shape within the hole crystal, leading to the full potential (FP) versions of most band structure methods, thus giving FPLAPW and FPLMTO, for example. A recently developed full-potential band structure scheme is called FPLO® [54, 32].

2.2.1 Methods of calculation

FPLO (Full Potential Local Orbital method) is based on the construction of the extended crystal wave-functions via a linear combination of overlapping non-orthogonal minimum basis orbitals, similar to the LCAO method (Section 2.1.1) [55]. The representation of the electronic density and the crystal potential is again a lattice sum of local overlapping contributions. But these contributions now exhibit non-sphericity via an angular momentum expansion. Thus the total lattice sum of these local functions converges in a controlled manner to the real crystal density and potential with increasing momentum cut-off. The core electrons are treated in the same manner as the valence electrons, which results in an all-electron band-structure scheme. Nevertheless, an algebraic transformation based on the fact that core orbitals from different sites do not overlap reduces the calculational effort considerably. The LSDA+U approximation (Section 2.1.1) was also implemented for computing the electronic structure of compounds with strong correlations. In order to consider relativistic effects, the FPLO scheme was also extended into a full relativistic version.

Full-Potential Local-Orbital Minimum-Basis Scheme (FPLO)

Starting point for the solution of the Kohn-Sham equation (2.37)

$$\hat{H} \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}) \quad (2.60)$$

is a trial density of states

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}_n \mathbf{s} l m} \rho_{s l m}(|\mathbf{r} - \mathbf{s} - \mathbf{R}_n|) Y_{l m}(\mathbf{r} - \mathbf{s} - \mathbf{R}_n), \quad (2.61)$$

obtained as a lattice sum of site densities in spherical harmonic representation. This is the result of a site-centering decomposing procedure of contributions from basis functions from the same site and overlap contributions from different sites. The maximum l -numbers used are 6 for the net contributions and 12 for the overlap contributions. Using the density in this form, the total potential with the atoms, Hartree and exchange terms of Eq. (2.37) is also expanded into spherical harmonics

$$V^{tot}(\mathbf{r}) = \sum_{\mathbf{R}_n \mathbf{s} l m} v_{s l m}(|\mathbf{r} - \mathbf{s} - \mathbf{R}_n|) Y_{l m}(\mathbf{r} - \mathbf{s} - \mathbf{R}_n). \quad (2.62)$$

The single-electron wave-function of a N -electrons crystal system is the Bloch state

$$\Psi_{\mathbf{k}\nu}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_n} \sum_{\mathbf{s}L} \psi_{\mathbf{s}L}(\mathbf{r} - \mathbf{s} - \mathbf{R}_n) C_{L\mathbf{s},\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{s})} \quad (2.63)$$

of wave-vector $\mathbf{k}$ and band index ν . The basis states $\psi_{\mathbf{s}L}$ are local orbitals centered at sites $\mathbf{s}$ in the elementary cell at the lattice vector $\mathbf{R}_n$. They are solutions of an atom-like Schrödinger equation and are denoted by a complete set of atomic quantum numbers $L = \{\rho, l, m\}$.

Introducing the ansatz (2.63) into the Kohn-Sham equation (2.37), the secular equation to be solved becomes

$$H C = E S C, \quad (2.64)$$

with H the Hamiltonian matrix from the left side of Eq. (2.37) and S the overlap matrix, since the basis is non-orthogonal. Considering that the overlapping between different core states usually disappears, the local basis states are divided into two classes, the valence states $\psi_{\mathbf{s}L_v}$ and the core states $\psi_{\mathbf{s}L_c}$. The core states are chosen among those which satisfy the condition

$$\int \psi_{\mathbf{s}'L_c'}^*(\mathbf{r} - \mathbf{s}' - \mathbf{R}_{n'}) \psi_{\mathbf{s}L_c}(\mathbf{r} - \mathbf{s} - \mathbf{R}_n) d\mathbf{r} = \delta_{cc'} \delta_{nn'} \delta_{ss'} \quad (2.65)$$

and can be then removed from the basis. The problem can be conveniently divided into one for core states and one for valence states. A crucial feature of the method is that the basis is readjusted at every iteration cycle and is optimized in the course of the iteration. The core states obey the equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\mathbf{s}}^{\text{tot}} \right] \psi_{\mathbf{s}L_c} = \psi_{\mathbf{s}L_c} E_{\mathbf{s}L_c} \quad (2.66)$$

with $V_{\mathbf{s}}^{\text{tot}}$ being the total crystal potential spherically averaged around the site centre $\mathbf{s}$

$$V_{\mathbf{s}}^{\text{tot}}(|\mathbf{r} - \mathbf{s}|) = \frac{1}{4\pi} \int d\Omega V^{\text{tot}}(\mathbf{r} - \mathbf{s}). \quad (2.67)$$

This definition assures that a Bloch sum of the core orbitals and the related core eigenvalues $E_{\mathbf{s}L_c}$ are very good approximations to the solution of the true crystal Hamiltonian.

On the contrary, the valence orbitals are defined in the following way

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\mathbf{s}}^{\text{tot}} + \left(\frac{r}{r_{\mathbf{s}L_v}} \right)^4 \right] \psi_{\mathbf{s}L_v} = \psi_{\mathbf{s}L_v} E_{\mathbf{s}L_v} \quad (2.68)$$

with $r_{\mathbf{s}L_v} = (r_{\text{NN}}(\mathbf{s}) x_0 / 2)^{\frac{3}{2}}$, where r_{NN} is the nearest neighbour distance and x_0 are dimensionless compression parameters. The scaling of the $r_{\mathbf{s}L_v}$ is the correct one for an empty lattice. The effect of the additional confining potential is to compress the long-ranging orbital tails of the valence orbitals⁴. A second effect is that the orbital resonance energies are pushed up to come close to the band centers, providing the optimum curvature of the orbitals.

The parameters x_0 enter the total energy via the basis expansion of the valence eigenstates. Therefore, the total energy depends on x_0 as long as the basis set is incomplete. The most important feature of the FPLO basis treatment is that the total energy is minimized with respect to the set $\mathbf{x}_0$ of compression parameters x_0 . In consequence FPLO is not a fixed basis scheme. In the self-consistent calculation, the basis is adapted to the best $\mathbf{x}_0$ set by a variational method

$$\frac{\partial E^{\text{tot}}}{\partial \mathbf{x}_0} = \sum_{\mathbf{k}\nu}^{E_F} \frac{\partial E_{\mathbf{k},\nu}}{\partial \mathbf{x}_0} - \int \rho(\mathbf{r}) \frac{\partial V^{\text{tot}}(\mathbf{r})}{\partial \mathbf{x}_0} d\mathbf{r} \quad (2.69)$$

using $\frac{\partial N}{\partial \mathbf{x}_0} = \int \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{x}_0} d\mathbf{r} \equiv 0$. The right-hand side of Eq. (2.69) turns out to be exactly zero for all x_0 if the basis orbitals form a complete set. Since the latter is obviously not the case, we require

⁴The power law potential has minor influence on the orbital in the core region, while in the region far from the nucleus the orbitals undergo a drastic change, compared to solutions without the confining potential. Actually, the valence orbitals are usually unbound states in the potential V_s alone.

$\frac{\partial E^{tot}}{\partial x_0}$ to vanish and obtain matrix equations for the calculations of the compression parameters, which then are solved simultaneously with the Kohn-Sham equations in every iteration steps. This method is very efficient in the basis optimization.

Solving Eq. (2.64) for each $\mathbf{k}$ -point of the irreducible part of the Brillouin zone produces the coefficients matrix C and the eigenvalues matrix E . These values are used to determine the Fermi energy, provided the condition $N = N(E_F)$ after equation (2.19) is fulfilled. The coefficients are then used to calculate the density of states. The integration over the reciprocal space of equation (2.18) for the density of states is implemented with the conventional tetraeder method. With the partitioning technique it will be decomposed into overlapping not-spherical site-centred contributions and inserted in the new iteration in form of the sum (2.62). The solution is self-consistent when the new density of state is equivalent to the previously calculated one.

Relativistic FPLO

The relativistic FPLO (RFPLO) solves the Kohn-Sham-Dirac equation (2.39) for the crystal

$$\hat{H}\Psi_i(\mathbf{r}) = \left[-i c \boldsymbol{\alpha} \cdot \nabla_{\mathbf{r}} + \beta m c^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC} + \frac{e \mu_0}{2 m} \beta \Sigma_z B^{tot} \right] \Psi_i(\mathbf{r}) = E_i \Psi_i(\mathbf{r}), \quad (2.70)$$

in a collinear approximation with the exchange field $\mathbf{B}_{XC} \equiv B^{tot} \hat{z}$ aligned along a fixed axis $\hat{z}$. The density $\rho(\mathbf{r})$, the magnetization density $\boldsymbol{\mu}(\mathbf{r})$, V^{tot} and B^{tot} are represented again as a lattice sum of overlapping, non-spherical localized site-centered functions like in (2.62), considering that

$$V_{XC} = \frac{1}{2} (V_{XC}^+[\rho, \mu] + V_{XC}^-[\rho, \mu]) \quad B^{tot} = \frac{1}{2} (V_{XC}^+[\rho, \mu] - V_{XC}^-[\rho, \mu]). \quad (2.71)$$

The same kind of ansatz for the wave-function $\Psi_{\mathbf{k}\nu}(\mathbf{r})$ as in the non-relativistic version (2.63) is used, but now in terms of atom-like four-spinor orbitals $\phi_{\mathbf{s}\Lambda}(\mathbf{r} - \mathbf{s} - \mathbf{R}_n)$ centered at the atomic positions $\mathbf{R}_n + \mathbf{s}$. The label $\Lambda = (\rho, \kappa, \mu)$ denotes a complete set of atomic quantum numbers in relativistic notation. In the relativistic method the minimum basis scheme is applied as well. In analogy to the non-relativistic FPLO method, the local spin-polarized basis states are defined as solutions of a single particle Kohn-Sham-Dirac equation

$$\left[-i c \boldsymbol{\alpha} \cdot \nabla_{\mathbf{r}} + \beta m c^2 + V_{\mathbf{s}\Lambda}^{tot} + \frac{e \mu_0}{2 m} \beta \Sigma_z B_{\mathbf{s}\Lambda}^{tot} \right] \phi_{\mathbf{s}\Lambda} = \pm \phi_{\mathbf{s}\Lambda} E_{\mathbf{s}\Lambda}, \quad (2.72)$$

in a spherical, orbital dependent potential $V_{\mathbf{s}\Lambda}^{tot}(|\mathbf{r} - \mathbf{s}|)$, which is the spherically averaged total potential $V_{\mathbf{s}}^{tot}(|\mathbf{r} - \mathbf{s}|)$ of Eq. (2.68) for the core states and for the valence states

$$V_{\mathbf{s}\Lambda_v}^{tot}(|\mathbf{r} - \mathbf{s}|) = V_{\mathbf{s}}^{tot}(|\mathbf{r} - \mathbf{s}|) + \frac{1 + \beta}{2} \left(\frac{|\mathbf{r} - \mathbf{s}|}{r_{\mathbf{s}\Lambda_v}} \right)^4. \quad (2.73)$$

The $r_{\mathbf{s}\Lambda_v}$ depends on the compression parameter $x_{0\Lambda_v}$, in analogy to the non-relativistic quantity. Further, the spherically averaged total exchange field is included,

$$B_{\mathbf{s}}^{tot}(|\mathbf{r} - \mathbf{s}|) = \frac{1}{4\pi} \int d\Omega B^{tot}(\mathbf{r} - \mathbf{s}). \quad (2.74)$$

Solving Eq. (2.72) gives rise to a set of four coupled differential equations, for which numerical standard methods exist. The relativistic method follows the same iteration steps of the non-relativistic procedure above described, additionally a magnetization density has to be calculated and analyzed for self-consistency.

2.2.2 Density of states and Fermi energy

Band structure calculations of LaRhIn_5 and the class CeTMIn_5 ($TM = \text{Co, Rh, Ir}$) revealed the advantages of the RFPLO scheme in considering relativistic contributions and using an optimal basis set [23], compared to other relativistic and non-relativistic full potential methods. Additionally, differences due to relativistic effects near E_F show the breaking of some band degeneracy or the broadening of $4f$ -band complexes [23].

Due to its character of reference compound, LaIrIn_5 was similarly studied ⁵ with RFPLO, although no strong relativistic effects are expected, but to enable direct comparisons with the other systems. The following basis set of the valence states is used:

$$\begin{aligned} \text{La:} & \quad 5s\,5p\,5d; 6s\,6p \\ \text{Ir:} & \quad 5s\,5p\,5d; 6s\,6p \\ \text{In:} & \quad 4s\,4p; 4d\,5s\,5d\,5p . \end{aligned}$$

In La , the $4f$ states important for the relativistic contributions mentioned in Section 2.1.1 are not occupied, while in In they are fully occupied and considered as core states. The orbitals $5s$ and $5p$ of La and Ir are both occupied, thus consisting of highly lying semicore orbitals that tend to hybridize with the $5d$ valence states. They are also included in the basis. For the same reason orbitals $4s\,4p\,4d$ are used too.

To build the basis for the lattice sites $\mathbf{R}_n$ and the atom sites $\mathbf{s}$, the experimental parameters of the crystal structure illustrated in Section 4.2.4 are used. The lattice constants are $a_1 = a_2 = 4.6854 \text{ \AA}$ and $a_3 = 7.5683 \text{ \AA}$. The cell is tetragonal and the space group is $P4/mmm$. The actual atom positions in the cell are established with the Wyckoff sites from the crystal structure refinement (refer to Section 4.2.4), which are $\text{La}(1a)$, $\text{Ir}(1b)$, $\text{In}(1c)$ and $\text{In}(4i)$. For the site-centered densities and potentials the lattice expansions in spherical harmonics reach the maximum l -number 12. The Perdew-Wang [74] parametrization of the exchange-correlation potential in the local spin density approximation (LSDA) was used. Solving the site-centred Kohn-Sham-Dirac equations (2.72), the basis set is additionally refined: compression parameters $x_0 \Lambda_v$ are optimized for each basis valence orbital separately by minimizing the total energy (2.69).

With this set the total Kohn-Sham-Dirac is then solved for a discrete mesh of inequivalent equally spaced $\mathbf{k}$ -points in the irreducible part of the Brillouin zone Fig. 2.4. The rest $\mathbf{k}$ -points of the Brillouin zone are then taken into account by simple use of the reciprocal-lattice symmetry. Once the energies $E_v(\mathbf{k})$ and the number of states $\nu(\mathbf{k})$ are known, the density of states is calculated by integration over the $\mathbf{k}$ -space. The Fermi energy is similarly calculated considering that the occupied states are equal to the number of valence electrons. A fine $\mathbf{k}$ -point mesh is necessary to obtain the density of states $n(E_F)$ at singularities and the density fraction of orbitals accurately. Increasing the density of the mesh, the results tend to converge but irregularly because of the discrete integration. The accurate result for a fine mesh of 1683 $\mathbf{k}$ -points is shown in Fig. 2.5. The atom-decomposed and total density of states (DOS) for the full zone is displayed in dependence of energy. The vertical line indicates the Fermi level E_F , here taken as the zero of energy. The density of states $n(E_F)$ is $2.33 \frac{\text{states}}{\text{V}_c \text{ eV}}$ and lies in a nearly flat interval between the strong peaks at -1.5 eV and 2 eV from the Fermi energy, thus not being sensitive to the $\mathbf{k}$ -points sampling. The partial DOS shows that the dominant contribution to the total density of states in the vicinity of E_F stems from the $5p$ states of the $\text{In}(4i)$ atoms ($\text{In}(2)5p$ in Fig. 2.5), placed on horizontal planes between the La and Ir layers (refer to the crystal structure in Section 4.2.4). The out-of-plane contribution comes from the $5d$ states of La and Ir as well.

⁵The calculations in the RFPLO scheme were performed by S. Elgazzar. The author benefitted from private discussions with S. Elgazzar and I. Opahle particularly regarding the technical content of the next sections.

Figure 2.4: The Brillouin zone of LaIrIn_5 with indexed high symmetry points and the inequivalent, equally spaced sampling with 1683 $\mathbf{k}$ -points of the irreducible part for the self-consistent calculation. Reciprocal-lattice basis vectors are also shown.

Figure 2.5: Total and partial density of states of LaIrIn_5 from the full-zone calculation.

Figure 2.6: The Brillouin zone of LaIrIn_5 with indexed high symmetry points and the fine point sampling at the edges of the irreducible part for the band-structure calculation. Reciprocal-lattice basis vectors are also shown.

Figure 2.7: Band structure of LaIrIn_5 .

Figure 2.8: Orbital weighted band structure: total (top) and La specific (bottom).

Figure 2.9: Orbital weighted band structure: Ir specific (top) and In specific (bottom).

2.2.3 Energy band structure

For the band structure, the self-consistent calculation is used to compute the energy eigenvalues of all the bands for a special linear $\mathbf{k}$ -points sampling of the irreducible zone. The lines connect the high symmetry points from the center Γ along symmetry directions ($\Gamma - M$, $M - X$, $X - \Gamma$, $\Gamma - Z$, $Z - A$, $A - R$, $R - Z$) and the $\mathbf{k}$ -points are equally spaced, refer to Fig. 2.6. The $E_\nu(\mathbf{k})$ when plotted as curves along the symmetry directions produce the well known band-structure as in Fig. 2.7. The orbital weight of the single elements influences the band character. It is graphically represented by a circle with center at coordinates $(\mathbf{k}, E_\nu(\mathbf{k}))$ and with radius the respective orbital extension parameter $x_{0,l,m}$. The total and element specific orbital weighted band-structures are shown in figures 2.8 and 2.9. The circles also show the discrete $\mathbf{k}$ -points sampling used for the calculation along the symmetry directions.

The band structure of LaIrIn₅ shows three bands which cross the Fermi level, thus generating the Fermi surface. These bands are denoted with $\nu = 131, 133$ and 135 , respectively, according to their number in the valence band complex of the fully relativistic calculation counted from below. All have mixed band character. From the different band weights illustrated in figures 2.8 and 2.9, the first orbital more strongly contributing to the Fermi energy is *In 5p*. That is especially true for the bands centered around A and M. Also pronounced is the *d* character at the Fermi energy, especially between $M - \Gamma$ and $M - X$, and between $R - Z$ as well.

2.2.4 Calculated Fermi surface

The Fermi surface collects the $\mathbf{k}$ -points which satisfy $E_\nu(\mathbf{k}) = E_F$. In order to refine the mesh of $\mathbf{k}$ -points in the irreducible Brillouin zone from the full-zone calculation, the tetrahedron method is used [66, 15]. According to this method each submesh cell is divided in tetrahedra, the shortest main diagonal is chosen as the common edge of the tetrahedra. Each tetrahedron is then identified by the quadrupole of irreducible $\mathbf{k}$ -points corresponding to the corners. The energy eigenvalues from the self-consistent calculation $E_\nu(\mathbf{k})$ at the four tetrahedral vertices are known. Their values of a fixed band index ν are interpolated linearly between each pair of vertices to find a $\mathbf{k}_F$ -point, so that the Fermi velocity $v(\mathbf{k})$ becomes constant and $E_\nu(\mathbf{k}_F) = E_F$. The Fermi surface is approximated by a plane cutting the tetrahedron at the $\mathbf{k}_F$'s. A plane can only be defined if three distinct $\mathbf{k}_F$ -points are found. It means that for this linear interpolation the energy eigenvalues at the four tetrahedral vertices must not be degenerate. If this is not the case, this degeneracy must be removed by shifting the degenerate eigenvalues slightly.

The calculated Fermi surfaces are shown in figures 2.10, 2.11 and 2.12. The colours indicate qualitatively the Fermi velocity magnitudes similarly to the representation in Fig. 2.2. The band 131-Fermi surface is a compensated electron-hole Fermi surface, consisting of the electron flower-like sheet centered at Z and a hole cushion-like sheet centered at Γ , with ellipsoidal branches in $\Gamma - X$ direction. The band 133 electron Fermi surface consists of elongated pockets centered at the points X and a not closed sheet stretching along $M - A$, with a strong corrugated part in the $M - \Gamma$ direction. The band 135 is an electron Fermi surface made of a corrugated sheet stretching along the $M - A$ direction.

LaIrIn₅ is thus a compensated metal with equal numbers of electron and hole carriers.

Figure 2.10: Full relativistic Fermi surface of LaIrIn₅ from band 131 and Fermi velocity.

Figure 2.11: Full relativistic Fermi surface of LaIrIn_5 from band 133 and Fermi velocity.

Figure 2.12: Full relativistic Fermi surface of LaIrIn₅ from band 135 and Fermi velocity.

Calculation of orbit areas and orbit integrals

The band structure provides the numerical dispersion relation of the band energy from which, by numerical derivation, the electron properties (mass and velocities) at points of the Fermi surface are calculated. Determination of the electron properties on particular contours, the so called orbits, assume much importance for experimental comparisons. Orbits are the result of the intersection of the Fermi surface and a plane in the $\mathbf{k}$ -space. The discrete Fermi surface from the tetrahedral method is used, which is approximated by planes delimited in tetrahedrons. Therefore only those tetrahedra of the irreducible Brillouin zone contribute to the orbit, which contains both the Fermi surface and the plane of intersection. The length of the intersection line for a given Fermi energy can be calculated from the $\mathbf{k}$ vectors and the band energies at the four tetrahedral vertices by simple analytical geometry. Open orbits are then closed by application of the point and translation symmetries at the intersection points found in the irreducible part (extended zone scheme). Orbits or "cuts" of the Fermi surface of LaIrIn₅ for planes intersecting the Brillouin zone in the vertical direction $\mathbf{b}_3$ are represented in Fig. 2.13 in the extended zone scheme, for which the irreducible part of the Brillouin zone of Fig. 2.6 is repeated in the reciprocal space by appliance of reflections and four-fold rotations. The planes from $(k_1 k_2 0)$ to $(k_1 k_2 0.5)$ at equal intervals in units of $[b_1 b_2 b_3]$ are illustrated.

In general, pictures of cuts in one direction (Fig. 2.13) and of the Fermi surfaces (Fig. 2.10, 2.11, 2.12) help to distinguish extremal orbits, the contours at which the cut areas assume a local maximum or minimum of their values. These cuts and their quasi-particle properties are actually those that can be measured of a Fermi surface by the de Haas-van Alphen effect, Chapter 7. For the area calculation a numerical orbit integration has to be performed over the intersecting $\mathbf{k}_F$ -points Ω of the Fermi surface and the intersection plane according to the equation (2.56) for $\mathcal{A}$. Another quantity that results from orbit integration is the orbit mass m_Ω by implementation of the equation (2.57). Orbit velocities are easily calculated from the values of the orbit area and average mass with relation (2.59). Calculated orbit quantities of LaIrIn₅ for two planes of Fig. 2.13 are summarized in Tab. 2.1. Orbit areas are also conventionally expressed in terms of the area of the Brillouin zone section produced by the orbit plane. In this case $\mathcal{A}_{BZ} = 2 \pi (b_1)^2$, $\mathbf{b}_1$ the basis reciprocal-lattice vector of LaIrIn₅.

Position	orbit Ω	$\mathcal{A}$ [nm ⁻²]	$\mathcal{A}$ [% $\mathcal{A}_{BZ}$]	m_Ω [m_o]	v_Ω [10^5m s^{-1}]
M	ϵ_1	132.32	73.58	-0.985	7.631
M	β_1	91.99	51.15	0.697	8.992
M	α_2	31.12	17.31	0.473	7.707
A	β_2	50.22	27.93	0.628	7.374
A	α_3	30.35	16.88	0.477	7.547
R	χ	2.51	1.40	0.149	6.951
Z	γ_1	6.64	3.70	0.235	7.164
Z	γ_2	1.36	-	-	-

Table 2.1: Calculated electronic properties from the full relativistic band structure of LaIrIn₅ for orbits perpendicular to the direction [001].

Figure 2.13: Orbits of all the Fermi sheets of LaIrIn_5 for cuts along the direction [001].

Chapter 3

Sample preparation of LaIrIn_5

SUMMARY

The model of the electronic structure introduced in the previous chapter develops from the assumption of long range order of the atomic matrix building the intermetallic compound. Only a high perfection single crystal reproduces these ideal conditions. The difficulty is then the realization of large size crystals, which enable measurements of the electronic system. Experimentally, one has to produce the conditions and to control the parameters, which command the atomic aggregation in the ordered crystal structure. This Chapter is dedicated to the description of the techniques used in the growing of large size single crystals of LaIrIn_5 .

Single crystals of the RETMIn_5 compounds (with $\text{RE} = \text{La, Ce and Pr}$; $\text{TM} = \text{Co, Rh and Ir}$) are successfully and economically produced by the self-flux method [42, 60, 43, 91].

3.1 The flux growth method

A common synthetic procedure for producing high-quality single-crystals of intermetallic compounds is the flux growth [16, 61]. The basis of flux growth is the higher diffusion of high-temperature-melting materials in a molten solute. Once in solution, the elements can interact

and by cooling single crystals grow. Complications come from the complexity of the phase diagram. By cooling the solution, many different phases solidify, which leads to an uncontrolled growth of different crystals. A controlled growth by a homogeneous or an inhomogeneous temperature gradient is usually ineffective on the crystal dimensions.

Typically, the starting materials, in elemental form, are placed into an alumina crucible. The crucible and its contents are then sealed into an evacuated quartz tube. In order to maintain a controlled growth environment, a few 1/4 bar Ar as protective gas is included and a rolled sacrifice Zr-foil is placed above the crucible in the tube. Zr interacts on a large surface with oxygen, preventing sample corrosion. The crystal growth follows a particular cooling ramp, which can be specific of the compound [43, 91].

Once the crystal growing process is finished, the crucible has to be cooled and the solute removed. Different procedures can be employed. The ampoule is removed from the furnace at a temperature higher than the melting point of the flux, and spun in a centrifuge to remove excess flux. Or the cold crucible is removed from the quartz tube and is heated on a plate to the melting point of the solute, which is then simply poured out. Actually, this procedure is suitable when the flux has a low melting point, so that the crystals are not strongly heated and subjected to oxidation. Flux specific wet etching is applied alone or in companion to the other processes to remove the remains of flux from the crystals.

3.2 Single crystal growth

In the synthesis of LaIrIn_5 , the constituents are prepared in a 1:1:34 ratio, where the excess of *In* works as solute (self-flux method). *Ir* metal (JMC 991, 99.998 %) was cut in small pieces and constituted the reference molar number (usually weighted mass of 500 – 700 mg). Then *La* metal (Ames Laboratory, 99.999 %) in pieces was prepared accurately (only in a small excess of 0.1 % mol) and put with the *Ir* into the crucible. The *In* metal (Heraeus, 99.999 %) was melted and casted onto the materials in the crucible, in order to prevent unwanted oxidation. The quartz tube with the crucible and the Zr-foil was evacuated and sealed under 260 mbar Ar atmosphere. The reaction tube was hung into an open vertical tube RF furnace.

The mixture was submitted to a slightly different heat process then reported in the literature [60, 91]. The tube was heated from room temperature to 1050 °C in 8 hours and held at this temperature for 24 hours. Then followed a very slow one-step cooling from 1050 °C to 700 °C at 1.82 °C /h. In particular, the crucible was held at this temperature for 24 hours and was then rapidly cooled down to room temperature at 100 °C /h without centrifugation. Excess of *In* flux was removed with wet etching. A diluted aqueous solution of HCl is element specific enough and different etching behaviour is observable in a reaction glass. The etching rate of *In*

Figure 3.1: Crucible with a batch of small single crystals of LaIrIn_5 . Detail of an exceptionally large crystal.

Figure 3.2: Large size crystal of LaIrIn_5 after cutting. Side dimensions $5.7 \times 3.8 \text{ mm}^2$.

predominates and the solution remains transparent. When the *In* is solved, the solution begins to etch LaIrIn_5 producing a dark solution.

Single crystals in cubic and plate-like form of $1 - 15 \text{ mm}^3$ volume are usually produced by the many attempts, as the batch of Fig. 3.1 illustrates. Two exceptional crystals were also obtained with dimensions $5.7 \times 5.3 \times 3.8 \text{ mm}^3$ and $6.1 \times 5.5 \times 4.2 \text{ mm}^3$ respectively.

The first crystal is shown integral in Fig. 3.1 and after the cut ¹ of some samples in Fig. 3.2. The revelation of *In* inclusions and evident embedded subgrains demanded a proof and an estimation of bulk perfection with γ -radiation diffractometry, to be explained in Section 4.4. X-ray diffraction methods were applied for crystal orientation, Section 4.3. Additional HCl wet etching removed the *In* from the inclusions and showed some grain boundaries. Thus, only the homogeneous zones were used for the physical property measurements to be reported: electric transport, heat capacity and de Haas-van Alphen effect.

The second large crystal showed more irregularities and subcrystals on the surface, thus was cut ² for inner bulk inspection, see Fig. 3.3. From the homogeneous part the samples for crystal structure definition and de Haas-van Alphen experiments were derived, refer to Section 4.2 and 7.6 respectively.

During the many attempts, changes in the preparation or in the growth procedure were executed. Separate pre-melting of *La* and *Ir* by arc melting them into a pill before *In* was joined

¹Cylindrical spark erosion.

²Planar spark erosion.

Figure 3.3: Large size crystal of LaIrIn_5 after planar cutting. Side dimensions $6.1 \times 5.5 \text{ mm}^2$.

into the crucible brought homogeneous growth of very small crystals in the region of the pill. Dimensions do not exceed 1 mm³ and larger samples are not observed. The attempt of forcing a spatial inhomogeneous crystal growth in order to favour building of large crystals was also approached by applying a temperature gradient. Thus the reaction was submitted to a temperature gradient by hanging the quartz off the middle of the vertical tube furnace. Only small plate-like crystals were observed with dimensions smaller than 1 mm³.

LaIrIn₅ has the properties common to transition metal compounds. It is highly refractory with a high melting temperature. Chemical stability in air and water did not show surface oxidation.

Chapter 4

Single crystal characterization and analysis

SUMMARY

Diffraction methods permit the characterization of the crystal structure of intermetallic compounds. The actual composition, structure and perfection of the crystal samples must be characterized with great accuracy and eventually considered in the calculation model, in order to make reliable interpretations of the measurements on the basis of the correct electronic structure. Three methods are used and their introductions explain the phenomena in the classical wave-matter interaction formalism. The experiments on LaIrIn_5 follow. Thus, the single crystal X-ray diffractometry determined the crystal structure of LaIrIn_5 , Section 4.2.4. The X-ray back-reflection Laue method permitted the orientation analysis of the samples, Section 4.3.3. γ -ray diffraction established the crystal homogeneity of LaIrIn_5 samples, see 4.4.3.

The diffraction of electromagnetic waves at the crystal lattice has become the essential experimental technique for the structural characterization of new materials.

Different radiations have been used for direct structure characterization, crystal orientation determination or bulk crystal perfection study, respectively. The different methods depend on the

⁰The experimental part of this Chapter was executed with the advice and co-work of H. Sowa, GZG Göttingen and the assistance of A. Gand, IPC Göttingen.

Figure 4.1: Wavelength spectrum of different radiations for diffraction experiments versus sample scale.

dimension of the crystal sample, use characteristic radiation or a continuous spectrum and apply X- or γ -radiation. Fig. 4.1 shows the wavelength spectrum of the different radiations used versus the crystal dimension.

The X-radiation from commercial equipments is generated by electronic transitions of a metal target, excited by a beam of energetic electrons accelerated from a source. Cu and Mo targets show, besides a background radiation, also a more intensive characteristic radiation, due to the K_α -transition. This constitutes the source of nearly monochromatic radiation at a specific wavelength for crystal structure determination experiments. The choice depends on the materials to be studied, which should not absorb the radiation. Interactions with the atomic core electrons give informations about the atomic positions. However, absorption of X-rays becomes stronger by increasing electronic number. Cu K_α ($\lambda = 1.542 \text{ \AA}$) is usually used for powder diffraction in reflection geometry. In transmission only for small single crystals, especially of organic substances. Mo K_α ($\lambda = 0.710 \text{ \AA}$) is more energetic and with shorter wavelength, thus being adapted for investigations at heavy elements systems. Employment of a W target produces an intense white radiation, which is necessary for the radiography of a crystal. Shorter wavelengths of the γ -radiation can interact with the matter on a large range without being absorbed. Besides the production at synchrotron facilities, emission of γ -radiation from radioactive decay is employed in special in-house installations.

4.1 Theory of crystal diffraction

Considering the incident radiation to the crystal as strongly collimated, it assumes the expression of a plane wave. Thus the radiation at a point $\mathbf{r}$ of the crystal is assumed

$$\mathbf{I}_i e^{i\mathbf{k}_i \cdot \mathbf{r}}, \quad (4.1)$$

with wave-vector $\mathbf{k}_i = \frac{2\pi}{\lambda} \hat{\mathbf{e}}_i$. The amplitude is the vector quantity $\mathbf{I}_i$, whose modulus is the intensity and the direction is the polarization with respect to the propagation direction $\hat{\mathbf{e}}_i$. λ is the

Figure 4.2: Monochromatic diffraction condition in the reciprocal space (Ewald construction) and in the real space of the crystal.

wavelength of the radiation. The radiation electric field, oscillating at a frequency $\nu = \frac{c}{\lambda}$, excites the atomic electron clouds, thus the atoms become point sources of electromagnetic spherical waves. These waves interfere and produce a plane wave which propagates in the diffracted direction $\hat{\mathbf{e}}_f$. Actually, the resulting wave is the superimposition of phase shifted waves scattering from the volume elements dV of the sample in the direction $\hat{\mathbf{e}}_f$ with amplitudes proportional to the number of electrons $\rho(\mathbf{r}) dV$ contained in the volume element dV at the position $\mathbf{r}$. The difference phase factor of the diffracted wave from a volume element dV at $\mathbf{r}$ is

$$e^{i(\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r}}. \quad (4.2)$$

The complete amplitude of the wave diffracted in direction $\hat{\mathbf{e}}_f$ is proportional to the scattering amplitude calculated in the Born approximation of perturbation theory [110]

$$F(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{-i\mathbf{Q} \cdot \mathbf{r}} dV \quad (4.3)$$

with scattering vector

$$\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i. \quad (4.4)$$

Within the lattice periodicity of the crystal, the electron density can be written as a Fourier series of the reciprocal lattice

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}_h} \rho_h e^{i\mathbf{K}_h \cdot \mathbf{r}} \quad (4.5)$$

as analogue to expressions for all periodic functions of a crystal, see Section 2.1.1. The scattering amplitude becoming

$$\begin{aligned} F(\mathbf{Q}) &= \sum_{\mathbf{K}_h} \int \rho_h e^{i(\mathbf{K}_h - \mathbf{Q}) \cdot \mathbf{r}} dV \\ &= \begin{cases} \rho_h V & \text{if } \mathbf{K}_h - \mathbf{Q} = 0 \\ 0 & \text{otherwise} \end{cases}. \end{aligned} \quad (4.6)$$

It means that diffracted radiation can only be observed in directions corresponding to wave-vectors $\mathbf{k}_f$ satisfying

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{K}_h. \quad (4.7)$$

Considering the case of elastic scattering, the energy of the diffracted beam is the same as the incident energy and the wave-vectors have the same length $|\mathbf{k}_f| = |\mathbf{k}_i| = \frac{2\pi}{\lambda}$. This means a condition for the angle of scatter. If 2θ is the angle between $\mathbf{k}_i$ and $\mathbf{k}_f$ then

$$|\mathbf{K}_h| = 2 |\mathbf{k}_i| \sin\theta . \quad (4.8)$$

The vector relation can easily be represented with the Ewald construction in Fig. 4.2, a sphere in the wave-vector space, where both the wave-vectors $\mathbf{k}_i$ and $\mathbf{k}_f$, which differ only in their direction, span the radius. In the same space the crystal is represented by the discrete reciprocal-lattice vectors $\mathbf{K}_h$. Thus the diffraction condition (4.7) is satisfied when a reciprocal-lattice vector between $\mathbf{k}_i$ and $\mathbf{k}_f$ passes on the Ewald sphere.

It is particularly convenient to notice that the length of a reciprocal-lattice vector is proportional to the reciprocal of the spacing d of the crystal planes to which it is perpendicular

$$|\mathbf{K}_h| = \frac{2\pi n}{d} , \quad (4.9)$$

where n is an integer. Thus if λ is the wavelength of the incident radiation, equations (4.8) and (4.9) give

$$n \lambda = 2 d \sin\theta , \quad (4.10)$$

also known as the Bragg reflection law. It is easily deduced by consideration of the phase relation between beams reflected off successive lattice planes. For coherent diffraction, the extra path $2d \sin\theta$ must be an integral number of the wavelength. θ corresponds to the angle between the incident radiation and the reflecting plane (Fig. 4.3).

The magnitude of the diffracted amplitude 4.6 depends on ρ_h . For electromagnetic radiation this is the Fourier component of the local electron density in the crystal. Considering the scattering crystal volume V composed of N unit cells, the scattering amplitude (4.6) becomes

$$F(\mathbf{K}_h) = N \int_{Cell} \rho(\mathbf{r}) e^{-i\mathbf{K}_h \cdot \mathbf{r}} dV . \quad (4.11)$$

Thus radiation is scattered only in the direction of reciprocal-lattice vectors. Moreover, knowledge of the position of the scattering atoms inside the unit cell and their spatial electron density distribution permit the definition of $\rho(\mathbf{r})$ and thus the intensity of the diffracted radiation. Considering the electrons concentrated around the atomic positions the integral can be conveniently substituted by a summation over the atoms inside the unit cell and the atom electron density by the atomic form factor f_j , thus

$$F(\mathbf{K}_h) = V \sum_j f_j e^{-i\mathbf{K}_h \cdot \mathbf{r}_j} \equiv F_h , \quad (4.12)$$

in this form also known as the structure factor. The value of f_j is normalized to the atomic number Z and decreases with increasing diffraction angle or radiation wave length.

4.2 Single crystal X-ray diffractometry

Single-crystal X-ray diffraction is an essential experimental technique for the structural characterization of a crystalline material. Its purpose is to apply the previous concept of radiation diffraction in order to derive quantitatively from the direction and intensity of the diffracted radiation structure and electron density of the crystal.

4.2.1 Theory

The electromagnetic diffraction of single crystals is understood in terms of the crystal reciprocal lattice defined through the vectors $\mathbf{K}_h$, stated in equation (2.7). In crystallography the coordinates of the index vector $\mathbf{h} = [h_1 \ h_2 \ h_3]$ are called the Miller indices h , k and l respectively. The amplitude and phase information of a scattered wave is included in the cell structure factor as stated in equation (4.12), but in a more realistic way in

$$F_{\mathbf{h}}^{Cell} = \sum_j g_j e^{i \mathbf{K}_h \cdot \mathbf{r}_j} = \sum_j g_j e^{i 2\pi (h x_j + k y_j + l z_j)}, \quad (4.13)$$

where $\mathbf{K}_h \cdot \mathbf{r}_j$ is always the resultant phase-shift for the wave scattered by atom j , and g_j refers to the temperature-corrected atomic scattering factor f_j for each atom j . The atomic form factors, which themselves fall off with increasing scattering angle, experience an additional weakening from atomic vibrations which can be represented by

$$g = f \cdot e^{-\frac{2\pi^2 \langle u \rangle^2}{d^2}}. \quad (4.14)$$

This formula implies that the atom is isotropic, vibrating equally in all directions. The square of the mean vibration amplitude $\langle u \rangle^2$ is called the atomic displacement factor U . Since it increases with temperature, it is often also called the temperature factor of the atom. Anisotropic vibrations can be represented by so-called vibration ellipsoids with three principal axes U_1 , U_2 and U_3 . In an orthogonal system they represent the extent of vibration along $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ respectively. An equivalent isotropic atom displacement parameter can also be referred to, which is approximately equal to $\frac{1}{3}(U_1 + U_2 + U_3)$. In general, shape and orientation of each atom ellipsoid are given by six U_i -parameters. Usually, d in expression (4.14) is replaced according to the Bragg condition (4.10), giving the form

$$g = f \cdot e^{-\frac{B \sin^2 \theta}{\lambda^2}} \quad (4.15)$$

where $B = 8\pi^2 U$ is the Debye-Waller factor, most commonly used as temperature factor due to thermal vibration of atoms.

The structure factor F is the amplitude of the scattered wave, and F^2 denotes the intensity of the wave. Considering equations (4.5) and (4.6), the structure factor (4.12) is also the Fourier transform of the periodic electron density $\rho(\mathbf{r})$. The Fourier series is stated in

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{h}} F_{\mathbf{h}} e^{-i \mathbf{K}_h \cdot \mathbf{r}} = \frac{1}{V_{Cell}} \sum_{\mathbf{h}} F_{\mathbf{h}}^{Cell} e^{-i \mathbf{K}_h \cdot \mathbf{r}} \quad (4.16)$$

where V_{Cell} is defined as the volume of the unit cell. Experimentally, the set of $F_{\mathbf{h}}$ and $\mathbf{K}_h$ is widely scanned by running the angle θ and rotating the crystal.

4.2.2 Instrumentation

For single-crystal X-ray diffraction several commercial in-house diffractometers are available. For the work performed here, a Bruker Smart Apex2 CCD diffractometer was used at the Center for Geoscience in Göttingen¹, Fig. 4.3. This diffractometer is equipped with a Mo X-ray tube, a three circle goniometer, and a charge-coupled device (CCD) detector. The CCD is a two-dimensional solid-state detector sensitive to visible light. A phosphor² plate in front of the camera converts X-ray photons into visible light, so that the reflections pattern can be detected. CCD allows for high speed and accuracy. The radiation used is monochromatic Mo K_{α} ($\lambda =$

¹University of Göttingen, GZG, Dept. of Crystallography, Prof. Dr. W. F. Kuhs.

²Typically, phosphors are composed of Gd_2O_3 doped with Tb [2].

Figure 4.3: Detail of the X-ray diffractometer. In the middle, the mounted sample on the goniometer.

0.71073 Å, graphite monochromator), particularly adapted for highly absorbing elements. The data collection is controlled with a computer interface. The settings for the generation of X-rays are 30 mA and 50 kV.

The data set presented in this chapter was collected within one night.

4.2.3 Data analysis

Once data are collected, data reduction is performed using the Apex 2 Suite program package [4]. Integration of the reflection spots yields intensity data. This enables, by assigning $h k l$ values to the diffraction spots in the pattern, the determination of lattice parameters of the unit cell using least squares refinement. Data are corrected for Lorentz and polarization effects and absorption due to variation in the path length through the detector faceplate. Polarization corrections are made when there is a loss of intensity due to polarization of the beam by reflection [100].

Structure solution

Typically, Patterson or direct methods are employed to obtain a structure solution. As described in [61], the Patterson method relies on interatomic vectors to determine the atomic arrangement. This can be very difficult with unit cells with more than twenty atoms. Many persons have contributed to the development of direct methods, but the key findings of Karle and Hauptman in the 1950's revolutionized the use of crystallography [51]. Direct methods employ normalized structure factors E to determine the phases of the Bragg reflections. The definition of E being

$$|E(\mathbf{h})|^2 \propto \frac{|F_{\mathbf{h}}|^2}{N \sum_j f_j^2 e^{-B_j \sin^2 \theta / \lambda^2}} \quad (4.17)$$

The scattered X-ray intensity proportional to $|F_{\mathbf{h}}|^2$ decreases with increasing scattering angle θ and temperature. The denominator in Eq. (4.17) is also θ -dependent and serves to normalize the structure factor F . Compared with F values, E can be quite large, particularly for ordinary small F values. This becomes advantageous when, as in direct methods, the solution is achieved by forming a vector triplet in reciprocal space. For centrosymmetric space groups, this translates into deducing the phase of the third vector if the phases of two other vectors for a particular $h k l$ are known. Thus, the phase of the scattered wave can be determined. A

point of maximum contribution from three signs at an intersection point corresponds to a region of high electron density. A complete X-ray data set can be imported into a direct methods program, such as SIR97 [3] or SHELXS [88], to obtain a structure solution.

Structure refinement

When the structure is solved or it is known through literature, the diffraction data has to be refined for the actual atomic positions in the cell, thermal vibrations and extinction factor. Atomic displacement due to thermal vibrations is described by the temperature factor B_j of atom j

$$B_j = 8 \pi^2 U_j, \quad (4.18)$$

where U_j is the mean displacement parameter. Each atomic U is considered anisotropically, so that it is described by the six parameter matrix. Extinction factors may be necessary to correct for attenuation of the X-ray beam by the crystal. Primary extinction is caused by X-rays being doubly reflected by multiple planes in the crystal. This ultimately leads to reduction in the intensity of the X-ray beam. The scattered X-ray can also be reduced by significant reflection of the beam by the first plane; subsequent parallel planes farther in the crystal receive less of the incident beam [57]. The refinement parameters enter calculated structure functions $F_{calc}(\mathbf{h})$ using formula (4.13). The refinement is then carried out as a function of errors of the intensities $|F_{obs}^2 - F_{calc}^2|$, while minimizing

$$\sum_{\mathbf{h}} w (F_{obs}^2 - F_{calc}^2)^2. \quad (4.19)$$

$F_{obs}(\mathbf{h})$ are the observed structure factors related to the reduced intensities. The mathematical description of the weighting function w , is given by

$$w(\mathbf{h}) = \frac{1}{\sigma^2 (F_{obs}^2(\mathbf{h})) + (A P)^2 + B P}, \quad (4.20)$$

where σ is the standard deviation, A and B are constants, and $P = (F_{obs}^2 + 2F_{calc}^2)/3$ [100].

The quality of a structure determination can be judged by the reliability R -factors and the differences in the electron density maps $\Delta\rho_{max, min}$. The factor R_{int} describes the deviation of the intensities among the observed symmetrical equivalent reflex. The conventional factor R_1 refers to the difference in observed and calculated structure-factor amplitudes. Its mathematical expression is [100]

$$R_1 = \frac{\sum_{\mathbf{h}} ||F_{obs}| - |F_{calc}||}{\sum_{\mathbf{h}} |F_{obs}|}. \quad (4.21)$$

The weighted R -factor wR_2 is directly related to the minimized function in the refinement and it is expressed by

$$wR_2 = \sqrt{\frac{\sum_{\mathbf{h}} w (F_{obs}^2 - F_{calc}^2)^2}{\sum_{\mathbf{h}} w (F_{obs}^2)^2}}. \quad (4.22)$$

Lower R -factors indicate higher degrees of agreement between observed and calculated structure factors. Typically, for a good data set of $R_{int} < 0.05$, the refined structure should give final values of 0.05 and 0.15 for R_1 and R_2 respectively. A further index used to indicate the quality of a refinement is the goodness-of-fit, that should be desirably close to 1.

As described in [61], positive and negative peaks in the electron density map correspond to residual electron density that is unaccountable [57]. Excessively large peaks indicate incorrect assignment of atomic positions. For structure determinations of organic compounds, residual electron density peaks $\Delta\rho$ rarely exceed $1 \text{ e}\text{\AA}^{-3}$; for the intermetallic compounds considered in this work, values of $\Delta\rho$ smaller than approximately $5 \text{ e}\text{\AA}^{-3}$ are considered reasonable. The program SHELXL97 [89] was used for the data refinement.

Figure 4.6: Precession images of the reflections of diffraction vectors in the planes $(hk0)$ and $(h0l)$.

$29.5 \text{ cm}^2\text{g}^{-1}$ respectively. For a calculated density of 9.047 g cm^{-3} , the linear absorption coefficient is $\mu = 43.12 \text{ mm}^{-1}$, for which a thickness of 0.1 mm in order to transmit an intensity of nearly 15% is advisable. The intermetallic compound here studied is brittle and samples can be easily prepared by cutting a crystal with a sharp-edged razor blade into fragments with dimensions smaller than 10^{-3} mm^3 . This limitation of the single-crystal diffractometry becomes an advantage for the experimentator. It permits the characterization of a big crystal by diffraction measurements with small pieces prepared from samples for physical properties experiments.

Or to characterize directly and not destructively one microcrystal to be used for investigations with microsensor techniques (superconducting quantum interference devices, cantilever magnetometry). Direct characterization is particularly requested in the description of physical and phase diagrams by changing stoichiometry or by non-stoichiometric materials, for which samples may strongly deviate in their properties and structure.

LaIrIn_5 and its analogous compounds LaTMIn_5 and REIrIn_5 ($TM = \text{Co, Rh}$; $RE = \text{Ce, Pr}$) are

Figure 4.7: View of the unit cell of the crystal structure of LaIrIn_5 . (La is represented red, Ir green and In yellow).

	Crystal data
Formula	LaIrIn ₅
Fweight [g mol ⁻¹]	905.21
Crystal system	Tetragonal
Space group	<i>P4/mmm</i>
<i>a</i> [Å]	4.6854(3)
<i>c</i> [Å]	7.5683(9)
<i>V</i> _{Cell} [Å ³]	166.15(2)
<i>Z</i>	1
<i>d</i> _{calc} [g cm ⁻³]	9.047
μ [mm ⁻¹]	43.12

Table 4.1: Summary of the crystal data of LaIrIn₅.

	Diffraction data
Crystal size [mm ³]	0.19×0.18×0.1
Temperature [°C]	23
Wavelength MoK α [Å]	0.71073
$2\theta_{max}$ [°]	66
No. of frames	1093
Counting time per frame [s]	10
<i>h</i>	-7 ... 4
<i>k</i>	-7 ... 6
<i>l</i>	-11 ... 11
Reflections read / rejected	1820 / 0
Unique reflections	232
Reflections @ $F_{obs} > 4\sigma(F_{obs})$	232
<i>R</i> _{int}	0.0313

Table 4.2: Diffraction data collected for LaIrIn₅.

	Least squares refinement
Refined parameters	12
atom positions	1
extinction factor	1
displacement parameters	9
Goodness-of-fit	1
Extinction factor	0.0061(8)
<i>R</i> ₁ @ $F_{obs} > 4\sigma(F_{obs})$	0.0184
<i>wR</i> ₂ @ 232	0.0440
Goodness-of-fit	1.307
$\overline{\Delta\rho}$ [e Å ⁻³]	0.00(40)
$\Delta\rho_{max}$ [e Å ⁻³] / site	2.55 / [0 0 0.145]
$\Delta\rho_{min}$ [e Å ⁻³] / site	-2.45 / [0.5 0 0.0661]

Table 4.3: Results of the structure refinement of LaIrIn₅.

Atom	Wyckoff site	x/a	y/a	z/c
La	1a	0	0	0
Ir	1b	0	0	1/2
In1	1c	1/2	1/2	0
In2	4i	0	1/2	0.30743(7)

Table 4.4: Refined atom positions of LaIrIn_5 in the unit cell.

Figure 4.8: Representation of the atoms of LaIrIn_5 as 100% probability vibration ellipsoids, refer also to Fig. 4.7.

Atom	(U_{11} U_{22} U_{33}) [$\text{\AA}^2$]	($\frac{U_{11}}{U_{eq}}$ $\frac{U_{22}}{U_{eq}}$ $\frac{U_{33}}{U_{eq}}$) $\cdot U_{eq}$ [$\text{\AA}^2$]
La	0.0055(2) 0.0055(2) 0.0043(3)	(1.08 1.08 0.84) $\cdot$ 0.0051(2)
Ir	0.0053(2) 0.0053(2) 0.0057(2)	(0.96 0.96 1.04) $\cdot$ 0.0055(1)
In1	0.0078(3) 0.0078(3) 0.0124(4)	(0.84 0.84 1.33) $\cdot$ 0.0093(2)
In2	0.0063(2) 0.0171(3) 0.0058(2)	(0.65 1.76 0.60) $\cdot$ 0.0097(2)

Table 4.5: Refined thermal parameters at 23 °C for atomic sites of Tab. 4.4. The components represent the extent of 50% probability vibration along the crystallographic axes.

Nearest neighbours polygon ¹	bond length ² [Å]		angle ² [°]
La-Ir (×2)	3.7841	In^a₁-La-In^b₁	90.00
	La-In₁ (×4)	3.3131	In^a₂-La-In^b₂	60.23
	La-In₂ (×8)	3.3018	In^a₂-La-In^c₂	90.39
			In^a₂-La-In^d₂	89.61
			In^a₂-La-In^e₂	119.77
			In^a₁-La-In^a₂	120.11
			In^a₁-La-In^c₂	59.89
			Ir-La-Ir	180.00
Ir-La (×2)	3.7841	La-Ir-La	180.00
	Ir-In₂ (×8)	3.3131	In^a₂-Ir-In^b₂	73.80
			In^a₂-Ir-In^c₂	116.23
			In^a₂-Ir-In^d₂	63.77
			In^a₂-Ir-In^e₂	106.20
In₁-La (×4)	3.3131	La^a-In₁-La^b	90.00
	In₁-In₂ (×8)	3.3018	In^a₂-In₁-In^b₂	60.23
			In^a₂-In₁-In^c₂	90.39
			In^a₂-In₁-In^d₂	89.61
			In^a₂-In₁-In^e₂	119.76
			La-In₁-In^a₂	59.89
			La-In₁-In^c₂	120.11
In₂-La (×2)	3.3018	In^a₂-In₂-In^b₂	90.00
	In₂-In₁ (×2)	3.3018	In^a₂-In₂-In^c₂	90.00
	In₂-Ir (×2)	2.7590	In^a₂-In₂-In^d₂	90.00
	In₂-In^a₂ (×4)	3.3131	In₁-In₂-In₁	90.39
	In₂-In^c₂	4.6535	La-In₂-La	90.39
	In₂-In^d₂	2.9148	In₁-In₂-La	60.23
			In₁-In₂-Ir	111.85
			Ir-In₂-Ir	116.23
			La-In₂-Ir	76.69

¹ FPLO (Refer to Section 2.2, [32]).² PowderCell 2.4 [80].**Table 4.6:** Selection of interatomic distances and bond angles from the refined structure of LaIrIn₅.

known to be isostructural with the HoCoGa_5 structure type in the tetragonal space group $P4/mmm$. The sample for diffraction was cut from a crystal to be used for de Haas-van Alphen effect measurements (Section 7.6.2). It was mounted on a thin nylon loop with a drop of grease at the top of a support, before being placed onto the goniometer, refer to Fig. 4.4 and Fig. 4.3.

A series of three runs with twelve frames per run were collected in order to determine rough unit-cell parameters. Intensity data were obtained by collecting frames with the CCD camera for diffraction angles 2θ up to 66° . The sample was successively rotated by the three circle goniometer in order to put all the reciprocal-lattice vectors in reflection. Two examples of frames for different crystal position and $2\theta \approx 0$ are shown in Fig. 4.5. The spots are the reflections produced by the corresponding reciprocal-lattice vectors indicated. The incident radiation is covered by a beam stopper. A total number of 1820 reflections was collected. They are displayed to simulate the precession images in the reciprocal space. Their positions for diffraction vectors in the planes $(hk0)$ and $(h0l)$ are shown in Fig. 4.6. Precession images constitute the undistorted representation of the reciprocal lattice. From a precession image the information about the diffraction vectors and the square of their scattering factors are thus immediately available from the hkl -indexed position and the intensity of the spots, respectively.

The knowledge of the space group and of the structure permitted the avoidance of using methods for structure solution. Thus the structure of LaIrIn_5 was refined using SHELXL97 beginning with the atomic positions taken from the literature [60] as the initial structural model. Additional correction for extinction and anisotropic displacement parameters was included. For all atoms, the displacement matrices U_{ij} are diagonal. The elements are the principal axes of the thermal ellipsoids, scaled as such that the ellipsoid represents the space in which the center of electron density can be localized with 50% probability. The refined structure is shown in Fig. 4.7. The crystal and diffraction data are summarized in tables 4.1 and 4.2.

LaIrIn_5 is a stoichiometric compound with atomic ratio 1 : 1 : 5 per unit cell. *La* and *Ir* atoms are located at Wyckoff positions $1a$ and $1b$, respectively. *In* atoms occupy two different sites, $1c$ and $4i$, which will be distinguished into In_1 and In_2 respectively, refer to Tab. 4.4. Tab. 4.5 summarizes the results with the coefficients of ellipsoid anisotropy. For more clarity Fig. 4.8 represents the atom sites with 100% probability vibration ellipsoids. In Tab. 4.3 the results and parameters for the refinement procedure are given, which present a quality up to 50% better than previously reported [60].

Interatomic distances and angles are listed in Tab. 4.6. As noticed in literature [60] the systems RETMIn_5 can be described as layered compounds. In LaIrIn_5 , the multilayers are seen as 8-coordinated Ir-In_2 rectangular prisms interleaved with layers of $\text{La-In}_{1,2}$ face-sharing cuboctahedra, refer to Tab. 4.6. The coordination of the *La* in the cuboctahedra is 12-fold to *In* altogether: four-fold to In_1 and eight-fold to In_2 .

The layered structure can also be viewed as alternating La-In_1 planes and planes of Ir-In_2 rectangular prisms. These sheets are stacked directly above one another; the transition metal atoms lie directly above the rare earth atoms.

4.3 X-ray back-reflection Laue method

The back-reflection Laue method is a convenient and accurate method of determining the orientation of a single crystal. The attainable accuracy is limited only by the perfection of the crystal and the instrumentation. Nevertheless, it also enables the study of large-scale imperfections and the relative orientations of twins.

Figure 4.9: Polychromatic diffraction condition in the reciprocal space (Ewald construction).

4.3.1 Theory of the Laue method

The Laue method uses a white incident radiation and considers the radiation back-scattered from the crystal [38, 11]. A family of crystal planes automatically select the correct wavelength to give a diffraction beam according to the fundamental Bragg equation (4.10). In accordance to Section 4.1, the vector relation can be easily represented with the Ewald construction in Fig. 4.9.

Figure 4.10: Back-reflection Laue pattern for hexagonal crystal ZrB_2 . (left) Origin of the hyperbolic pattern. (right) Developed Laue image for crystal-to-film distance 3 cm.

Each wavelength of the radiation gives rise to an Ewald sphere, but only those components, for which reciprocal-lattice vectors pass on their sphere, are diffracted. The crystal lattice works as a monochromator and produces a discrete angular dispersion of the radiation. Using a collimated spotlike white X-radiation (point focus), the back-reflection pattern on a planar surface perpendicular to the incident radiation is represented in Fig. 4.10. The diffracted spots lie exclusively on hyperbolas or straight lines, degenerate hyperbolas. The reciprocal-lattice vectors lying on a plane produce a diffraction cone of reflections with axis perpendicular to the plane. The intersection of this cone with the detector plane is a hyperbola. Reciprocal-lattice planes parallel to the incident radiation produce degenerate flat cones of diffracted reflexes. Their intersection with the perpendicular detector plane gives straight lines. If the incident radiation is parallel to a high symmetrical crystal axis, the diffraction spot pattern reproduces the axis symmetry, since the symmetry is reproduced by the disposition of the reciprocal-lattice planes. This readily permits the identification of important diffraction spots from the visual inspection of the symmetry. Relative angular positions are solved through the use of a special coordinate plate with hyperbolic meridians and parallels, called the Greninger net [38]. Fig. 4.10 shows a back-reflection Laue pattern for hexagonal ZrB_2 , with incident X-ray radiation parallel to the two-fold axis $[110]$. The spots vertical line is produced by the plane (001) .

4.3.2 Instrumentation

The experimental set up is illustrated in Fig. 4.11. It consists of a track mounted onto the tube tower of a commercial X-ray generator. A goniometer head is used for precise positioning of the crystal in the X-ray beam. A commercial camera Polaroid XR-7, model 57-3 is used. Tungsten target X-ray tubes are best suited for Laue, but any tube giving appreciable general radiation with or without characteristic radiation can be used. Sensitive films (approx. 3000

Figure 4.11: System for back-reflection Laue photographs to be mounted onto a X-ray tube tower. Crystal is adjustable in height, distance and angle through a movable goniometer.

Figure 4.12: Laue photographs as used to orient a LaIrIn_5 crystal in the $[001]$ direction.

ASA equivalent) should be used. An integral part of the camera is an intensifying screen with a high-speed, high-resolution phosphor coating³. During exposure the coating fluoresces, reproducing a visible light pattern. A hole in the center of the picture area permits the passage of the incident beam through the camera while a thin cover prevents the penetration of normal light. Four reference marks are present on the intensifying screen around the hole, two on the vertical axis and two on the horizontal axis. These are recorded as small distinct dots. The intersection of lines drawn between two pairs of dots locates the center of the photograph. To reduce the fogging from the secondary X-radiation emitted by the crystal, efficient filtering is obtained by using thin aluminium sheet in front of the film.

Laue images in this work are produced on Polaroid 9×12 cm black & white instant sheet films, model Polapan 57. A Cu tube with a 2 mm focal spot radiation was operated at 30 mA 30 kV using a Philips generator PW 1830. The radiation is additionally collimated at the entrance into the cassette by a pinhole 0.5 mm diameter 1 cm long nozzle. The crystal is placed at 3 cm distance from the film. Standard exposure time of 15 min was required. Some images were also produced with a new W tube, for which exposure time of 5 min was sufficient for accurate photographs. After exposure the film is withdrawn from the cassette and left to develop within its protective envelope. The procedure of developing transforms the negative film into print within seconds, permitting immediate analysis. Negative and print are shown in Fig. 4.10.

4.3.3 Orientation analysis of LaIrIn_5 samples

The Laue method was used as a quality test on crystals after the growth and in determining the orientation of crystals to be prepared for physical measurements. The procedure follows the analysis of the picture in relation to the required symmetrical pattern. Identification of particular high symmetry directions is considerably facilitated by use of tables from Laue atlas [81]. The use of the independent graduate circles of the goniometer head helps to set the reflection of

³Fluorazure.

Figure 4.13: Short wavelength diffraction condition in the reciprocal space (Ewald construction).

interest parallel to the incident beam, into the middle of the Laue image, thus moving the relative reciprocal vector parallel to the vertical axis of the goniometer head. Fig. 4.12 illustrates the procedure of orienting a LaIrIn_5 single crystal in the $[001]$ direction. The angular deviation was interpreted with use of the Greninger chart. The pictures are the scans of Laue photographs with inverted colours thus to enhance the reflection spots.

The oriented crystal is then directly transferred with the goniometer to a spark cutting machine. High accurately oriented samples, which are needed for electric transport or de Haas-van Alphen measurements, are then cut from the crystal.

4.4 Single crystal γ -ray diffraction

The γ -radiation, thanks to its high energy, is capable to easily penetrate matter without remarkable dispersions, thus becoming a best diffractive radiation for non-destructive analysis of materials and bulk perfection.

4.4.1 Theory

A particular characteristic of the nuclear emission of radiation is the relative long time of life (between days and years) of the excited states. Since the wavelength spread of the radiation emitted by the decay is inversely proportional to the life, γ spectral lines are very narrow, with typical spreads of $\frac{\Delta\lambda}{\lambda} \approx 10^{-6}$. The lines are generally well separated so that additionally monochromators are normally not necessary. At the same time great collimation on long distances can be achieved without loss of intensity.

Due to the intrinsic small wavelength of the γ -radiation, the diffraction angles from the Bragg condition (4.10) are consequently very small too and the scattering reciprocal-lattice vectors usually possess high Miller indices. In the vector relation of the Ewald construction, the Ewald sphere radius is much larger than a reciprocal vector, as Fig. 4.13 illustrates. A longitudinal scan of a scattering vector by multiple index, such as for the determination of the lattice parameters, is not accurate. But the transversal scan of a vector in order to investigate relative reflex positions is very precise, since the diffraction condition is very narrow by transpassing the Ewald

Figure 4.14: View of the γ -diffractometer.

sphere, compare Fig. 4.13. The consequent intensity distribution of a diffraction vector is called rocking curve.

4.4.2 Instrumentation

The work here presented was executed at the γ -diffractometer at the Institute of Physical Chemistry in Göttingen ⁴ [25], here illustrated in Fig. 4.14. The source is a commercial capsule with ^{192}Ir , as commonly available for non-destructive material testing. It is stored in a massive lead shielding. ^{192}Ir emits a series of spectral lines. The most intensive one, used in the experiments, has energy of 316 keV and wavelength $\lambda = 0.0392 \text{ \AA}$. The radiation is conducted to the

⁴University of Göttingen, IPC, Dept. of Physical Chemistry of Solids, Prof. Dr. G. Eckold.

Figure 4.15: Schematical functionality of the γ -diffractometer.

Figure 4.16: Rocking curve measured at the $hkl = 200$ reflection of the LaIrIn_5 crystal of Fig. 3.2. The side peaks indicate the mosaicity relative to the main peak $hkl = 200$.

sample along a collimating lead shielded tube, equipped with shutters and slit diaphragms. The divergence can be varied by shifting the source along the tube and by the choice of using diaphragms of different width. At a distance of 4 m to the sample and with diaphragms of 0.5 mm, the incident divergence of the radiation is $\delta_x = 0.014^\circ$ [25]. The sample on a goniometer is mounted on the diffractometer, as schematically shown in Fig. 4.15. It consists of a goniometer with two independent and high accurate rotators for the vertical rotation ω and the tilting ϕ of the sample. Both are precise to nearly 0.005° . The goniometer is mounted on a x -, y -translation stage for centering the sample. The y -translation permits the radiation to scan the sample in its length. The diffraction zone is surrounded by a lead shielding on nearly its complete length of 2 m. At this distance, the diffracted γ -radiation reaches the detector. A slit diaphragm protects from background radiation and scattering from the sample. The detector is a Ge crystal. The range of detection is between 40 keV and 10 MeV. The energy sensitivity permits the distinction of the different spectral lines. The detector system is mounted on a y -translational stage for perpendicular shifting from the direction of the incident radiation. The maximal shift is 25 cm, corresponding to a maximal diffraction angle of 7° . The absolute accuracy of the positioning system is 0.002° .

The measurement settings and the data collection are controlled with a computer interface.

4.4.3 Crystal homogeneity in LaIrIn_5 samples

The γ -ray diffraction is particularly useful for the analysis of the single crystal homogeneity in the big samples of LaIrIn_5 , where In inclusions and subgrains are noticed to grow.

Rocking-curve measurements reveal the relative angular misorientation of subgrain blocks and quantifies the mosaic distribution in the crystal. Rocking curves are measured by recording the scattered γ -ray intensity of a Bragg reflection, with scattering vector $\mathbf{K}_h$ and a fixed 2θ , while rotating the sample. This means a rotation of the reciprocal-lattice vector across the Ewald sphere around the vertical ω rotation axis, Fig. 4.13. If other mosaic blocks with the $\mathbf{K}_h$ vector lying in the plane would exist in the crystal, they would produce intensity peaks at a relative angle $\Delta\omega$, their misorientation. A total angular range of 0.3° was covered. Tilting the sample for several different azimuth angle ϕ settings, the rocking curves reveal the misorientation in other scattering planes. Additionally, the use of the y -translation permits the scanning of the sample on its length. In this way, and by investigating complementary Bragg reflections $\mathbf{K}_h$, a picture of the anisotropic mosaicity η_h of the crystal can be obtained.

Figure 4.17: Intensity maps of rocking curves of the reflection with diffraction vector [200] as function of position along the sample length for set $\phi = 0^\circ$ and $\phi = 90^\circ$ respectively.

The crystal illustrated in Fig. 3.2 was studied with the rocking procedure. A rocking curve for the diffraction vector [200] is shown in Fig. 4.16. The profile of the intensity was registered for two perpendicular scattering planes at $\phi = 0^\circ$ and $\phi = 90^\circ$ and across the full length of the crystal. The result is shown with the intensity colour maps of Fig. 4.17. Narrow, nearly Gaussian curves represent wide highly-perfect crystalline lattices. The wider rocking curves of the LaIrIn_5 sample show a less perfect crystal through its length. These curves display various kinds of deviations from the ideal narrow Gaussian profile, such as double and triple peaks or a wide shoulder of side peaks. Side peaks in the rocking curve are generated by single crystallites (mosaic blocks), the crystal lattices of which have a slightly different orientation than the main part of the sample (central peak). The angular separation $\delta\omega$ of the peaks in the rocking curve is a measure of the relative misorientation of the crystallites. Broad profiles of a single peak curve can be understood as the envelope function of a continuous distribution of small peaks or mosaic blocks with width η . In general, the measurable rocking-width values are given by a convolution of the sample mosaicity profile with the instrumental resolution function. Thus in the realistic case, many effects superimpose and the experimentally measurable width w is given in terms of the sample mosaicity η , the incident beam divergence δ_x , the wavelength spread $\frac{\Delta\lambda}{\lambda}$, the Bragg diffraction angle θ and the Darwin width w_D by the relation

$$w^2 = \eta^2 + \delta_x^2 + \left(\frac{\Delta\lambda}{\lambda}\right)^2 \tan^2\theta + w_D^2. \quad (4.24)$$

The Darwin width w_D is the theoretical width of a reflection for a hypothetical perfect crystal and a perfectly parallel and monochromatic radiation [59]. For the measurement setup used the parameters are $\delta_x = 0.014^\circ$, $\frac{\Delta\lambda}{\lambda} \tan\theta = 1.2 \cdot 10^{-7}$ and $w_D \approx 0.00001^\circ$. The cumulative effect of these instrumental contributions constitutes the lower limit of the measured rocking widths. It accounts for about 30% of the smallest measured full-width at half-maximum (FWHM) and for 10% of the experimental peak shifts. Thus the experimental peak widths are to be interpreted in terms of the crystal mosaicity η . Thus η of the peak $hkl = 200$ is estimated to be in average 0.05° , while side peaks reach shift values of 0.1° . The full-width at 10% of the maximum intensity (FW10M) gives a more representative measure in the case of wide shoulders and near side peaks. In this case values of 0.3° are found, hinting at the presence of many small strongly misoriented mosaic blocks.

A potential cause of peak broadening are lattice-parameter differences $\frac{\Delta d}{d}$, which cannot be distinguished from mosaicity. In the case of LaIrIn_5 , a stoichiometric phase, the variations are expected to be very small. The range can be estimated by comparing the measured parameters from single crystal diffraction of Section 4.2.4 with the values in the literature [60]. This contribution amounts to a maximum of $\Delta w = \frac{\Delta d}{d} \tan\theta = 0.00015^\circ$, thus not affecting the measured mosaicity η .

Fig. 4.18 shows a colour map of rocking curves measured in the middle of the same crystal but

Figure 4.18: Rocking-curves intensity map of the [003] diffraction vector reflection as function of the azimuthal rotation.

for a different reflection $hkl = 003$ and at different azimuth angles ϕ in the range $0^\circ - 360^\circ$. The horizontal angular distribution of the intensity gives the mosaicity relative to the peak $hkl = 003$ in the diffraction planes at ϕ , where $\phi = 0^\circ$ is arbitrary. The vertical angular distribution shows a 180° periodicity as it is expected for the azimuthal rotation of scattering planes. While all the curves show a single peak, the relative widths change in different scattering planes. Some side peaks can be superimposed to the main peak in a particular scattering geometry and in the plane of misorientation they appear separated. The values of FWHM range between 0.015° and 0.05° .

Considering also Fig. 4.16, where side peaks for [100] direction are also present at nearly 0.1° distance, the mosaic blocks seems to be less misoriented along the perpendicular [001] direction. This also demonstrates that crystal mosaicity can be highly anisotropic. In order to obtain representative description of a crystal mosaicity, measurements along non-coplanar directions of reciprocal space, at many positions of the crystal and for different scattering planes, are required. Actually, the relation of the anisotropy of mosaicity to the direction of crystal growth is not clear, because a preferential direction in LaIrIn_5 was not observed by the flux method.

The observation and evaluation of the mosaicity was fundamental in the choice and preparation of samples for the measurement of anisotropic physical properties of the electronic structure. Samples were cut from regions of high homogeneity, away from In inclusions, cavities and grain boundaries.

Chapter 5

Electric transport measurement

SUMMARY

The electronic structure determines the electrons behaviour in the charge transport. Relations to quantities of the electronic structure and lattice properties, like Fermi surface, Fermi velocities and Debye temperature involve model functions from the Bloch-Grüneisen-Einstein model parallel to transport theory concepts. Their description and analysis in Section 5.1 were partly previously published by the author [31]. The study of the models enables the interpretation of the data and the implementation of an analysis method, in order to determine the first results about the electronic structure of LaIrIn_5 from the measured transport properties illustrated in Section 5.5.

5.1 Theory

The Bloch-Grüneisen model

Matthiessen rule states that the measured resistivity ρ at a given temperature T consists of the temperature-dependent resistivity $\rho(T)$ and the temperature-independent residual resistivity ρ_o as

$$\rho = \rho_o + \rho(T) . \quad (5.1)$$

ρ_o is caused by impurities and crystal imperfections and $\rho(T)$ is due to electron scattering by lattice vibrations, when magnetic effects and/or impurities are not present.

In 1930 Bloch [14] developed a theory for the lattice resistance of a pure metal as a function of temperature which led to the formula

$$\rho(T) = (m-1) \rho' \Theta_D \cdot \left(\frac{T}{\Theta_D} \right)^m \cdot J_m\left(\frac{\Theta_D}{T}\right) \quad (5.2)$$

$$J_m\left(\frac{\Theta_D}{T}\right) = \int_0^{\Theta_D/T} \frac{z^m dz}{(e^z - 1)(1 - e^{-z})} \quad (5.3)$$

where $m = 5$ and $J_m(x)$ is another of the class of Debye integrals [52] for specific heat [108], (see Section 6.1). The temperature depending part of the resistivity has the form of the general Bloch-Grüneisen (BG) formula

$$\rho_{BG} = (m-1) \rho' T \cdot \left(\frac{T}{\Theta_D} \right)^{m-1} \cdot J_m\left(\frac{\Theta_D}{T}\right) \quad (5.4)$$

with $m \leq 5$ and $J_m(\frac{\Theta_D}{T})$ from Eq. (5.3), which can be simplified by transformations and substitutions¹ into

$$J_m\left(\frac{\Theta_D}{T}\right) = 2^{m-1} \int_0^{\Theta_D/2T} z^{m-2} \left[\frac{z}{\sinh z} \right]^2 dz. \quad (5.8)$$

Integral (5.8) cannot be solved analytically into a tractable function, but limiting curves are found. For $T > \Theta_D$, the expansion

$$\left[\frac{z}{\sinh z} \right]^2 = 1 - \frac{z^2}{3} + O(z^4) + \dots \quad (5.9)$$

approaches 1 rapidly and Eq. (5.8) can be integrated:

$$J_m\left(\frac{\Theta_D}{T}\right) = \frac{2^{m-1}}{m-1} \left[z^{m-1} \right]_0^{\Theta_D/2T}, \quad (5.10)$$

thus Eq. (5.4) becomes

$$\rho_{BG} = \rho' T. \quad (5.11)$$

For $T \leq 0.1 \Theta_D$, $J_m(\frac{\Theta_D}{T})$ tends to a definite numerical value j_m , thus the resistivity follows the Grüneisen empirical power law dependence [39]

$$\rho_{BG} = (m-1) j_m \rho' T \cdot \left(\frac{T}{\Theta_D} \right)^{m-1}. \quad (5.12)$$

The power index $m = 5$ for free-electron metals can assume values between 3 and 5 when including the quasi-particle effects, and reduces to 2 as disorder increases [17]. $m = 3$ is particularly associated to interband electron-phonon scattering [68, 106].

¹ The transformation consists of a series of substitutions applied when the Debye integral is expressed as in (5.3). The development of the integral (5.3) to

$$J_m\left(\frac{\Theta_D}{T}\right) = \int_0^{\Theta_D/T} \frac{z^m dz}{e^z + e^{-z} - 2}, \quad (5.5)$$

after considering that

$$\cosh z = \frac{e^z + e^{-z}}{2} \quad \text{and} \quad \sinh^2\left(\frac{z}{2}\right) = \frac{\cosh z - 1}{2}, \quad (5.6)$$

reduces into

$$\int_0^{\Theta_D/T} \frac{z^m}{2^2 \sinh^2\left(\frac{z}{2}\right)} dz = \int_0^{\Theta_D/T} z^{m-2} \left[\frac{\frac{z}{2}}{\sinh\left(\frac{z}{2}\right)} \right]^2 dz. \quad (5.7)$$

Using $\frac{z}{2}$ as the integration variable, $J_m(\frac{\Theta_D}{T})$ assumes the form in Eq. (5.8).

Figure 5.1: Numerical solution of the integral (5.8) as a function of reduced temperature $\frac{T}{T_0}$.

Figure 5.2: Numerical solution of the BG formula as a function of reduced temperature $\frac{T}{T_0}$.

The numerical solution of the integral (5.8) is represented in Fig. 5.1 as a function of reduced temperature $\frac{T}{T_o}$, together with the analytical limits. It thus permits the calculation of the total BG dependence through the formula (5.4). The result as a function of reduced temperature $\frac{T}{T_o}$ is shown in Fig. 5.2(a), together with the analytical limits (5.11) and (5.12). Eq. (5.4) (solid line) is calculated for $m = 5$, $\Theta_D = T_o$ and a given ρ' . Broken lines are the limiting curves (5.11) and (5.12). The first derivative of (5.4) and of the functions (5.11) and (5.12), scaled to the high temperature limit ρ' , are shown in Fig. 5.2(b). The numerical result of the BG formula predicts that the resistivity changes curvature at an inflection point inside the interval $\frac{\Theta_D}{4} < T < \Theta_D$. The first derivative has a maximum and decreases to the limit ρ' for $T > \Theta_D$. These informations are necessary for a correct interpretation of the measured resistivity curves. Measurements are commonly limited to temperature intervals $T \ll \Theta_D$, because of the usual Debye temperatures $\Theta_D < 400$ K of the intermetallic materials. Thus measurements lie commonly in the range of the maximum slope of the BG formula. When the Debye temperature is large, the maximum becomes flatter. In good approximation the derivative is considered constant above $\frac{\Theta_D}{4}$ and the resistivity is practically linearly dependent of the temperature.

The influence of the parameters Debye temperature Θ_D and index m on the BG formula is made clear once the Eq. (5.4) is scaled to the high temperature approximation Eq. (5.11)

$$\sigma_{BG} = \frac{\rho_{BG}}{\rho' T} \quad (5.13)$$

and is represented, as in Fig. 5.2(c) and 5.2(d), in dependence of the Debye temperature and of the index m respectively.

Figure 5.3: σ and σ_{BG} inflection characteristics as a function of Debye temperature and index m .

We found similarity to the Hill sigmoid function

$$\sigma = \frac{\left(\frac{T}{\Theta_D}\right)^{m-1}}{1 + \left(\frac{T}{\Theta_D}\right)^{m-1}}. \quad (5.14)$$

Both are step functions of temperature with a smooth change of curvature (positive maximum of the first derivative) at the inflection point T_i^{BG} and T_i respectively. Multiplication of the maximum derivative with the inflection point value results in the dimensionless inflection factor. Inflection point and factor are temperature independent functions of Θ_D and m . The details are illustrated in Fig. 5.3 for σ and for σ_{BG} . Inflection point T_i , function value $\sigma(T_i)$ and inflection factor of function (5.14) are compared with inflection point T_i^{BG} , function value $\sigma_{BG}(T_i^{BG})$ and inflection factor of function (5.13) respectively. (See also Fig. 5.2(c) and Fig. 5.2(d) for σ_{BG}). T_i shows a kind of direct proportionality with both Θ_D and m . The value of σ and of the inflection factor at T_i grow with m but are constant in Θ_D . It follows that increasing Θ_D (or T_i), the slope of σ at the inflection is inversely proportional to T_i . Fig. 5.3 also shows that σ_{BG} behaves like σ only for m between 2 and 3. T_i^{BG} , in contrast, has lower values so that the inflection factor gives such values a steeper maximum slope. For m larger than 3, the inflection point T_i^{BG} behaves differently than T_i and becomes independent from m . Also, the inflection factor is approximately constant with m , so that m has no influence in the actual maximum slope of σ_{BG} . The value of σ_{BG} at the inflection point reaches a local maximum for $3 < m < 4$.

The transport theory model

In the formal transport theory the kinetic method presented in [109] results in a simple expression of the electron average drift velocity

$$\langle \delta v \rangle = \frac{e v_x \tau}{\partial E / \partial v} E_x, \quad (5.15)$$

due to the energy gain ∂E in the applied electric field E_x along a crystal direction x and for the scattering relaxation time τ . For the N electrons per unit cell, this means a current density $j_x = N e \langle \delta v \rangle$, which defines the electrical conductivity

$$\sigma = \frac{N e^2 v_x \tau}{\partial E / \partial v} \quad (5.16)$$

of the macroscopic transport relation $\mathbf{j} = \boldsymbol{\sigma} \otimes \mathbf{E}$. The conductivity is generally a tensor which reduces to a scalar along high symmetry crystal directions and overall in crystals having cubic symmetry. Eq. (5.16) simplifies to the well known relation $\frac{N e^2 \tau}{m_e}$ for free-electron conductivity. Considering realistic quasi-particles energy bands $E_v(k)$, velocities $v_v(k)$ and density of states $n(E)$, for which the density-of-states equations 2.18 and 2.19 are valid, we obtain the general relation

$$\sigma = 2 n(E_F) \langle v_x^2 \rangle e^2 \tau. \quad (5.17)$$

$n(E_F) \langle v_x^2 \rangle$ is the weighted mean square velocity, averaged over the density of states for given spin-direction at the Fermi-level,

$$n(E_F) \langle v_x^2 \rangle = \int_0^{v_F} n(E) v_x dv \cong \sum_{v,k} v_x^2(k) \delta(E_F - E_v(k)), \quad (5.18)$$

and τ the electron relaxation time for impurity and phonon dominated scattering

$$\frac{1}{\tau} = \frac{1}{\tau^{imp}} + \frac{1}{\tau^{ep}} + \dots, \quad (5.19)$$

both evaluated in the applied electric field E_x direction. For a complete discussion see [9] for example. Here τ^{imp} is a temperature independent term, while τ^{ep} is the temperature dependent term for the electron-phonon interaction.

F.J. Pinski, P.B. Allen and W.H. Butler [78] presented calculations in the lowest-order variational approximation (LOVA), which show the use of realistic phonons, energy bands, and matrix elements for the scattering time τ^{ep} , as opposed to traditional approximations such as the BG formula. The resulting LOVA formula for (6.17) is

$$\frac{1}{\tau^{ep}} = \frac{2\pi k_B T}{\hbar} 2 \int_0^\infty \frac{d\omega}{\omega} \alpha^2(\omega) F(\omega) \frac{x^2}{\sinh^2 x} \quad (5.20)$$

with $x = \frac{\hbar\omega}{2k_B T}$, ω the phonon frequency. The integral is evaluated in terms of the transport spectral function $\alpha_{tr}^2(\omega)F(\omega)$ which is analogous to the electron-phonon spectral function of the superconductivity theory [87] and defined in [65]. Therefore, after (5.17) and (5.20), the LOVA expression for the electrical resistivity is

$$\rho^{ep} = \frac{2\pi k_B T}{\hbar n(E_F) \langle v_x^2 \rangle e^2} \int_0^\infty \frac{d\omega}{\omega} \alpha_{tr}^2(\omega) F(\omega) \frac{x^2}{\sinh^2 x}, \quad (5.21)$$

which is also known as the Boltzmann equation. By analogy with the superconducting notation, the parameter λ_{tr} is defined as follows

$$\lambda_{tr} = 2 \int_0^\infty \frac{d\omega}{\omega} \alpha_{tr}^2(\omega) F(\omega). \quad (5.22)$$

The parameter λ_{tr} is the transport analogous of the dimensionless parameter λ which determines the superconducting transition temperature T_c [65].

In the high temperature limit (small x) the series expansion of $\frac{x^2}{\sinh^2 x}$ is conveniently used in Eq. (5.20)

$$\frac{1}{\tau^{ep}} = \frac{2\pi k_B T}{\hbar} 2 \int_0^\infty \frac{d\omega}{\omega} \alpha^2(\omega) F(\omega) \left[1 - \frac{1}{3} \left(\frac{\hbar\omega}{2k_B T} \right)^2 + \dots \right] \quad (5.23)$$

and again by analogy to (5.22) we introduce the definition

$$\lambda_{tr} \langle \omega^n \rangle_{tr} = 2 \int_0^\infty d\omega \omega^{n-1} \alpha_{tr}^2(\omega) F(\omega). \quad (5.24)$$

$\langle \omega^n \rangle_{tr}$ is a weighted mean phonon frequency at the n -th order. It follows that at high temperatures Eq. (5.20) and Eq. (5.21) become respectively

$$\frac{1}{\tau^{ep}} = \frac{2\pi k_B T}{\hbar} \lambda_{tr} \left[1 - \frac{\hbar^2 \langle \omega^2 \rangle_{tr}}{12 k_B^2 T^2} + \dots \right] \quad (5.25)$$

$$\rho^{ep} = \frac{2\pi k_B T}{2\hbar n(E_F) \langle v_x^2 \rangle e^2} \lambda_{tr} \left[1 - \frac{\hbar^2 \langle \omega^2 \rangle_{tr}}{12 k_B^2 T^2} + \dots \right]. \quad (5.26)$$

Considering that in the LOVA procedure a typical phonon energy $k_B \Theta_D = \hbar \omega_D$ leads to the identification $\omega_D^2 = \frac{3}{2} \langle \omega^2 \rangle_{tr}$, we found a relation for the high temperature interval $T \geq \frac{\Theta_D}{2}$. For these temperatures all the terms in the expansion can be neglected and equations (5.25) and (5.26) reduce to a linear temperature dependence

$$\frac{1}{\tau^{ep}} = \frac{2\pi k_B T}{\hbar} \lambda_{tr} \quad (5.27)$$

$$\rho^{ep} = \frac{2\pi k_B T}{2\hbar n(E_F) \langle v_x^2 \rangle e^2} \lambda_{tr}. \quad (5.28)$$

Equation (5.28) is a modern version of the equation (5.2) or (5.4) derived earlier by Bloch. It is generalized to include realistic (nonspherical) energy bands, phonons and electron-phonon matrix elements but it is based on a model employing Debye phonons, a spherical Fermi surface and deformation-potential electron-phonon coupling via longitudinal phonons only, with no umklapp scattering [78]. Thus, assuming a spherical Fermi surface, the factor $v_x^2(k)$ in Eq. (5.18) can be replaced by a constant v_F^2 . The integrals that conduce to the transport spectral function result in the Debye approximation in

$$\alpha_{tr}^2(\omega)F_D(\omega) = 2\lambda_D \left(\frac{\omega}{\omega_D}\right)^4 \Theta(\omega_D - \omega), \quad (5.29)$$

where ω_D is the Debye frequency, $\lambda_D \approx \lambda_{tr}$. The step function $\Theta(\omega_D - \omega)$ is equal to unity for $0 < \omega < \omega_D$ and zero outside. For a comparison of Eq. (5.29) with real spectral functions see [78].

Using the spectral function (5.29), the expression for the resistivity (5.21) becomes

$$\rho_D = \frac{2\pi k_B T}{\hbar n(E_F) \langle v_x^2 \rangle e^2} \int_0^{\omega_D} \frac{d\omega}{\omega} \frac{x^2}{\sinh^2 x} 2\lambda_{tr} \left(\frac{\omega}{\omega_D}\right)^4. \quad (5.30)$$

Elementary substitutions² transform it into

$$\rho_D = \frac{2\pi k_B T}{2\hbar n(E_F) \langle v_x^2 \rangle e^2} \lambda_{tr} 4 \left(\frac{T}{\Theta_D}\right)^4 2^4 \int_0^{\frac{\Theta_D}{2T}} x^3 \frac{x^2}{\sinh^2 x} dx, \quad (5.31)$$

which reproduces equation ρ_{BG} in (5.4) for $m = 5$, thus giving an expression for the temperature coefficient

$$\rho' = \frac{2\pi k_B}{2\hbar n(E_F) \langle v_x^2 \rangle e^2} \lambda_{tr}. \quad (5.32)$$

Although Eq. (5.31) for the resistivity is based on a highly simplified model, it captures the correct trends of the temperature dependence and, considering Eq. (5.28), reproduces the LOVA calculated result in the high temperature limit

$$\rho^{ep} \cong \rho_D = \rho_{BG} = \rho' T. \quad (5.33)$$

The electrical resistivity of a crystalline metal is related to the quasi-particle transport scattering rate $\frac{1}{\tau}$ and the Drude plasma frequency Ω_p with

$$\rho = \frac{1}{\epsilon_0 \Omega_p^2 \tau}, \quad (5.34)$$

according to the Drude relation [48]. Considering ρ to stand for the lattice resistance $\rho(T)$, $\frac{1}{\tau}$ can then be related to the transport electron-phonon coupling parameter λ_{tr} through the high-temperature expansion (5.25), thus leading in the linear region [64] to

$$\rho(T) = \frac{2\pi k_B T}{\hbar \epsilon_0 \Omega_p^2} \lambda_{tr} \quad (5.35)$$

and in general after (5.33) to

$$\frac{\partial \rho}{\partial T} = \frac{2\pi k_B}{\hbar \epsilon_0 \Omega_p^2} \lambda_{tr} = \rho'. \quad (5.36)$$

As seen in the previous numerical analysis of the Bloch-Grüneisen formula, considering equation (5.36) in the range $T > \frac{\Theta_D}{4}$, the first derivative approximates ρ' of Eq. (5.11) and also the

² The substitution in (5.30) of the integration variable $\omega \rightarrow x = \frac{\hbar\omega}{2k_B T}$ and the introduction of the Debye frequency $\omega_D = \frac{k_B}{\hbar} \Theta_D$ produces the resistivity formula (5.31).

constant λ_{tr} at an upper limit. But if the plasma frequency Ω_p is known from energy-band theory calculations or optical measurements, Eq. (5.36) can be introduced into Eq. (5.4) and be used in a least-squares method (Section 5.5.2) to obtain from an experimental curve of ρ , empirical values of Debye temperature and electron-phonon coupling constant as fitting parameters.

If the material is superconducting, the resulting λ_{tr} may then be compared with a value for λ obtained from the experimental T_c according to the McMillan equation [65]

$$T_c = \frac{\Theta_D}{1.45} \exp\left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right). \quad (5.37)$$

Θ_D is the Debye temperature and μ^* is the Coulomb pseudopotential strength representing a repulsive electron-electron interaction. It was shown by R.C. Dynes [21] that the agreement between the calculated T_c and the experimental values of the transition temperatures of a large number of elements and compounds can be considerably enhanced by replacing the prefactor $\frac{\Theta_D}{1.45}$ of the McMillan equation (5.37) by $\frac{\hbar\langle\omega\rangle}{1.2k_B}$. The average phonon energy $\hbar\langle\omega\rangle$ is related to the transport electron-phonon coupling constant λ_{tr} of Eq. (5.22) and defined by [21] with

$$\hbar\langle\omega\rangle = \frac{\int_0^\infty \alpha_{tr}^2(\omega)F(\omega) d\omega}{\int_0^\infty \frac{\alpha_{tr}^2(\omega)F(\omega) d\omega}{\hbar\omega}}. \quad (5.38)$$

This reflects the fact that $\hbar\langle\omega\rangle$ is one particular way of weighting the whole phonon spectrum, whereas Θ_D , if calculated from the Bloch-Grüneisen or low-temperature heat capacity, is determined by the shape of $F(\omega)$ at extremely low energies. For the superconducting elements the calculated values of T_c from the Dynes-corrected McMillan equation are typically smaller than the T_c values from the McMillan equation by a factor of 1.5 – 2.0.

Developing the model: optical-phonons contribution

Since LaIrIn₅ has more than one atom per unit cell, it is likely that an additional scattering due to highly energetic optical mode phonons [53] occurs. To take the optical-phonon contribution explicitly into account [67, 5, 63], the transport spectral function of the general Boltzmann expression for the resistivity (5.21) is extended to

$$\alpha_{tr}^2(\omega)F(\omega) = \alpha_{tr}^2(\omega)F_D(\omega) + \alpha_{tr}^2(\omega)F_E(\omega), \quad (5.39)$$

thus distinguishing the acoustic and optical phonon dominated scattering

$$\frac{1}{\tau^{ep}} \cong \frac{1}{\tau_D} + \frac{1}{\tau_E}, \quad (5.40)$$

because of the assumption that the contributions from acoustic and optical modes are additive (Matthiessen rule). The first term of (5.39) is the Debye approximation (5.29) which results in the BG equation (5.31), the second term represents the Einstein approximation

$$\alpha_{tr}^2(\omega)F_E(\omega) = \frac{1}{2}\lambda_E \omega_E \delta(\omega - \omega_E), \quad (5.41)$$

with ω_E a characteristic Einstein phonon frequency, λ_E the electron-phonon coupling constant for the Einstein phonons and $\delta(\omega - \omega_E)$ a delta-function at $\omega = \omega_E$. For a comparison with the complete spectral function, see [6].

In analogy with (5.30), the optical mode term of the resistivity becomes

$$\rho_E = \frac{2\pi k_B T}{\hbar n(E_F) \langle v_x^2 \rangle e^2} \int_0^{\omega_{max}} \frac{d\omega}{\omega} \frac{x^2}{\sinh^2 x} \frac{1}{2} \lambda_E \omega_E \delta(\omega - \omega_E). \quad (5.42)$$

The resistivity formula can be easily written ³ as

Figure 5.4: The Einstein formula as a function of the reduced temperature $\frac{T}{T_1}$ in comparison with the Bloch-Grüneisen function of Fig. 5.2.

$$\rho_E = \frac{2\pi k_B T}{2\hbar n(E_F) \langle v_x^2 \rangle e^2} \lambda_E \frac{\left(\frac{\Theta_E}{2T}\right)^2}{\sinh^2\left(\frac{\Theta_E}{2T}\right)}, \quad (5.45)$$

which we call the Einstein formula. The result is illustrated in Fig. 5.4(a) as a function of the reduced temperature $\frac{T}{T_1}$ in comparison with the Bloch-Grüneisen function of Fig. 5.2 for $m = 5$, $\rho'_E = \rho'$, $\Theta_E = 2 \Theta_D$ (solid lines). Dotted lines are the respective high temperature limiting curves ρ'_E and ρ' . In analogy to the Bloch-Grüneisen for high temperatures, we substituted the last term of (5.45) with the series expansion (5.9). At $T > \Theta_E$, Eq. (5.45) is a linear function

$$\rho_E = \rho'_E T \quad \text{with} \quad \rho'_E = \frac{2\pi k_B}{2\hbar n(E_F) \langle v_x^2 \rangle e^2} \lambda_E. \quad (5.46)$$

³ ← After writing the integration variable of (5.42) explicitly, $\omega = \frac{2k_B T}{\hbar \omega} x$, and introducing the Einstein frequency as $\omega_E = \frac{k_B}{\hbar} \Theta_E$, the use of the relation $\delta(kx) = \frac{1}{|k|} \delta(x)$ transforms the delta function into

$$\delta(\omega - \omega_E) = \frac{\hbar}{2k_B T} \delta\left(x - \frac{\Theta_E}{2T}\right). \quad (5.43)$$

Considering that

$$\int_{-\infty}^{+\infty} f(x) \delta(x - a) dx = f(a) \quad \text{with} \quad -\infty < a < +\infty, \quad (5.44)$$

the resistivity formula reduces to (5.45).

A comparison of the first derivatives of functions (5.45) and (5.4), scaled to the high temperature limits ρ'_E and ρ' respectively, are shown in Fig. 5.2(b).

At intermediate temperatures, the second order term of the expansion (5.9) must be considered and the Einstein resistivity can be approximated with

$$\rho_E = \rho'_E T \left[1 - \frac{\Theta_E^2}{12T^2} \right], \quad (5.47)$$

an inverse function of the type $aT - bT^{-1}$.

At very low temperatures $T < 0.1 \Theta_E$, the terms of higher order cannot be neglected and a better approximation can be reached with the exponential representation

$$\rho_E = 2\rho'_E T \frac{\left(\frac{\Theta_E}{T}\right)^2}{\frac{1}{2}e^{\frac{\Theta_E}{T}} - 1}. \quad (5.48)$$

The limit curves and function (5.45) are scaled to Eq. (5.46) and are represented in Fig. 5.4(c), in analogy to Fig. 5.2(c) for the function (5.13) (solid lines). The Einstein term is also compared to the approximating functions (5.47) and (5.48) for middle-high and low temperature range (dashed lines). This procedure permitted the isolation of the sigmoid term dependent on the parameter Θ_E

$$\sigma_E = \frac{\left(\frac{\Theta_E}{2T}\right)^2}{\sinh^2\left(\frac{\Theta_E}{2T}\right)}. \quad (5.49)$$

Figure 5.5: σ_E inflection characteristics as a function of Einstein temperature.

Fig. 5.5 shows the characteristics of σ_E . Plots for the inflection point T_i^E , function value $\sigma_E(T_i^E)$ and inflection factor of the function (5.49) are compared with the characteristics of σ_{BG} , see Fig. 5.4(c). The representation agrees with Fig. 5.3, although σ_E does not depend on the index m . The inflection point T_i^E increases more rapidly with the temperature parameter, see Fig. 5.4(c). The value of σ_E and of the inflection factor at T_i^E are constant and comparable to the constant values of σ_{BG} for $m > 3$. It follows that the inflection factor gives, in the physically significant interval $\Theta_E > \Theta_D$, a smaller slope at the inflection point, except for $m \approx 2$. The use of the spectral function (5.39) leads, with relations (5.40), (5.34) and (5.35), to very important relations

$$\rho^{ep} \cong \rho_{BG} + \rho_E \quad (5.50)$$

$$\lambda_{tr} \cong \lambda_D + \lambda_E = \frac{\hbar \epsilon_0 \Omega_p^2}{2\pi k_B} (\rho' + \rho'_E). \quad (5.51)$$

Thus considering the composition of the two formulas (5.4) and (5.45) for the resistivity, one can obtain the total electron-phonon coupling by summation of the single terms.

5.2 The measurement technique

The resistivity measurement is made by passing a known current through the sample and measuring the voltage drop across the sample in one direction, usually in the current direction. The resistivity ρ of the sample is thus calculated by the Ohm's law

$$\rho = \frac{A}{l} \frac{\mathcal{V}}{I}, \quad (5.52)$$

where $\mathcal{V}$ is the measured voltage drop across the sample and I the current through the sample. The other two parameters are fixed: l is the voltage lead separation and A the cross-sectional area through which the current passes.

Resistivity measurements take particular advantage from the alternating current four-terminal option. The geometric configuration requires that two leads pass the current through the sample and two separate leads are used to measure the potential drop through the sample. The voltage leads draw very little current, so the current applied through the sample and the potential drop measured across the sample are known with a high degree of accuracy, virtually eliminating the effects of lead and contact resistance. The alternating bias current, selectable from 1 Hz up to 1 kHz, provides greater measurement sensitivity than the direct current option because filtering and phase sensitive detection of the signal voltage can be employed. For a sampling current

$$I = I_o e^{i\omega t}, \quad (5.53)$$

with I_o resistively stabilized, so that I_o remains constant during the measurement, the voltage response has a form similar to the driving form. The voltage component of frequency ω

$$\mathcal{V} = \mathcal{V}_o e^{i\phi} e^{i\omega t}, \quad (5.54)$$

is isolated by appropriate filtering from all the other components of the sample signal, frequency-dependent noise, and instrumental offset and drift. Phase sensitive detection permits to solve the amplitude $\mathcal{V}_o$ with its dephasing factor. Insertion of I_o and $\mathcal{V}_o$ in formula (5.52) gives the resistivity of the sample.

Nevertheless, when the frequency is commensurate with the power line and its harmonics, noise effects result and it should be avoided while measuring very small signals.

5.3 Cryogenic facility and experiment control

The measurement system available is constituted of a commercial cryogenic can, equipped with a vertical track, on which a travelling holder is driven by a step motor and an endless screw. When the long probe is mounted, the holder drives the sample into the exchange gas of the liquid-helium bath of the cryostat. Thus, temperatures from room ambient to 4.2 K are performed. The probe is a long sealed stainless steel tube which conveys the conduction leads and supports the sample holder. The sample holder is a capsule of copper, where a Si diode thermometer⁴ and the sample are mounted. The system is fully automated, with control of a lock-in phase-sensitive detector, the thermometer hardware and the step motor.

5.4 Data analysis

The measured data set of the sample electric resistivity $\rho(T)$ is conveniently plotted as a function of temperature T . At low temperatures a power dependence is expected. At high temperatures the dependence is linear. In the total temperature range the resistivity follows the Bloch-Grüneisen expression, refer to Section 5.1. A least-squares fit permits the estimation of the values of the transport parameters like Debye temperature Θ_D and Einstein temperature Θ_E and the temperature coefficients ρ' from which the quasi-particle coupling constants are deduced.

5.5 Electrical resistivity of LaIrIn₅

The anisotropy of the resistivity in LaIrIn₅ was measured as a function of temperature using the four-terminal technique.

5.5.1 Sample preparation

Because the big dimensions of the crystals available, bar-shaped samples with axis in the principal crystal directions [001] and [100] were preferred for accurate resistivity measurement. Particularly, regular faces of the large crystal in Fig. 3.1 were cut with flat spark erosion and analysed for perfection. Wet etching with HCl removed the *In* inclusions, when present. The most homogeneous zone was oriented with the Laue method, as illustrated in Section 4.3. Thus using spark erosion, bar-shaped samples of dimensions approximately $0.5 \times 0.5 \times 5 \text{ mm}^3$ were cut. The sample with axis parallel to the [100] direction is shown in Fig. 5.6. By this sample geometry the current leads are easily attached to contact the entire ends of the sample. This configuration of the current leads passes a more uniform current through the sample. Then, the voltage leads contact the sample in-line and parallel to the ends, Fig. 5.6, in order to maximize the potential drop length l . Additionally, thanks to the sample geometry, is $l \gg \sqrt{A}$, which enhances the resolution of the resistivity from equation (5.52). The voltage contact surface must be narrow, thus thin copper leads (50 – 125 μm diameter) are curled around the sample. Silver paste was used to patch the copper leads onto the sample. Soft-soldering contacts them onto the sample chip to be mounted in the probe capsule. At room temperature, the contacts should be tested for low resistivity: values between 0.5 – 1 Ω are required. Intermetallic compounds can also be contacted by soft-soldering, when the silver paint does

⁴Lakeshore.

Figure 5.6: Bar-shaped sample cut from a planar face of crystal in Fig. 3.1. Detail of the sample on the measurement chip.

not cover the surface. Two pairs of narrow nickel stripes must be previously electrolytically plated around the samples at their ends, then, the copper leads can be soft-soldered around the samples on to these stripes, producing very narrow contacts. The use of nickel improves the wetting action of the solder to the contacts. Lowest resistance contacts are necessary for very low temperature electrical measurements, in order to reduce warming effects and a temperature gradient to the thermometer clamped next to the sample.

5.5.2 Data interpretation

The electrical resistivities measured for current flow $\mathbf{I}$ along the $[001]$ and $[100]$ axes show a characteristic “simple metal” temperature dependence and exhibit very little anisotropy, as expected from the density-of-states and band structure calculations reported in sections 2.2.2 and 2.2.3.

Figure 5.7: Rescaled resistivity curves of LaIrIn_5 crystal samples for current flow $\mathbf{I}$ parallel to direction $[100]$ in the low temperature range down to 4.2 K.

Figure 5.8: Temperature dependence of the resistivity of LaIrIn₅ for current flow **I** parallel to direction [100] down to 4.2 K (cooling curve). Inset: the low temperature resistivity.

Measurements down to 4.2 K for the resistivity in the direction [100] delivered different values of the residual resistivity ratio $RRR = \rho(300\text{K})/\rho(4.2\text{K})$ of about 125, 340 and 450, which can be considered as a measure of the quality of the crystal samples. A comparison of their rescaled resistivities $\rho(T)/\rho(300\text{K})$ in the low temperature range is illustrated in Fig. 5.7. The sample shown in Fig. 5.8 delivers the small residual resistivity $\rho_o \approx 0.03 \mu\Omega\text{cm}$ and the very large residual resistivity ratio $RRR \approx 560$, indicating the high quality of the crystal sample. Thus it was considered for electronic structure characterization.

By fitting Eq. (5.11) to the data set of Fig. 5.8 inside $\frac{\Theta_D}{4} < T < \Theta_D$, as is often done in the literature [63, 64], the resulting value ρ' is close to the maximum of the slope, compare Fig. 5.2(a) and Fig. 5.2(b). The resistivity curve of LaIrIn₅ in Fig. 5.8 has a linear temperature dependence above $T \approx 140$ K, with a temperature coefficient ρ' of nearly $0.05 \mu\Omega\text{cm/K}$. According to the extended linearity condition for $T \geq \Theta_D/4$, we would obtain a Debye temperature $\Theta_D \approx 560$ K. But this is only a qualitative estimation. As discussed in the previous Section 5.1, by a large Θ_D the temperature interval of the measurement is usually insufficient for a comparison with the linear function (5.11) and, in general, an estimation of Θ_D through graphical interpretation of the linearity is not reliable [63].

A more precise evaluation of Θ_D follows from numerical analysis of the data on the basis of equations (5.4) and (5.8) with a fitting procedure, where the parameters are m , ρ' and Θ_D . Their physical interpretation was previously developed from the electrical transport theory presented in the Section 5.1. The temperature dependence of the resistivity curves was fitted in two steps to the function (5.1) using for $\rho(T)$ the BG limit (5.12) and then formula (5.4) with (5.8). The least-squares method minimizes the mean squared error

$$S(m, \rho', \Theta_D) = \frac{1}{N-2} \sum_k \left(\rho_{calc}(T_k) - \rho_{interp}(T_k) \right)^2 \quad (5.55)$$

between the calculated resistivities and the linear interpolated data values at a regular mesh of N sampling temperatures T_k . The total relative error of the best fit is

$$\bar{S}(m, \rho', \Theta_D) = \frac{1}{N-2} \sum_k \left(\frac{\rho_{calc}(T_k) - \rho_{interp}(T_k)}{\rho_{calc}(T_k)} \right)^2, \quad (5.56)$$

that would be zero if a true solution existed. Up to nearly 30 K the curve is well fitted by the

Figure 5.9: Low temperature resistivity of LaIrIn₅ and the fitted Bloch-Grüneisen function in the low temperature limit (5.12).

power law (5.12) $\rho = \rho_o + a \cdot T^m$ with $m = 3.4$, as can be seen in Fig. 5.9(a). Fig. 5.9(b) shows the relative deviations of the experimental data from the fit. The complete data set was then fitted to the Bloch-Grüneisen function (5.4), using the fixed $m = 3.4$ as to reduce the number of fitting parameters. We obtained the best fitting curve with the parameters listed in Tab. 5.1 [82]. The result is shown in Fig. 5.10(a). In Fig. 5.10(b) the relative deviation of the experimental data from the fit is illustrated. The bars indicate intervals of maximum or growing deviation. The fit reproduces the experimental curves very well, except for deviations between 1 and 15 % in the temperature interval from 25 to 75 K and above 250 K, see Fig. 5.10(b). This is due to the

direction	residual resistivity	BG-fit	error
I [100]	$\rho_o = 0.0268 \mu\Omega\text{cm}$ $RRR = 556$	$m = [3.4]$ $\rho' = 0.0506 \mu\Omega\text{cm/K}$ $\Theta_D = 235.4 \text{ K}$	$\bar{S} = 2 \cdot 10^{-3}$

Table 5.1: Resistivity parameters from the fitted Bloch-Grüneisen function. The m value in square brackets is held constant during the fitting procedure.

Figure 5.10: Resistivity of LaIrIn_5 and the fitted total Bloch-Grüneisen function.

change of curvature in the BG curve around $\Theta/4$, as shown in Fig. 5.2.a and Fig. 5.2.b, which is not completely reproduced from the data. With increasing temperature, the deviation from the BG increases monotonically. Since LaIrIn_5 has more than one atom per unit cell, it is likely that an additional scattering due to highly energetic optical mode phonons [53] occurs, which causes the steady departure of the data from the Bloch-Grüneisen behaviour with increasing temperature. The BG model represents for LaIrIn_5 an approximation and the Einstein term should be introduced in order to complete the model. The resistivity data are analysed using the expression (5.1) extended with (5.50) to

$$\rho = \rho_o + \rho_{BG} + \rho_E. \quad (5.57)$$

Equation (5.57) is fitted to the data using the previous least-squares method for the Bloch-Grüneisen formula. Fitting parameters are now ρ' , Θ_D , ρ'_E , Θ_E , while $m = 3.4$ is fixed. We obtained the best fitting curves with the parameters listed in Tab. 5.2. The result is shown in Fig. 5.11(a). Fig. 5.11(b) shows the relative deviation of the experimental data from the fit. The fitting is considerably improved in comparison to the previous calculation for Fig. 5.10, which refers to the same wide temperature range.

The obtained $\Theta_D = 223$ K in this approximation refines the estimation from a simple Bloch-Grüneisen approximation, and is closer to 218.7 K obtained from the specific heat measurement of one sample of the same crystal, compare with Section 6.5. The deviation of the fit from the data is considerably reduced and equally distributed around zero in the wide range above 75

Figure 5.11: Resistivity of LaIrIn₅ and the fitted function with the Bloch-Grüneisen and the Einstein terms.

K, and at low temperatures it amounts to 4 – 6 %.

Total electron-phonon coupling constant in LaIrIn₅

Considering the two analogous expressions (5.32) and (5.36) for the resistivity temperature coefficient, the relation for the plasma frequency

$$\hbar \epsilon_0 \Omega_p^2 = 2 \hbar n(E_F) \langle v_x^2 \rangle e^2 \quad (5.58)$$

explicitly relates the plasma frequency, actually an experimental quantity from optical experiments, to quantities from band-structure calculations. Then together with the Debye and Einstein formulation of the total temperature coefficient (5.51), the transport coupling constant λ_{tr} is obtained.

In Eq. (5.58), the density of states at the Fermi energy is given by $n(E_F) = 2.33 \frac{\text{states}}{V_e \text{ eV}}$. The average square velocity is the average of the square Fermi velocities components $v_{F,[100]}^2$, over the bands ν , following formula (5.18). Referring to the considerations about velocities and Fermi surface in Section 2.1.2, we regarded only the places of the Fermi surface in LaIrIn₅ with the gradient in direction [100], thus the corresponding velocities were calculated by derivation of

direction	BG E-fit	error	el. - ph. properties
$\mathbf{I} \parallel [100]$			$\langle v_{F,[100]}^2 \rangle = 3.4 \cdot 10^5 \frac{\text{m}}{\text{s}}$
			$n(E_F) = [2.33] \frac{\text{states}}{\text{V}_c \text{ eV}}$
	$m = [3.4]$	$\bar{S} = 3 \cdot 10^{-4}$	$\hbar\Omega_p = 5.189 \text{ eV}$
	$\rho' = 0.05 \frac{\mu\Omega \text{ cm}}{\text{K}}$		$\lambda_D = 0.316$
	$\Theta_D = 223 \text{ K}$		
	$\rho'_E = 3.8 \cdot 10^{-3} \frac{\mu\Omega \text{ cm}}{\text{K}}$		$\lambda_E = 0.024$
	$\Theta_E = 1129 \text{ K}$		
coupling constant :			$\lambda_{tr} = 0.34$

Table 5.2: Resistivity parameters from the fitted Bloch-Grüneisen-Einstein function. Values in square brackets are held constant during the fit.

the relative band dispersion curves at E_F in accordance to the definition of band velocity (2.49). The average over the bands is then approximated to the average over these values and gives $\langle v_{F,[100]}^2 \rangle = 3.4 \cdot 10^5 \frac{\text{m}}{\text{s}}$. From relation (5.58) follows a plasma frequency $\hbar\Omega_p$ of 5.189 eV, which is consistent to the common value of 5 eV for related intermetallic compounds [77]. Thus, λ_D and λ_E estimated from Eq. (5.51) are 0.316 and 0.024 respectively for the [100]-direction coupling, giving a total coupling constant of 0.34. The results are listed in Tab. 5.2.

In analogy to other layered crystal structures ([31] and references therein), λ_D is likely to quantify the coupling to in-plane vibrations, while λ_E is the coupling to the out-of-plane vibrations and the relative vibrations of the elements sublattices. In LaIrIn_5 , the smaller λ for the Einstein phonons indicates a negligible contribution of the optical phonons in the total electron-phonon coupling. The coupling to the acoustic modes alone is in LaIrIn_5 a factor 13 larger than the coupling to the optical mode. This conclusion is a confirmation of the strong anisotropy of the atomic thermal vibration illustrated by crystal structure refinement of X-ray diffraction data, Section 4.2.4. The in-plane vibration of the $\text{In}(4i)$ atoms is in fact predominant, as shown with the displacement ellipsoids in Fig. 4.8. Additionally, from Section 2.2.2 and following, the $\text{In}(4i)$ 5p states constitute the prevalent component of the density of states at the Fermi energy, thus giving also a dominant contribution to the in-plane conductivity.

A direct comparison with In based intermetallic compounds is not possible, because the complete set of transport properties is not available, except for specifications about RRR ranging between 350 – 1350 [91] for the series LaTMIn_5 ($TM = \text{Co}, \text{Rh}, \text{Ir}$) and the value of T_c , when existing in the range 0.4 – 2.3 K with Ce as rare-earth element.

Chapter 6

Heat capacity measurement

SUMMARY

The electronic structure determines the electrons behaviour in the heat capacity. Relations to quantities of the electronic structure and lattice properties, like Fermi surface, density of states and Debye temperature involve model functions from the Debye and the Einstein model. Their description and revision in Section 6.1 in terms of the electronic structure quantities enables the interpretation of the data, in order to determine results of the electronic structure of LaIrIn_5 from the measured heat transport properties illustrated in Section 6.5.

At low temperatures the total heat capacity of a crystal consists of the sum of two terms:

$$C = \gamma T + bT^3, \quad (6.1)$$

the γT term arising from the conduction electrons and depending on the density of states at the Fermi energy $n(E_F)$ (2.18) with

$$\gamma = \frac{\pi^2}{3} N_A k_B^2 n(E_F). \quad (6.2)$$

N_A and k_B are the Avogadro and the Boltzmann constant respectively.

The bT^3 term introduces the contribution from the lattice vibrations (phonons) through their

Debye temperature Θ_D and the number of atoms in the unit cell n_c with

$$b = \frac{12 \pi^2}{5} N_A k_B \frac{n_c}{\Theta_D^3} . \quad (6.3)$$

ω_D being the maximum phonon frequency, $\Theta_D = \hbar \omega_D$ is a measure of the temperature above which all modes begin to be excited, and below which modes begin to be "frozen". At sufficiently low temperatures $T \ll \Theta_D$ the linear term of the electronic contribution is dominant, so that the experimental determination of the coefficient γ is most accurately carried out at very low temperatures.

The quasi-particle nature is more properly the characteristic assigned to the electrons in a solid. It is used to include real interactions that enhance the calculated density of states $n(E_F)$. The quasi-particle properties directly related to the experiments are thus denoted γ^* and $n^*(E_F)$.

6.1 Theory

The heat capacity is the heat or internal energy required to raise the temperature of a sample by one degree Celsius. It can also be written as

$$C = \frac{\partial U}{\partial T} . \quad (6.4)$$

The heat capacity per mole, internal energy, and temperature are designated as C , U , and T , respectively. Although the specific heat is typically defined as the heat capacity per gram of sample, the molar heat capacity is often referred to as the specific heat. In this discussion, the specific heat is considered to be the partial derivative of the energy with respect to temperature at constant pressure as stated in Eq. (6.4).

Electron and phonon contribution

The electronic contribution γT to the specific heat is derived by application of the Fermi-Dirac statistics (Section 2.1.1), which regulates the energy states occupation. Thus the total internal energy of the electron system reduces to the integral

$$U = \int_0^\infty E n(E) f(E, T) dE , \quad (6.5)$$

where E is the energy, $n(E)$ the density of states and $f(E, T)$ the Fermi-Dirac distribution. Solving the integral and substituting it into equation (6.4) gives the γT term. One should notice that the correct derivation of γ only depends on whether the real density of states is introduced into integral (6.5). Experiments on γ deliver the real density of states $n^*(E_F)$, while band-structure calculations give an approximation of γ through the band density of states $n(E_F)$.

The phonon contribution bT^3 to the specific heat is an approximation at low temperature of the Debye model. It refers to quantized lattice vibrations of frequency ω (or wave-vector k) by analogy to the quantum theory of the harmonic oscillator. In analogy to expression (6.5), the internal energy per unit volume of the vibrating lattice system is

$$U = \int_0^{k_{max}} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} p(k) dk , \quad (6.6)$$

with the density of states $p(k) = 3k^2/2\pi^2$, or, using the Debye approximation $\omega = v_0 k$, it is

$$U = \frac{3\hbar}{2\pi^2 v_0^3} \int_0^{\omega_{max}} \frac{\omega^3}{e^{\hbar \omega / k_B T} - 1} d\omega , \quad (6.7)$$

with v_0 a constant medium wave-velocity. Equation (6.7) is conveniently reduced ¹ using $x = \hbar\omega/k_B T$ to

$$U = 9n_c N_c k_B \frac{T^4}{\Theta_D^3} \int_0^{x_{max}} \frac{x^3}{e^x - 1} dx, \quad (6.8)$$

where Θ_D is the characteristic Debye temperature ². Differentiating the expression (6.8) with respect to temperature, the phonon molar heat capacity is

$$C = 9n_c k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_{max}} \frac{e^x x^4}{(e^x - 1)^2} dx. \quad (6.9)$$

At high temperatures $T \gg \Theta_D$, the heat capacity approaches the classical Dulong and Petit value of $3R \text{ mol}^{-1}$.

At very low temperatures $T \ll \Theta_D$, the internal energy (6.8) may be approximated by letting the upper limit x_{max} go to infinity. The integral approaches a finite number $\pi^4/15$, thus reducing the energy to

$$U = \frac{3\pi^4 n_c k_B T^4}{5\Theta_D^3} \quad (6.10)$$

and from expression (6.4) follows a molar heat capacity

$$C = \frac{12\pi^4 n_c k_B T^4}{5} \left(\frac{T}{\Theta_D} \right)^3, \quad (6.11)$$

showing the Debye T^3 dependence.

Developing the model: optical-phonons contribution

As a high temperature approximation, the Einstein formula for heat capacity is appropriate for the contribution of optical modes. In the Einstein model, each atom of the lattice is vibrating in the average field of its neighbours as if these were at rest in their equilibrium positions. The molar internal energy

$$U = n_c \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \quad (6.12)$$

leads by differentiation with respect to temperature to the molar heat capacity

$$C = n_c k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}. \quad (6.13)$$

Introducing a definite quantity in form of the Einstein temperature $\Theta_E = \hbar\omega/k_B$ of the mode ω , equation (6.13) becomes

$$C = n_c k_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}. \quad (6.14)$$

The contribution of this term for the optical modes is particularly reasonable when the mass ratio of the ions differs considerably from unity ³.

¹The upper limits k_{max} and ω_{max} are determined by the condition that the total number of modes be equal to $3n_c N_c$, where n_c is the number of atoms per unit cell and N_c is the number of cells per unit volume. Therefore $k_{max}^3/2\pi^2 = 3n_c N_c$. $v_0 = (c/\rho)^{1/2}$ is the wave-velocity, which depends on the elastic stiffness c and the density ρ of the lattice.

²The definition of Debye temperature being:

$$x_{max} = \hbar\omega_{max}/k_B T = (\hbar v_0/k_B T)(6\pi^2 n_c N_c)^{1/3} = \Theta_D/T.$$

³In a previous study at ZrB₂ [31], where the ion masses are very different, an Einstein term had to be introduced for the correct interpretation of the transport measurements.

Figure 6.1: *Microcalorimeter sample stage.*

6.2 Measurement technique and facility

The specific heat can be measured with the commercially available Physical Property Measurement System (PPMS) from Quantum Design. It performs the measurement in dependence of temperature in a wide range, from room temperature down to 2K and up to 400K. The technique developed by Quantum Design [102] for measuring the heat capacity controls the heat added to and removed from a sample while monitoring the resulting change in temperature. During a measurement, a known amount of heat is applied at constant power for a fixed time, and then this heating period is followed by a cooling period of the same duration, see the following Section 6.3.

The probe is the microcalorimeter sample stage of Fig. 6.1, dimensions $4 \times 4 \text{ mm}^2$. It contains heater and Cernox-thermometer to control and monitor the temperature of the sample. Supporting wires connect the sensor platform to a messing puck (thermal bath) and provide a small thermal link to the sample platform. On the back side are the connectors. A socket is placed at the bottom of the ^4He -kryostat chamber. The puck with the sample has to be mounted at the end of a holding stab, used to introduce it into the cryostat onto the socket connector.

The PPMS *Turbo Pump* or *Cryopump High-Vacuum* options provide a sufficient vacuum so that the thermal conductance between the sample platform and the thermal bath (puck) is totally dominated by the conductance of the wires. This gives a reproducible heat link to the bath with a corresponding time constant large enough to allow both the platform and sample to achieve sufficient thermal equilibrium during the measurement.

6.3 Experiment control

For heat capacity measurements, Quantum Design developed a relaxation technique optimized for different sample sizes and high resolution versus accuracy [102].

After each measurement cycle at an experimental temperature - which is a heating period followed by a cooling period - mathematical models are used to interpret the temperature function of time. The measurement software fits the entire temperature response of the sample platform to the Two-tau modelTM [102] that accounts for both the thermal relaxation of the sample platform to the bath temperature (puck) and the relaxation between the sample platform and the sample itself [90, 46]. The effect of the relaxation between the platform and sample must be considered when the thermal connection shared by the sample and platform is poor. When the analysis fails to find a fit to a two-tau solution, the simple-tau model is used [90]. It assumes that the sample and the platform are in good thermal contact with each other and are at the

same temperature during the measurement or that the platform is empty (background measurement).

In the simple-tau model [90], the temperature T of the platform as a function of time t obeys equation

$$C_{total} \frac{dT}{dt} = -K_w(T - T_b) + P(t), \quad (6.15)$$

where C_{total} is the total heat capacity of the sample and the platform, K_w is the thermal conductance of the heat leak (supporting wires); T_b is the experimental temperature of the thermal bath (puck frame) and $P(t)$ is the power applied by the heater. The heater power $P(t)$ follows a step function equal to P_0 during the heating portion of the measurement and equal to zero during the cooling portion. If the power P_0 is applied until a steady-state temperature T_0 is reached, then, by turning off the heating power, the measured time dependence of the cooling curve is the exponential decay of T to T_b

$$T(t) - T_b = (T_0 - T_b)e^{-\frac{t}{\tau_1}} \quad (6.16)$$

with a characteristic time constant

$$\tau_1 = \frac{C_{total}}{K_w}. \quad (6.17)$$

The model assumes that the heat leak is massless and constant with temperature and the temperature differences $T_0 - T_b$ are small compared to T_b , so that equations (6.16) and (6.17) give the total heat capacity at the experimental temperature T_b . The thermal conductance K_w may be calculated from measurements $T_0 - T_b$ and the applied power P_0 according to $K_w = \frac{P_0}{T_0 - T_b}$. Generally the software uses the simple-tau model to measure the most samples. Thus the sample heat capacity is computed from the measured total heat capacity of the fit by subtracting the background heat capacity, as retrieved from a previously measured reference table of the platform used.

6.4 Data analysis

The measured data set of the sample heat capacity $C(T)$ is conveniently plotted as function C/T versus T^2 . At low temperatures a linear dependence is expected, compare to function (6.1). Thus a linear fit permits the estimation of the values of the quasi-particle γ^* and b directly from the quote and the slope of the curve, respectively. According to formula (6.3), the value of b leads to the estimation of the Debye temperature Θ_D .

6.5 Heat capacity in LaIrIn₅

As a probe for the dispersive electron-electron and electron-phonon interactions in LaIrIn₅, a coupling constant λ_{hc} can be obtained from heat capacity measurements. It depends on the experimental value γ^* of the electronic specific-heat zero temperature coefficient γ (6.2) and the band-theoretical value of the density of states at the Fermi energy $n(\epsilon_F)$ (2.18), [85].

γ^* is proportional to the true quasi-particle density of states at the Fermi energy $n^*(\epsilon_F)$ through Eq. (6.2). Many-body effects make $n^*(\epsilon_F)$ larger than $n(\epsilon_F)$ so that the ratios give

$$\frac{\gamma^*}{\gamma} = \frac{n^*(\epsilon_F)}{n(\epsilon_F)} = 1 + \lambda_{hc} \geq 1. \quad (6.18)$$

λ_{hc} is equal to zero if $n(\epsilon_F)$ is calculated from an exact quasi-particle band structure which also considers all electron many-body effects ⁴ correctly, included the electron-phonon interaction

⁴Electron many-body effects are described with exchange-correlation interactions and relativistic effects. They are only taken into account with approximations like the Hartree potential or the L(S)DA (see Section 2.1).

Figure 6.2: Single crystal sample of LaIrIn_5 . Detail of the sample mounted on the calorimeter.

[87]. Thus in general, a coupling constant is only relative to the band model used and quantifies the physics not taken into account.

6.5.1 Sample preparation

The sensor platform accommodates small, but not microscopic, samples weighing approximately 1 to 200 mg [102]. This range of masses produces, for most solids, varying relaxation time constants τ_1 that may be a fraction of a second at 2 K or many minutes at 300 K. Measuring very large samples can thus be very time consuming. The background heat capacity, however, limits the size of the smallest samples. Measurement accuracy, which is generally a percentage of the total heat capacity, is sacrificed when the sample heat capacity is small compared to the background heat capacity. Additionally, to get a correct heat capacity, the geometry and the thermal diffusivity of the sample must be as such that the sample reaches internal thermal equilibrium at each temperature T_b in a small time, compared to the time constant τ_1 of the measurement. Otherwise, by materials with long thermal diffusion time, samples with wide contact surface and flat geometry should be used.

Following the previous considerations, a suitable flat sample of dimensions $2 \times 1.5 \times 0.6 \text{ mm}^3$ and mass 25.3 mg was used, see Fig. 6.2. It was the remanence of the preparation of a de Haas-van Alphen sample (refer to Section 7.6.2) from the homogeneous larger piece illustrated in Fig. 5.6 of the planar face also used for transport measurements and originating from the crystal of Fig. 3.1. A small *In* inclusion was entirely removed by wet etching with diluted HCl aqueous solution until the LaIrIn_5 began to be attacked, details in Section 3.2. The sample is mounted on its wide flat face onto the sensor platform by using a thin layer of grease (Apiezon), which provides the required thermal contact to the platform, Fig. 6.2.

6.5.2 Data interpretation

The heat capacity of LaIrIn_5 was measured between 2 K and 300 K and is represented in Fig. 6.3. Its dependence of temperature is regular without hinting to transitions. However, it does not reach saturation at high temperatures, which is to be ascribed to the participation of the Einstein term. Major interest was directed to the low temperature behaviour of the heat capacity, for which the simple model formula (6.1) is valid. As in the procedure explained in Section 6.4, the data were linearly fitted. The result is shown in Fig. 6.4. The simple cubic function (6.1) reproduces the data very well up to a temperature of 4.5 K, refer to Fig. 6.3 again. From the

Figure 6.3: Temperature dependence of the measured heat capacity C and the interpolation curve from the Fermi-Dirac statistic and the Debye model. Inset: low temperature interval.

Figure 6.4: T^2 -dependence of the scaled heat capacity C/T .

residual heat capacity	linear fit	error	electron properties
$C(300\text{ K}) = 198.5 \frac{\text{J}}{\text{mol K}}$	range 2.02 – 4.47 K $n_c = [7]$ $\gamma^* = 0.00691 \frac{\text{J}}{\text{mol K}^2}$ $b = 0.0013 \frac{\text{J}}{\text{mol K}^4}$	$\bar{S} = 1.75 \cdot 10^{-4}$	$n(E_F) = [2.33] \frac{\text{states}}{V_c \text{ eV}}$ $n^*(E_F) = 2.935 \frac{\text{states}}{V_c \text{ eV}}$ $\Theta_D = 218.7\text{ K}$
coupling constant : $\lambda_{hc} = 0.26$			

Table 6.1: Parameters from the linear fit of the scaled heat capacity data of LaIrIn₅. Values in square brackets are constants.

slope of the linear curve and formula (6.3), the Debye temperature $\Theta_D = 218.7$ K is estimated. It is, interestingly, a very low value, if compared to an experimental value of approximately 600 K for the intermetallic compound ZrB_2 [31], which has a strong in-plane covalent bonding in common to the diboride systems. Thus LaIrIn_5 shows a low excitation energy of the crystal lattice vibrations, despite the high atomic weight. *In*-based compounds show low Debye temperatures, like also the RuIn_3 with $\Theta_D = 258$ K, we recently investigated.

The quote of the fit, γ^* , is directly related to the real electron density of states $n^*(E_F)$, in analogy to expression (6.2). The obtained value is $2.935 \frac{\text{states}}{\text{V}_c \text{ eV}}$. Thus, referring to the calculated band-structure value $n(E_F) = 2.33 \frac{\text{states}}{\text{V}_c \text{ eV}}$ of Section 2.2.2, the additional density of states due to the quasi-particle nature of the electrons can be quantified in the formula (6.18).

The enhancement parameter λ_{hc} of LaIrIn_5 , or more properly coupling constant of the quasi-particle interactions, amounts to 0.26 from the heat capacity measurement.

The list of the fitting parameters and the deduced electron properties is then represented in Tab. 6.1.

Chapter 7

Angle-Resolved Electron-Diamagnetic-Oscillation Spectrometry (AREDOS)

SUMMARY

The electronic structure determines the electrons behaviour by the de Haas-van Alphen effect. Relations to quantities of the electronic structure and dispersive interactions, like Fermi surface and effective masses involve a complex formulation from the Lifshitz-Kosevich theory. A quantitative description on the basis of the electronic structure model follows in Section 7.1. The non-linear magnetic field dependence of the effect establishes the foundation for the AREDOS method of detection presented in Section 7.2. The AREDOS is the most powerful method in the determination of the electronic structure properties of LaIrIn_5 , as illustrated in Section 7.6, thus also becoming its most direct experimental proof.

7.1 Theory of the de Haas-van Alphen effect

Quantum oscillations in the magnetic susceptibility versus an applied magnetic field were first observed in a single crystal of bismuth by de Haas and van Alphen [19]. They are due to the

Figure 7.1: Quantum oscillations of the nearly-free electrons diamagnetism periodic in $1/B$.

quantization of the electronic states near the Fermi surface in a magnetic field. The quantitative description of the de Haas-van Alphen (dHvA) effect for conduction electrons with arbitrary dispersion relation $E(\mathbf{k})$ and spin was first derived in 1956 by Lifshitz and Kosevich (LK), [58]. They determined the thermodynamic potential Ω making use of the usual formula of statistical mechanics

$$\Omega = -\Theta \sum_s \ln \left[1 + e^{\frac{\mu - E(s)}{\Theta}} \right], \quad (7.1)$$

where $E(s)$ is the energy of the electron in the state s , μ is the chemical potential, $\Theta = k_B T$, and the summation is performed over all the possible states s of the individual electron. Considering Ω in the general formulation

$$\Omega = U - TS - \mu N, \quad (7.2)$$

its variation

$$d\Omega = -M dB - S dT - N d\mu \quad (7.3)$$

can be expressed in terms of the external magnetic field. Thus from the formula of Ω , a magnetization is derived according to the relation

$$\mathbf{M} = -(\nabla_{\mathbf{B}} \Omega)_{\mu, T}, \quad (7.4)$$

for constant temperature and chemical potential. At low temperatures $T \approx 0$ K the LK equation [97, 96, 95, 29] calculated with respect to the Fermi energy $\mu = E_F$ has the general form

$$\mathbf{M}(B, \theta, \phi) = \mathcal{M} \tilde{\mathbf{M}}, \quad (7.5)$$

for a given magnetic field strength B and magnetic field orientation (θ, ϕ) given in spherical coordinates with respect to the fundamental crystallographic axes or the Fermi surface sheet coordinate system (refer to Section 2.1.2). The description of equation (7.5) follows easier when applied to the ellipsoidal Fermi surface, considering the general character of the nearly-free-electron model of Section 2.1.2, for which Fig. 7.1 represents the special case $\mathbf{M}(B, \frac{\pi}{2}, \phi)$.

Figure 7.2: Cross-section variation for the ellipsoidal Fermi surface (reciprocal space). Detail of the extremality condition for the cross-section function $\mathcal{A}$.

In general, the vector term

$$\tilde{\mathbf{M}}(B, \theta, \phi) = \hat{\mathbf{M}}(\theta, \phi) \sin \left[2\pi \frac{F(\theta, \phi)}{B} + \beta(\theta, \phi) \right] \quad (7.6)$$

contains the vector direction of the quantum magnetization and the expression of the quantum oscillations, both depending on the dimension and topology of the Fermi surface. The dependence of $\hat{\mathbf{M}}(\theta, \phi)$ will be described below. In the phase $2\pi \frac{F(\theta, \phi)}{B} + \beta(\theta, \phi)$ of the oscillations, the frequency $F(\theta, \phi)$ is related to the extremal cross-sectional area $\mathcal{A}_{ext}(\theta, \phi)$ of the Fermi surface in planes normal to $\mathbf{B}$ by the Onsager relation

$$F(\theta, \phi) = \frac{\hbar}{2\pi e} \mathcal{A}_{ext}(\theta, \phi). \quad (7.7)$$

The extremality condition for the closed Fermi surface is illustrated in Figure 7.2, with respect to the variation of wave-vector k along $\mathbf{B}$. The additive phase is

$$\beta(\theta, \phi) = -2\pi\gamma + p\frac{\pi}{4}, \quad (7.8)$$

where γ is the Onsager phase factor ($= \frac{1}{2}$ for free electrons) and $p = \text{sign } \mathcal{A}_{ext}''(\theta, \phi)$ is the sign of the rate of change of the cross-sectional area of the Fermi surface at the extremum ($= -1$ at a maximum, $+1$ at a minimum). $\beta(\theta, \phi)$ of an ellipsoid is thus independent of (θ, ϕ) , but in general it is expected to vary within 2π over the entire range of variation of θ and ϕ .

The amplitude of the oscillating quantum magnetization, in terms of the **Bohr magneton** μ_B ¹, is

$$\mathcal{M}(B, \theta, \phi) = \mu_B \frac{4}{\pi} \left(\frac{e}{\hbar} \right)^{\frac{3}{2}} \frac{F(\theta, \phi)}{\sqrt{|\mathcal{A}_{ext}''(\theta, \phi)|}} \frac{B^{\frac{1}{2}}}{m^*(\theta, \phi)}. \quad (7.10)$$

It is determined by the dimension of the extremal cross-section through the frequency $F(\theta, \phi)$ and the geometry of the Fermi surface in the immediate neighbourhood of the extremal plane

¹The Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \cdot 10^{-24} \left[\frac{\text{J}}{\text{T}} \right] \quad (7.9)$$

is the smallest possible magnetic moment of the electron orbital motion and therefore is regarded as the elementary unit of magnetic moment.

Figure 7.3: Angular dependence of dHvA quantities for the ellipsoidal Fermi surface.

through the curvature factor $\mathcal{S}_{ext}''(\theta, \phi)$. It also depends on the energy variation of the extremal cross-section through $m^*(\theta, \phi)$, the extremal orbit effective mass in units of m_e (the free electron mass)

$$m^*(\theta, \phi) = \frac{\hbar^2}{2\pi} \left(\frac{\partial \mathcal{S}_{ext}(\theta, \phi)}{\partial E} \right) \frac{1}{m_e}, \quad (7.11)$$

according to the dispersion relation (2.58). Additional factor is the external magnetic field B . The angular dependence of $F(\theta, \phi)$, $\mathcal{S}_{ext}''(\theta, \phi)$ and $m^*(\theta, \phi)$ for the ellipsoidal Fermi surface is illustrated in figure 7.3. For $\mathbf{B}$ parallel to an ellipsoid principle axis a , b or c , the effective mass is simply

$$m^*(\theta_a, \phi_a) = \sqrt{m_b m_c} \quad (a, b, c \text{ cyclic}). \quad (7.12)$$

The magnitude $\mathcal{M}$ of the magnetization $\mathbf{M}$ is modulated by expression $\tilde{\mathbf{M}}$, which is an essential sinusoidal oscillation if the magnitude of $\mathbf{B}$ is changed. Then, the oscillation is easily described by changes of an integer quantum number n in the part of the phase

$$\varphi = 2\pi \frac{F(\theta, \phi)}{B} = 2\pi n \quad n = 0, 1, 2 \dots \infty. \quad (7.13)$$

A single complete oscillation in $\mathbf{M}$ results when n changes to the nearest integer. For a fre-

Figure 7.4: Constant-phase quantum surface for the ellipsoidal Fermi surface in the magnetic field B space for $n = 1$ quantum number. In detail, portion of the family of quantum surfaces and gradient vectors.

quency $F(\theta, \phi)$ of 10^4 T and in fields of the order of 10 T, the quantum index varies around the value of 10^3 .

In the magnetic field space, described in spherical coordinates (B, θ, ϕ) , contours of constant phase φ are contours of constant quantum index number n . Surfaces of constant phase for the ellipsoidal Fermi surface are shown in figure 7.4. The shape of a constant phase contour is determined by the extremal cross-sectional areas of the Fermi surface which give rise to the quantum oscillation for the directions (θ, ϕ) . Thus for a given (θ, ϕ) the value of B on the contour is directly proportional to the extremal cross-sectional area of the Fermi surface for the same (θ, ϕ) . In general, oscillations in $\mathbf{M}$ will be observed when $\mathbf{B}$ changes magnitude B or direction (θ, ϕ) by an amount sufficient to move it from one contour to the next, see figures 7.5 and 7.6.

The magnetic field space is a convenient coordinate system for describing changes in the mag-

Figure 7.5: The dHvA effect appears when the field B is held constant and the field direction (θ, ϕ) is varied.

Figure 7.6: Quantum oscillations from the ellipsoidal Fermi surface for B varying in the plane $(\frac{\pi}{2}, \phi)$. In detail, the dHvA effect appears when the field direction (θ, ϕ) is held constant and the field magnitude B is varied.

netization $\mathbf{M}(B, \theta, \phi)$. The contours of constant phase in the (B, θ, ϕ) -space are also contours of vanishing constant magnetization. Locally, the magnetization is a monotone function of the phase, thus its magnitude follows the phase gradient

$$\nabla_{\mathbf{B}} \varphi = -\frac{2\pi F(\theta, \phi)}{B^2} \left(\hat{\mathbf{B}} - \frac{1}{F} \frac{\partial F}{\partial \theta} \hat{\boldsymbol{\theta}} - \frac{1}{F \sin \theta} \frac{\partial F}{\partial \phi} \hat{\boldsymbol{\phi}} \right). \quad (7.14)$$

The vector direction of the magnetization is in the direction of the phase gradient

$$\hat{\mathbf{M}} = \frac{\tilde{\mathbf{M}}}{|\tilde{\mathbf{M}}|} = \frac{\nabla_{\mathbf{B}} \varphi}{|\nabla_{\mathbf{B}} \varphi|} = -\left(\hat{\mathbf{B}} - \frac{1}{F} \frac{\partial F}{\partial \theta} \hat{\boldsymbol{\theta}} - \frac{1}{F \sin \theta} \frac{\partial F}{\partial \phi} \hat{\boldsymbol{\phi}} \right), \quad (7.15)$$

showing the diamagnetic nature of the de Haas-van Alphen effect, as also illustrated in figure 7.4. For an anisotropic Fermi surface, $\hat{\mathbf{M}}$ and thus $\mathbf{M}$ is generally not parallel to the external magnetic field $\mathbf{B}$, at least for those $\mathbf{B}$ away from symmetrical directions for which $\frac{\partial F}{\partial \theta}$ and $\frac{\partial F}{\partial \phi}$ is zero. These vector relations enable the measurement of the dHvA effect in its components separately. The component parallel to the magnetic field is easily measured by the induced voltage in a coil and the normal components by a system of perpendicular coils or by the torque generated on a cantilever. More about the measurement technique in Section 7.2.

A typical measurement of the dHvA effect in a material is performed by holding θ and ϕ constant and varying the magnitude of B . Successive variation of one angle permits the scan of a plane like in figure 7.6 for the ellipsoidal Fermi surface. The measured oscillations of the magnetization are periodic in the reciprocal of B and occur as B cuts through successive constant phase contours. The frequency spectrum of these oscillations then gives by using equation (7.7) the extremal cross-sectional area of the Fermi surface in the direction (θ, ϕ) . This procedure was developed in this work.

Another way in which the dHvA effect is measured is to hold B constant and vary the field direction (θ, ϕ) . In this case, the vector $\mathbf{B}$ traverses a circle in (B, θ, ϕ) -space. An oscillation in the magnetization will occur each time $\mathbf{B}$ crosses one of the constant phase contours, as shown in figure 7.7 at different constant values B for the ellipsoidal Fermi surface. The oscillations result solely from changes in the frequency $F(\theta, \phi)$ with changing angle (θ, ϕ) ; these in turn are related to the extremal cross-sectional area of the Fermi surface through equation (7.7). A rotation experiment only gives informations about the relative change of the extremal cross-section of the

Figure 7.7: Oscillating magnetization amplitude on surfaces of constant magnetic field magnitude B .

Fermi surface with angle.

The general LK formula does not consider the effects of perturbations and degeneracies. These result in damping contributions to the amplitude $\mathcal{M}(B, \theta, \phi)$ of the dHvA effect, thus

$$\mathcal{M}(B, \theta, \phi, T) = \mathcal{M}(B, \theta, \phi) R_T R_D R_S. \quad (7.16)$$

The amplitude reduction factors are

$$R_T = \frac{b m^* T / B}{\sinh[b m^* T / B]}; \quad R_D = \exp\left[-\frac{b m^* T_D}{B}\right]; \quad R_S = \cos\left[\frac{\pi}{2} g^* m^*\right], \quad (7.17)$$

with $b = \frac{\pi^2 k_B}{\mu_B} = 14.69 \text{ TK}^{-1}$, being R_T , R_D and R_S in modulus smaller than one. R_T gives the contribution of a finite temperature T by a value of effective mass m^* and magnetic field B . This consists of the most striking reduction factor, that requires, at moderate magnetic fields, a temperature below the fluid-helium temperature also for a free electron gas. For systems with great dispersive interactions, the effective masses can be considerably greater than the respective calculated orbit masses and in general the free electron mass, so that special low temperature cryostats are necessary. R_D takes into account a finite electron relaxation time τ , due to scattering, that results, according to the uncertainty principle, into an energy broadening of the occupied states at the E_F . So that the average of the electronic scattering rate $\tau(\mathbf{k})^{-1}$ on the extremal area contour at E_F reduces to the so called Dingle temperature [20]

$$T_D = \frac{\hbar}{k_B} \left\langle \frac{1}{\tau_{ext}(\mathbf{k})} \right\rangle_{\Omega} = 0.7638 \cdot 10^{-11} [\text{K} \cdot \text{s}] \cdot \frac{1}{\tau}. \quad (7.18)$$

With typical relaxation times within $10^{-11} \dots 10^{-13}$ seconds the Dingle temperature has a magnitude of $10^{-2} - 1 \text{ K}$. Heavy electrons are easily scattered and high magnetic fields and pure crystals are necessary to increase R_D . In a magnetic field B the spin degeneracy of the electronic states is lifted and it comes to an energy splitting

$$\Delta E = \pm \frac{1}{2} g M_B B, \quad (7.19)$$

for spin-up and spin-down electrons at E_F , with g being the spin-splitting factor (≈ 2 for free electrons). Oscillations from spin-up and spin-down electrons superimpose, producing a wave with the same frequency but an amplitude reduction factor R_S , that contains the extremal area contour averaged g -factor g^* .

7.1.1 Total de Haas-van Alphen effect

In general the Fermi surface may be so complex that many extremal cross-sectional areas or orbits Ω exist simultaneously for any field direction (θ, ϕ) . Each of them produces a quantum oscillation of own frequency F_j , which then superimpose. Expression (7.5) is immediately generalized by adding an extra suffix j to $\hat{\mathbf{M}}$, $\mathcal{M}$, F , γ and p and then summing over j

$$\mathbf{M} = \sum_j \mathbf{M}_j. \quad (7.20)$$

In polyvalent metals, the dHvA frequencies F_j normally range from about 0.1 kT to 10 kT. Thus in fields of the order of 1 T, the corresponding phases in expression (7.20) will range from 200π to 20000π . Typically, the smaller dHvA frequencies can be observed at fields lower than 1 T, while the oscillations with larger dHvA frequencies are only becoming observable at fields of about 5 T, for which values the sinusoidal dependence stretches out conveniently to show the oscillations when the field is changed.

Harmonic content

Because of the non-linearity behaviour of the dHvA oscillations, the actual magnetization of the component j , or equivalently of the orbit Ω_j is more properly a harmonic series

$$\mathbf{M}_j = \sum_{q=1}^{\infty} \frac{1}{q^{\frac{3}{2}}} \mathcal{M}_{j,q} \tilde{\mathbf{M}}_{j,q}, \quad (7.21)$$

with

$$\tilde{\mathbf{M}}_{j,q} = \hat{\mathbf{M}}_j \sin \left[q(\varphi_j - 2\pi\gamma_j) + p_j \frac{\pi}{4} \right] \quad (7.22)$$

and $\mathcal{M}_{j,q}$ being the traditional amplitude (7.16) now with reduction factors

$$R_{T,j} = \frac{q b m_j^* T / B}{\sinh \left[q b m_j^* T / B \right]}; \quad R_{D,j} = \exp \left[-\frac{q b m_j^* T_{D,j}}{B} \right]; \quad R_{S,j} = \cos \left[\frac{q \pi}{2} g_j^* m_j^* \right]. \quad (7.23)$$

The total expression is thus more correctly

$$\mathbf{M} = \sum_j \sum_{q=1}^{\infty} \frac{1}{q^{\frac{3}{2}}} \mathcal{M}_{j,q} \tilde{\mathbf{M}}_{j,q}, \quad (7.24)$$

becoming the extended Lifshitz-Kosevich relation.

Magnetic interactions

Shoenberg [92, 95] and Pippard [79] showed that the total magnetic field appearing in the extended LK expression (7.24) should really be the total magnetic flux density $\mathbf{B} + \frac{\mu_0}{V} \mathbf{M}$ rather than simply being the applied flux density $\mathbf{B}$. The amplitudes $\mathcal{M}_{j,q}$ and the arguments

$$\varphi_j = 2\pi \frac{F_j}{B + \frac{\mu_0}{V} M} \quad (7.25)$$

become functions of the total magnetization $\mathbf{M}$ and Eq. (7.24) transforms to a self consistent relation in $\mathbf{M}$.

In order to simplify the question, we consider the interaction due to the harmonic content $q = 1..∞$ or the extremal multiplicity $j = \alpha, \beta, \gamma, \dots$ separately. Thus for a singular frequency $j = \alpha$ and all its harmonics q , the starting point is assuming amplitude $\mathcal{M}$ so that the quantity $\frac{\mu_0}{V} \mathcal{M}$ is comparable to the field interval of any dHvA oscillation, nearly $\Delta B = \frac{B^2}{qF}$. Additionally, the fact that the magnetization produces a magnetic field smaller than the applied flux density B , as it is always the case, replacing B by the total flux density will hardly affect the slowly varying amplitudes $\mathcal{M}$; however the small contribution to the magnetizing field in the phase can markedly affect the values of the term $\tilde{\mathbf{M}}$. The result is that the net amplitudes found for the self consistent solution of expression (7.24) may be very different from the ideal amplitudes $\mathcal{M}$.

Developing the phase expression (7.25) after Taylor in the lowest order with M , Phillips [76] has derived a general solution in which an arbitrary number of harmonic terms could be retained. As Phillips reported, any expansion of his expression will contain terms involving powers and cross products of the ideal amplitudes $\mathcal{M}$. Since the ideal amplitudes are affected approximately by exponential damping factors (7.23), the various terms of the expansion were classified in orders $O(i)$ according to the index i of the resulting negative exponentials. In a limiting case involving only the fundamental amplitude $\mathcal{M}$ for $q = 1$, the first three obtained expansion amplitudes given in terms of the LK ideal amplitude are

$$\mathcal{M}_1 = \mathcal{M}_1 + O(3) + \dots \quad (7.26)$$

$$\mathcal{M}_2 = \pi k \mathcal{M}_1^2 + O(4) + \dots \quad (7.27)$$

$$\mathcal{M}_3 = \frac{3}{2} \pi^2 k^2 \mathcal{M}_1^3 + O(5) + \dots, \quad (7.28)$$

which are different from the ideal harmonics amplitudes $\mathcal{M}_q$ for $q = 1, 2, 3$, refer to relations (7.21) and (7.23). $k = \frac{F \mu_0}{B^2 V}$ is an expansion constant.

From these relations the temperature dependence of the q -th harmonic should be given by

$$R_{T,j} \approx \frac{(b m_j^* T / B)^q}{\exp[q b m_j^* T / B]} \quad (7.29)$$

rather than by the equivalent expression $q T / \exp[q b m_j^* T / B]$, the approximation of R_T in (7.23) from the normal LK theory.

Magnetic interactions do not only cause modification of the harmonic content. Another effect is the generation of combination tones from the various fundamental terms which arise from different extremal sections j through the Fermi surface.

For two extremal sections denoted α and β , two expressions from Phillips for the fundamental amplitudes $q = 1$ have to be summed. Lowest order expansion and neglect of all terms beyond the first order show the presence of two simplest combination terms with dHvA frequencies $F_\alpha \pm F_\beta$ and with amplitudes

$$\mathcal{M}_{\alpha \pm \beta} = \pi \mathcal{M}_\alpha \mathcal{M}_\beta (k_\alpha \pm k_\beta), \quad (7.30)$$

k_α and k_β the relative expansion constants. The temperature variation of the amplitudes of these combination tones are given similarly to relation (7.29) by a curve $T^2 \exp[-b (m_\alpha^* + m_\beta^*) T / B]$. So that harmonics and combination tones are always stronger suppressed than the relative fundamental or component frequencies. Moreover the situation is made very complex since the amplitudes of the individual components j can differ by two, four orders of magnitude. Thus combinations terms are very strong too. The basic experimental problem is thus the spectrum analysis of expression (7.24) into each of its components.

7.2 The measurement technique

7.2.1 Principles of magnetometry

The susceptibility of a medium expresses the proportionality of the response (magnetization $\mathbf{M}$) to the excitation (magnetic field $\mathbf{H}$) after

$$\mathbf{M} = \boldsymbol{\chi} \otimes \mathbf{H}, \quad (7.31)$$

$\mathbf{B} = \mu_o \mathbf{H}$ being the applied flux density.

Since anisotropy in the medium, the magnetization is not necessarily parallel to the magnetic field, thus the susceptibility is generally a 3×3 tensor matrix with also out-of-diagonal elements. A time- and space-varying magnetic field [104, 107]

$$\mathbf{H}(\mathbf{r}, t) = \frac{1}{2\pi V} \sum_{\mathbf{q}} \int d\omega \mathbf{H}(\mathbf{q}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} \quad (7.32)$$

produces a spatial-temporal magnetization

$$\mathbf{M}(\mathbf{r}, t) = \frac{1}{2\pi V} \sum_{\mathbf{k}} \int d\Omega \mathbf{M}(\mathbf{k}, \Omega) e^{i(\mathbf{k} \cdot \mathbf{r} - \Omega t)}, \quad (7.33)$$

whose generalized wave-vector- and frequency-dependent susceptibility is defined by

$$\mathbf{M}(\mathbf{k}, \Omega) = \sum_{\mathbf{q}} \int d\omega \boldsymbol{\chi}(\mathbf{k}, \mathbf{q}; \Omega, \omega) \otimes \mathbf{H}(\mathbf{q}, \omega), \quad (7.34)$$

with components

$$M_\nu(\mathbf{k}, \Omega) = \sum_{\mathbf{q}} \int d\omega \sum_{\mu} \chi_{\nu\mu}(\mathbf{k}, \mathbf{q}; \Omega, \omega) H_\mu(\mathbf{q}, \omega) \quad (7.35)$$

where ν and $\mu = x, y$, and z . If the magnetization is directly proportional to the exciting field, the susceptibility is independent of the field (paramagnetism, diamagnetism). Generally the susceptibility is a functional of the field (non-linearity, ferromagnetism, de Haas-van Alphen effect). Furthermore, since the magnetization may be out of phase with the exciting field, the susceptibility is also complex. If the magnetic medium is isotropic and stationary, thus $\mathbf{q} = \mathbf{k}$ and $\Omega = \omega$, the susceptibility takes the form

$$\boldsymbol{\chi}(\mathbf{k}, \mathbf{q}; \Omega, \omega) = \boldsymbol{\chi}(\mathbf{q}, \omega) \Delta(\mathbf{k} - \mathbf{q}) \delta(\Omega - \omega) \quad (7.36)$$

and in case of simple excitation at ω , Eq. (7.34) reduces to

$$\mathbf{M}(\mathbf{r}, t) = \sum_{\mathbf{q}} \boldsymbol{\chi}(\mathbf{q}, \omega) \otimes \mathbf{H}(\mathbf{q}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)}. \quad (7.37)$$

Since the spatial modulation with reciprocal vector $\mathbf{q}$, the field penetrates with a gradient producing a magnetic force $\mathbf{F}(\mathbf{r}, t) = \mathbf{M}(\mathbf{r}, t) \cdot \nabla_{\mathbf{r}} \mathbf{H}(\mathbf{r}, t)$, easily detectable with a torque balance.

If the magnetic medium possesses anisotropy but translational invariance, the presence of a homogeneous magnetic field conducts to a macroscopic magnetism, while function (7.37) and more generally (7.33) reduces to

$$\mathbf{M}(t) = \boldsymbol{\chi}(\omega) \otimes \mathbf{H}(\omega) e^{-i\omega t}. \quad (7.38)$$

Torque magnetometry assumes that the magnetization and field are not parallel, for which a torque $\boldsymbol{\tau}(t) = V \mathbf{M}(t) \times \mu_o \mathbf{H}(t)$ results. Induction magnetometry requires a coil surrounding the medium of volume V , thus the voltage is induced by the time rate of change of $\mathbf{M}(t)$

$$\mathcal{V}(t) = \mu_o V \dot{\mathbf{M}}(t) \cdot \mathbf{c} = \mu_o V \dot{H}(t) \nabla_{\mathbf{H}} \mathbf{M}(t) \cdot \mathbf{c} = V \dot{B}(t) \nabla_{\mathbf{H}} \mathbf{M}(t) \cdot \mathbf{c}, \quad (7.39)$$

where $\mathbf{c}$ is the vectorial form of the gain factor for the coil detection system. Thus measuring the voltage $\mathcal{V}$ is a direct measurement of the susceptibility because

$$\nabla_{\mathbf{H}} \mathbf{M}(t) = \boldsymbol{\chi}. \quad (7.40)$$

7.2.2 Field modulation magnetometry

The induced voltage in the coil system depends directly on the time rate of change of the flux density $\mathbf{B}(t)$. In order to enhance this rate, a modulating component $\mathbf{b}(t)$ is superimposed to a steady or slow varying field $\mathbf{B}$, thus the magnetic field is

$$\mathbf{H}(t) = \mathbf{H} + \mathbf{h}(t), \quad (7.41)$$

where

$$\mathbf{h}(t) = \mathbf{h} e^{i\omega t}, \quad (7.42)$$

with the assumption of homogeneous magnetic fields through the medium. A convenient coordinate system for describing the magnetization $\mathbf{M}$ is given by the spherical coordinate system (H, θ, ϕ) with respect to fundamental symmetry axes of the medium, like cristallographic or magnetic easy axes. Thus giving for Eq. (7.33)-(7.35) the expression

$$\mathbf{M}(t) = \chi \otimes \mathbf{H}(t) \quad (7.43)$$

with components

$$M_\nu(t) = \sum_{\mu} \chi_{\nu\mu} H_\mu(t), \quad (7.44)$$

where ν and $\mu = H, \theta$, and ϕ . Actually the detection succeeds on the time-varying part of the magnetization, nevertheless without loosing the information content from the susceptibility, since

$$\Delta \mathbf{M}(t) = \chi \otimes \mathbf{h} e^{i\omega t}. \quad (7.45)$$

The induced voltage in the coil system reduces to

$$\mathcal{V}(B, \theta, \phi, b, \omega, t) = V_e \Delta \dot{\mathbf{M}}(t) \cdot \mathbf{c}. \quad (7.46)$$

V_e is the effective volume of the sample, that the oscillating component $\mathbf{b}(t)$ penetrates. The modulation field is comparable to an electromagnetic radiation which propagates into the sample from the surface. Its magnitude b decays of a factor e^{-1} at the depth

$$\delta = \sqrt{\frac{2\rho(B)}{\mu_r \mu_o \omega}} \quad (7.47)$$

the "skin depth", dependent from the magnetoresistivity and the relative permeability of the sample material and the modulation frequency. The modulation field is homogeneous through the sample and the effective volume equals the sample volume V only when δ is much larger than the average sample radius.

The complex susceptibility produces a phase shift in the induced signal. A phase sensitive detection permits to resolve the real and the complex components χ' and χ'' , respectively, of the total amplitude $|\chi| = \sqrt{\chi'^2 + \chi''^2}$. Moreover, phase sensitive detection of the varying coil voltage at harmonics of ω then yields more gain in signal-to-noise for non-linear media. In order to employ function (7.46), the magnetic field has to be applied in any direction with respect to the specimen axis. Furthermore, using the vector direction and amplitude of $\mathbf{b}$ and the orientation $\mathbf{c}$ of the pick-up coil axis with respect to the medium, permits a selective detection of anisotropic components of $\mathbf{M}$, since components perpendicular to $\mathbf{c}$ do not produce induction. So many degrees of freedom are difficult to realise experimentally. In common low temperature cryostats the assembly consists of a solenoid producing the modulation field parallel to the field generated by a superconducting magnet, Section 7.3. But additional Helmholtz pairs can be used producing transverse modulation fields. In the equipment described here, refer to figures 7.13 and 7.14, a rotator turns specimen and pick-up coil about an axis perpendicular to the field, thus changing θ . While $\mathbf{B}$ and $\mathbf{c}$ remain in the rotation plane, a specimen axis can be moved to this plane by turning the sample about an axis parallel to $\mathbf{c}$, thus changing ϕ . Actually the components of $\mathbf{M}$ inside the plane being not distinguishable.

The problem of precise orientation of the specimen in the magnetic field becomes extremely important and it is illustrated in Section 7.2.5.

7.2.3 Magnetic oscillation spectrometer for AREDOS

The convenience of the field modulation method is particularly noticeable when the magnetization has a non-linear nature, like the oscillating magnetization in the dHvA effect [93, 94, 37, 97, 95]. It enables the selective detection of any particular dHvA frequency component.

The effect of modulating $\mathbf{B}$ by a small amount $\mathbf{b}$ is to change the dHvA phase of

$$\nabla_{\mathbf{B}}\varphi \cdot \mathbf{b} = -\delta\varphi. \quad (7.48)$$

Assuming a modulation field of the form $\mathbf{b} \cos\omega t$, its magnitude must be small in comparison to B , thus $b \ll B$. Secondly, the modulation frequency ω must be sufficiently low so that the skin depth in the sample is much larger than the largest sample dimension, refer to Section 7.2.2. With this condition satisfied, the modulation field will be uniform throughout the bulk of the sample.

The time dependent portion of the dHvA phase that results from this modulation field is

$$\delta\varphi(t) = -\nabla_{\mathbf{B}}\varphi \cdot \mathbf{b} \cos\omega t = -\delta\varphi \cos\omega t, \quad (7.49)$$

thus the total dHvA phase is given in first approximation by

$$\varphi(t) = \varphi - \delta\varphi \cos\omega t + \beta \quad (7.50)$$

and the total magnetization is given by

$$\mathbf{M}(t) = \frac{\chi_o}{\mu_o} (B + b \cos\omega t) \hat{\mathbf{B}} + \mathcal{M}(B, \theta, \phi, T) \hat{\mathbf{M}} \sin[\varphi - \delta\varphi \cos\omega t + \beta], \quad (7.51)$$

composed of the spin susceptibility contribution and the LK formula of the dHvA oscillation. The total phase is a periodic function of t and can therefore be expanded to a Fourier series. It turns out that the corresponding Fourier coefficients can be expressed in terms of Bessel functions leading for the time-dependent magnetization to

$$\begin{aligned} \Delta\mathbf{M}(t) = & \frac{\chi_o}{\mu_o} b \cos\omega t \hat{\mathbf{B}} + \mathcal{M}(B, \theta, \phi, T) \hat{\mathbf{M}} \left(J_0(\delta\varphi) \sin[\varphi + \beta] + \right. \\ & \left. + 2 \sum_{k=1}^{\infty} J_k(\delta\varphi) \cdot \sin\left[\varphi + \beta + k\frac{\pi}{2}\right] \cdot \cos\left[k\omega t + k\frac{\pi}{2}\right] \right), \end{aligned} \quad (7.52)$$

where $J_k(\delta\varphi)$ is the Bessel function of the first kind and of order k . The voltage induced by the rate of change of magnetization (7.52) along the axis of the pick-up coil after equation (7.46) is

$$\begin{aligned} \mathcal{V}(B, \theta, \phi, b, \omega, t) = & -\frac{\chi_o V_e}{\mu_o} b \sin\omega t \hat{\mathbf{B}} \cdot \mathbf{c} - \mathcal{M}(B, \theta, \phi, T) V_e \hat{\mathbf{M}} \cdot \mathbf{c} \times \\ & \times 2 \omega \sum_{k=1}^{\infty} k J_k(\delta\varphi) \cdot \sin\left[\varphi + \beta + k\frac{\pi}{2}\right] \cdot \sin\left[k\omega t + k\frac{\pi}{2}\right], \end{aligned} \quad (7.53)$$

which can be easily summarized in the expression

$$\mathcal{V}(B, \theta, \phi, b, \omega, t) = \sum_{k=1}^{\infty} \mathcal{V}_k \cdot \sin\left[k\omega t + k\frac{\pi}{2}\right]. \quad (7.54)$$

The measurement of the magnetization follows by phase sensitive detection with a lock-in amplifier of the pick-up signal $\mathcal{V}$, which resolves the time-independent amplitudes $\mathcal{V}_k$ of the k -th harmonic frequency $k\omega$. The susceptibility χ_o only contributes to the fundamental $k = 1$ component and produces a strong background signal proportional to the modulation amplitude b and the effective volume V_e . For $k \geq 2$ only the dHvA effect contributes to the signal, which oscillates as a function of B by the term $\sin[\varphi + \beta + k\frac{\pi}{2}]$. The detected amplitude from the oscillating

k	$J_k(\delta\varphi)_{max}$	$\delta\varphi_{max}$	$\delta\varphi_{zero}$
1	0.58152	1.8	3.8
2	0.48621	3.1	5.1
3	0.43439	4.2	6.2
4	0.39906	5.4	7.6

Table 7.1: Variation with k for the first maximum of the Bessel function and the corresponding argument $\delta\varphi_{max}(k)$, together with the variation of the argument $\delta\varphi_{zero}(k)$ for the Bessel function zero [1].

$\mathcal{V}_k(B)$ is not only the dHvA amplitude $\mathcal{M}(B, \theta, \phi, T)$, but also the multiplicative Bessel function factor $J_k(\delta\varphi)$ and the geometrical factor $\hat{\mathbf{M}} \cdot \mathbf{c}$. If the Fermi surface shows a j -multiplicity of extremal cross-sections, the total detected voltage $\mathcal{V}_k$ is the sum of the k -th harmonic components of the various $\mathcal{V}_j(t)$, such as

$$\mathcal{V}_k(B, \theta, \phi, b, \omega) = 2 \omega \sum_j k J_k(\delta\varphi_j) V_e \mathcal{M}_j(B, \theta, \phi, T) \hat{\mathbf{M}}_j \cdot \mathbf{c} \sin \left[\varphi_j + \beta_j + k \frac{\pi}{2} \right]. \quad (7.55)$$

Since the terms φ_j and $\hat{\mathbf{M}}_j$ are different for the j -contributions, the relative factors $\delta\varphi_j$ and $\hat{\mathbf{M}}_j \cdot \mathbf{c}$ are also different so that, by adjusting $\delta\varphi_j$ and/or $\mathbf{c}$, the detection of any particular dHvA frequency component can be favoured despite the others. General selectivity results from the variation of $J_k(\delta\varphi_j)$ with $\delta\varphi_j$. For $\delta\varphi_j \leq 1$, the Bessel factor $J_k(\delta\varphi_j) \approx \delta\varphi_j^k$. Thus, detection at a high harmonic results in factor $J_k(\delta\varphi_j)$ to become vanishingly small for small $\delta\varphi_j$. $J_k(\delta\varphi_j)$ is an oscillatory function of $\delta\varphi_j$ and becomes identically zero for a series of values $\delta\varphi_j$. Thus when $\delta\varphi_j$ is set at one of the values such that $J_k(\delta\varphi_j) = 0$, no dHvA signal will be detected on the k -th harmonic from the j -th extremal cross-section of the Fermi surface.

In the case of longitudinal modulation $\mathbf{b}$ parallel to $\mathbf{B}$ as performed in the present work, equation (7.48) reduces to

$$\delta\varphi_j = \frac{2 \pi F_j(\Theta, \phi) b}{B^2}. \quad (7.56)$$

Thus for a given value of field B , $\delta\varphi_j$ can be set to any value by the appropriate choice of modulation amplitude b . In particular, b can be chosen such that $J_k(\delta\varphi_j)$ is either a maximum or zero, see table 7.1. For small $\delta\varphi_j$, $J_k(\delta\varphi_j)$ suppresses the lower frequency dHvA components in favour of the higher frequency components, for large values of k . Since in the measurement system to be described the pick-up coil axis is fixed to the rotator, the orientation $\mathbf{c}$ with respect to the sample and $\hat{\mathbf{M}}_j$ cannot be changed, thus further selection happens only indirectly when $\hat{\mathbf{M}}_j \cdot \mathbf{c} = 0$.

Eq. (7.55) considers only the fundamental frequency components for $q = 1$. But from the total dHvA effect the summation must be extended to all the harmonics q . The harmonic content is also submitted to spectral selection through Bessel functions $J_k(q\delta\varphi_j)$. By fast Fourier transform of the dHvA signal (7.55), extended to the harmonics content q and as a function of reciprocal magnetic field $\frac{1}{B}$, the dHvA frequency spectrum of amplitudes

$$\mathcal{U}_k(qF_j) = 2 \omega k J_k(q \delta\varphi_j) V_e \mathcal{M}_{j,q} \hat{\mathbf{M}}_{j,q} \cdot \mathbf{c} \quad (7.57)$$

is obtained. The non-linear characteristic of the dHvA effect thus permits, with the field modulation method, to spectrum analyse and empirically separate the dHvA components of equation (7.55). Experimentally, it establishes the foundation for the **Angle-Resolved Electron-Diamagnetic-Oscillation Spectrometry (AREDOS)**. AREDOS implies the realization of a high-sensitivity inductive sensor and an accurate rotator for use in high magnetic fields and low temperatures of a cryogenic apparatus.

7.2.4 The inductive sensor

A high resolution coil system quite totally compensates the parasitic fluxes due to the magnet, the modulation field and mechanical vibrations. The detection coil consists of two sections connected in series opposition. These coils must be mounted rigidly and concentrically together so that they detect the noise spectrum coherently, which cancels at the output of the coupled coils. The flux produced in the inner (*i*) and outer (*o*) section of the coil system by a homogeneous applied magnetic field **H** is

$$\Phi_{i,o} = \mu_o \eta_{i,o} H \quad (7.58)$$

for the field parallel to the unit vector $\hat{\mathbf{S}}$, the coil axis. The fluxes $\Phi_{i,o}$ depends on the geometrical factor

$$\eta_{i,o} = f A_{i,o} n_{i,o} = f A_{i,o} l_{i,o} \delta . \quad (7.59)$$

$f < 1$ is the fill factor of the real coil, considering that the metal wire does not fill completely. f is indirectly the gain coefficient. $A_{i,o} = \pi r_{i,o}^2$ are the cut section areas depending on the respective radius of the inner or outer coil. $n_{i,o}$ refers to the number of wire turns. Introducing the density pro layer δ , the geometrical factors depend on the layers numbers $l_{i,o}$. The compensation condition implies that

$$\eta_i = \eta_o . \quad (7.60)$$

The inner coil is closely wound to the sample while the outer concentric coil only weakly wound, thus typically giving $A_i < A_o$ and $n_i > n_o$ or $l_i > l_o$. Considering the coil sections geometrically similar, Eq. (7.60) reduces to the condition

$$r_i^2 l_i = r_o^2 l_o \quad (7.61)$$

where the radii

$$r_{i,o} \approx \bar{r}_{i,o} = b_{i,o} + \frac{l_{i,o} \cdot d}{2} = b_{i,o} + l_{i,o} \cdot \epsilon \quad (7.62)$$

are actually functions of the body radii $b_{i,o}$, the layers numbers and the wire diameter d (ϵ the radius). The compensation condition thus becomes the zero condition for the curve

$$F_{\epsilon, b_i, b_o, l_i}(l_o) = \epsilon^2 l_o^3 + 2\epsilon b_o l_o^2 + b_o^2 l_o - \left[\epsilon^2 l_i^3 + 2\epsilon b_i l_i^2 + b_i^2 l_i \right] . \quad (7.63)$$

The geometrical characteristics of the coil bodies and the turn number of the inner coil are constants, while l_o becomes the variable for the compensation. Since the sign of the constant term is negative, there is only one zero value. Other formulations for the function F (models B and C) are represented in Tab. 7.2 together with the previous model (A). They differ in the expressions of the radius (7.62) and thus the effective section areas of the coils. The models for the wire "packaging" are represented in sections along the coil axis. Models B and C cannot be solved analytically and solutions have to be calculated numerically. The zero value satisfies the compensation condition in these simple models and is used to indicate the number of turns necessary for a cylindrical coil system in good approximation.

At first, two cylindrical body forms are machined from Vespel® as support for the coils. The inner cylinder body has a hole along its axis to contain the sample with diameters up to 1.2 mm. The outer diameter supporting the wiring is 2 mm. The outer cylinder body has a hole along its axis with a diameter of 5 mm to contain the inner coil. The length available for the wiring is 3.5 mm. When the system is mounted its height is 5 mm. The inner coil was performed to fill the whole body form employing 20 layers or 1167 turns of 50 μm copper wire. The outer body of 6 mm diameter was then concentrically fixed on the inner one and the same wire was directly counterwound on the outer body. From the diagramm of Fig. 7.8, plotting the calculated inner and outer area formulas for the coil system and considering $l_i = 20$, the graphical value l_o satisfying the compensation relation (7.61) is approximately of 4 – 5 layers. The outer coil was thus performed with compensating turns exceeding the calculated number l_o of two layers. The number of turns was then adjusted at room temperature to give a minimum induced

model	$r_{i,o}$	$A_{i,o} \cdot l_{i,o}$	$F_{\epsilon, b_i, b_o}(l_i, l_o)$
<p>A</p>
	$b_{i,o} + l_{i,o} \cdot \epsilon$	$\pi r_{i,o} l_{i,o}$	$\epsilon^2 l_o^3 + 2\epsilon b_o l_o^2 + b_o^2 l_o - [\epsilon^2 l_i^3 + 2\epsilon b_i l_i^2 + b_i^2 l_i]$
<p>B</p>
	$b_{i,o} + (l_{i,o} - 1) d$	$\pi \sum_{k=1}^{l_{i,o}} [b_{i,o} + (k - 1) d]^2$	numerical
<p>C</p>
	$b_{i,o} + (l_{i,o} - 1) \sqrt{3} \epsilon - \frac{1}{2} \pi \sum_{k=1}^{l_{i,o}} [(b_{i,o} + (k - 1) \sqrt{3} \epsilon)^2 + (b_{i,o} + (k - 1) \epsilon)^2]$		numerical

Table 7.2: Models for the wire superposition during the coil winding. Related compensation conditions.

Figure 7.8: Effective coil cross-section versus layers number for the models of Tab. 7.2. Dash lines delimitate the compensation range.

signal when the coil system was subjected to an alternating magnetic field parallel to the axis $\hat{\mathbf{S}}$. Figure 7.9 shows the experimental calibration accurate to one turn on a total of 290 turns. It corresponds to a layer number l_o of 4.8. The result is summarized in figure 7.10. The grey surface delimited by the model curves for $F(l_i, l_o) = 0$ gives a narrow range where the experimental point (l_i, l_o) satisfies the compensation relation. The inner coil, after being wound, and the outer coil after balancing has to be fixed and were thoroughly impregnated with varnish, a procedure necessary to prevent vibrations of loose turns and consequent electrical noise. Test of compensation was also performed by cooling down the system to liquid nitrogen temperature. The growth in induced voltage during thermal contraction approaches 20 % and is illustrated in Fig. 7.11. The technical data of the coil system are then summarized in Tab.7.3.

Since the finite volume of the sample, with section A being nearly the inner coil section area A_i , the coupling to the coils is different ($A_o > A_i$), resulting in an inhomogeneous magnetic flux. This produces a voltage signal at the output of the coils pair proportional to the difference of

Figure 7.9: Experimental determination of the compensation condition for the inductive sensor for AREDOS.

Figure 7.10: Diagram of the compensation range, delimited by the model functions, versus the layers numbers. The circle indicates the compensation of the real inductive sensor.

Figure 7.11: Loss in compensation of the induction coil system with temperature (cooling curve down to liquid nitrogen temperature).

geometry	d [μm]	b_i [mm]	b_o [mm]	L [mm]
	60	0.95	3.0	3.5
compensation	l_i	l_o	n_i	n_o
model A-C	20	4-5	-	-
experiment	20	4.8	1167	290

Table 7.3: Technical data of the inductive sensor.

Figure 7.12: Insertion probe system for AREDOS.

the number of turns. Furthermore, the effective flux originates from the component parallel to the system axis. Thus the inductive response of the coil system is expressed by the vector

$$\mathbf{c} = f(n_i - n_o) A \hat{\mathbf{S}} \quad (7.64)$$

entering relation (7.46). From Eq. (7.57), the induced voltage amplitude per magnetic moment is typically around $1 \text{ V}/\text{Am}^2$. Voltages of a few 10^{-11} V can typically be resolved with lock-in phase sensitive detection, thus the moment sensitivity is around 10^{-11} A m^2 .

7.2.5 The rotation system

Much attention was invested in the development of a miniature orienting apparatus which could set the variables θ and ϕ of the crystal orientation accurately in the high magnetic field and at the low temperatures of a cryostat. At the same time it has to perform comfortable sample mounting and to be capable of the most accurate adjustment of the sample at room temperature. This is only assured when the system permits both orientation and characterization of the sample in the sensor itself. The resulting plug-in probe system with connectors and drive coupling is illustrated in the photograph of Fig. 7.12 and in detail in Fig. 7.13. The probe system is plugged-in to the end of a top loading probe for our ^3He -cryostat hosting a shaft run and conducting the electrical wiring from the top. The geometry allows the positioning of the probe inside the solenoids for the modulation and the steady magnetic field in vertical geometry. The plug-in-unit illustrated alone in Fig. 7.14 is contemporarily sample holder and rotator of the inductive sensor, which contains the sample. The rotator head, detail in Fig. 7.14, permits the field to be pointed in any crystallographic direction from the machined sample cylinder axis.

The rotator is a cylindrical barrel machined from Vespel®² with a side bore to contain the sample-coil system. It performs the θ -rotation using a rotating shaft in German Silver³ with worm drive gear at the end. The driven worm gear is milled directly on the barrel side. Drive shaft and rotator are matched together through a force fit in Delrin®⁴. A passing frame in Delrin® permits to attach the rotator to the long probe. A sliding plug junction with inner square section was spark erosion machined and couples the short rotator shaft to the long probe drive shaft. The potential leads are plugged through adapted commercial connectors⁵. A bronze spring and Vespel® bushing on the axles of the rotator assure gear engagement though seizing at low temperatures. Thus a rotation of the drive shaft from outside the long probe top results

²Polyimide in the resin designation SP-22: 40%, by weight, graphite filler. It provides low wear and friction, dimensional stability and lowest coefficient of thermal expansion. DuPont™.

³Metal alloy $\text{Cu}_{65}\text{Ni}_{18}\text{Zr}_{17}$, (Alloy No. 752).

⁴Acetal polyoxymethylene (POM) of DuPont™.

⁵Ultra miniature strip connectors with 2 or 4 contacts of Microtech, Inc.

Figure 7.13: Exploded view of the insertion probe system and the tail of the long probe.

Figure 7.14: Detail of the insertion probe system and of the inductive sensor in the rotator.

in a rotation of the coil (and crystal sample) about an axis perpendicular to the magnet axis. Refer also to Section 7.3. The ϕ -rotation of the crystal corresponds to the azimuthal rotation of the coil system parallel to the axis c and is accomplished with a transversal worm drive gear screw. The driven worm gear is machined directly on to the coil cylinder edge. The rotations are only slightly geometrically limited: θ performs 310° also at low temperatures while ϕ , extending within 300° , is only adjustable at room temperature, refer to the detail in Fig. 7.14.

The plug-in probe unit hosts 8 leads twisted in pairs. One lead is the grounding and acts also as current negative pole for the ^3He heater wound on the in-let cone cover. The voltage output of the inductive sensor occupies only one pair of leads.

The reason for mounting the rotator on a removable insert is to accurately control the crystallographic plane (ϕ) in which the sample is tilted (θ) and to reduce the time for this operation. By extracting the long probe from the cryostat, the new tilting plane can thus be quickly adjusted for the next measurement. After being demounted, the entire rotation assembly can be

Figure 7.15: Insertion probe system mounted inside the adjusting holder used for in-situ Laue imaging of the sample, refer to Fig. 4.11.

Figure 7.16: Laue images of a ZrB_2 sample in the rotator indicating the effect of the ϕ -rotation (top, from left to right) and of the θ -rotation (bottom, from left to right).

precisely transferred to an adjustable frame, like in Fig. 7.15, which has to be mounted on the track of the X-ray unit of Fig. 4.11. Because the sample in the central hole of the sensor is machined and mounted with an arbitrary crystallographic direction parallel to the sensor axis c , any tilt plane within 300° through this direction can be adjusted by the small side screw and controlled with the Laue back-reflection technique. This procedure was also used for the calibration of the apparatus at room temperature by inserting a cylinder sample of ZrB_2 oriented in $[0001]$ into the coil system and counting the number of drive gear revolutions needed to rotate the sample to known symmetrical directions. Refer to the pictures of Fig. 7.16 from top left to bottom right. From the calculated crystallographic angles between these directions conversion factors of $\Delta\theta = 5.1^\circ$ and $\Delta\phi = 6.4^\circ$ for θ - and ϕ -shaft revolution are estimated respectively. The figures also show the precise adjustment allowed by the system. Including errors in X-radiating and spark cutting the samples, a crystal direction can be known within 1° . The accurate calibration was performed directly in the low temperature environment at 400 mK for the θ -rotation in the (0001) crystal plane of a ZrB_2 crystal oriented in the $[11\bar{2}0]$ direction. The dHvA frequency dispersion versus drive shaft rotation is illustrated in Fig. 7.17. Because of the anisotropy of the Fermi surface at directions $[11\bar{2}0]$ and $[10\bar{1}0]$, the dHvA oscillation frequency ξ changes noticeably and gives an angular reference of 30° for the rotation. The rotation is measured at the long probe top outside the cryostat. Thus, the conversion factor is $\Delta\theta = 5.167^\circ$ per rotation. Other branches are attributed to harmonics or combination frequencies of the spectrum. The sample is mounted with axis $[11\bar{2}0]$ parallel to c and B while cooling. The nearly 1-rotation shift of B from $[11\bar{2}0]$ at zero rotation is a torsion hysteresis effect after opposite rotation, while effects of thermal contraction during cooling are suppressed by the gliding junction system of the drive shaft.

The use of prevalent insulating materials throughout the high field region was dictated by the need to avoid eddy currents effects (forces, heating and field distortion in the sample space). It also assures the necessary thermal insulation from the outer ^4He bath at 4.2 K, while the rotation system is immersed in the liquid ^3He bath for temperatures of 0.4 – 1.5 K. Refer to Sections 7.3 and 7.4.

The rotation system is conveniently mounted and introduced into the cryostat with the sensor

Figure 7.17: Low temperature calibration curve of the θ -rotation from the angular dispersion of the dHvA frequency of ZrB_2 for rotation in the (001) plane. (Description of amplitude maps in Section 7.6.3).

axis vector $\hat{\mathbf{S}}$ parallel to the field $\mathbf{B}$. This is also the reference position $\theta = 0^\circ$ for the measurement. As the detection system axis is tilted at an angle θ in the rotation plane with respect to the magnetic field, the vector $\hat{\mathbf{S}}$ tilts with respect to the magnetic moment direction $\hat{\mathbf{M}}$, which projection $\hat{\mathbf{M}} \cdot \hat{\mathbf{S}} < 1$ gives the effective measured flux fraction. This amount only depends on the anisotropy of the Fermi surface from formula (7.15) for $\hat{\mathbf{M}}$.

7.3 The cryomagnetic facility

The complete assembly producing high magnetic fields and low temperatures and the detail of the insertion long probe system for AREDOS measurements are illustrated in Fig. 7.18. The system is immersed in the liquid ^4He bath of a commercial nitrogen cooled stainless steel cryostat⁶. The low bath temperature furnishes the operation temperature for the superconducting magnet, the red cylinder in Fig. 7.18, and constitutes the starting cooling stage for the ^3He refrigerator.

The main magnetic field B at the sample reaches 13.5 T⁷ with a homogeneity at the magnet centre of one part in 10^4 over 10 mm diameter sphere volume. The homogeneity is very important to prevent phase smearing of the dHvA signal: an inhomogeneous field causes a radial field gradient inside the sample. The sample produces phase-shifted dHvA signals along the gradient direction, their superposition giving a weaker total signal.

The modulation field b for AREDOS is produced by an additional solenoid⁸. It guarantees great field homogeneity at the sample, since it is wound directly on the thin stainless steel cover of the vacuum can of the cold plate and is very close to the sample, see the detail of the insert tail in Fig. 7.19. Field values of 5 mT are reached by 100 mA alternate current.

The sample is supported at the centre of the solenoid within the sample rotator, which is in turn plugged-in to a long probe suspended from the top of the dewar in the central ^3He tube. The sample rotator enables the rotation of the sample continuously about an axis perpendicular to the magnetic field and remain immersed in the liquid ^3He .

The measurement temperature bath is constituted of the ^3He bath. The low temperature is reached through three stages: the first is constituted by the surrounding ^4He bath, the second uses a cold plate and the third, applied in this order, uses the ^3He evaporative cooling. The second-stage assembly is illustrated in Fig. 7.20. The condensation coldplate is the gold-plated copper ring tank with a massive wall acting as a junction in the central tube. The tank holds approximately 2.7 cm³ of ^4He vapour and is continuously refilled by a flow limiting capillary connected to the ^4He bath at 4.2 K. The tank is kept under dynamic pumping by a sealed pump⁹. Due to the pressure difference, the helium is kept circulating. The flow limiting device has to be properly chosen in order to determine, together with the pumping performance, the cooling power of the coldplate, which has to overcome the heat load. The device consists of a CuNi-capillary of an inside diameter of 0.3 mm and a length of 25 cm. The flow impedance is increased with an inside CrNi-wire of 0.2 mm diameter. The evaporative cooling reduces the coldplate temperature from liquid ^4He temperature to about 1.3 K, the working temperature is controlled with an Allen-Bradley resistor directly on the coldplate. The massive central tube junction remains at the same temperature as the coldplate. The coldplate and that length of the central tube below the tank are thermally insulated from the ^4He bath by a vacuum space inside the stainless steel cover.

The end section of the central tube which extends down from the coldplate is a glass tube. This tube completely eliminates eddy current heating of a metal tubing, enhancing the lasting time

⁶Cryogenic Model R160N: 160 mm neck reservoir cryostat with nitrogen cooled radiation shields.

⁷Oxford Instruments Ltd. : High Field Solenoid System S12/13.5L/26/13 and Magnet Power Supply IPS 120-10; NbTi superconducting solenoid, magnetic field to current ratio of $k = 0.1597 \text{ T/A}$.

⁸Four layer copper solenoid with inner diameter 22 mm and length 100 mm with a total winding number of 3200. The calculated magnetic field to current ratio is $\kappa = 0.049978 \text{ T/A}_{rms}$.

⁹Alcatel 2030, pumping speed 28 m³/h.

Figure 7.18: The AREDOS assembly and the detail of the insert long probe used for rotation $dH\nu A$ measurements.

Figure 7.19: Detail of the central tube end part, which contains the insertion sample rotation system.

Figure 7.20: Detail of the coldplate used for the second refrigeration stage (^3He condensation).

for liquid ^3He . It also eliminates magnetic effects causing local field inhomogeneities near the sample. When ^3He is let into the central tube, it condenses at the junction walls and runs into the glass Dewar, where the liquid gathers at the sample. This liquid can be pumped through the central tube with a sealed mechanical pump¹⁰ to reduce the temperature by evaporative cooling down to 400 mK. The combination of a turbo molecular pump¹¹ to the mechanical pump reduces the temperature to 350 mK. The long probe is constructed as to minimize heat leaks down its length to the liquid ^3He . It is constructed of thin wall, stainless steel tubing over most of its length. Alongside it many baffles are mounted at the central tube and are used as radiation shields. Two copper block junctions heat-sink the probe with bronze spring clamps at two points. Above the coldplate vacuum chamber, thermal contact is made to the central tube at the ^4He bath temperature, and further down, at the copper condensing junction, thermal contact is made to the 1 K coldplate. Between the two junctions and down to the sample rotator the probe wall is made of glass fiber tube.

To experimentally determine the cyclotron effective masses, it is important to know the sample temperature as accurately as possible over a reasonable temperature range. The presence of high magnetic fields prevents the use of electric devices to measure the temperature near the sample. ^3He vapour pressure constitutes a useful temperature characteristic. In the temperature range used (from 0.35 K to 1.5 K) the thermal conductivity of liquid ^3He is smaller than of ^4He , since ^3He becomes superfluid only at 3 mK. Only the continuous mixture of the boiling ^3He compensates any vertical temperature gradients in the liquid. The sample temperature can be assumed to be the same as the surface temperature of the liquid as determined by the vapour pressure of the gas in thermal equilibrium with the surface. For the purpose of vapour pressure thermometry, one needs to reach the liquid surface avoiding the flow resistance of the pumped gas. The long probe tube immersed in the liquid ^3He extends from the central tube out of the top of the cryostat. At this point the pressure is measured. The pressure measuring line has a conveniently large diameter wherever a substantial temperature gradient exists, in order to minimize thermomolecular effects. The pressure measurement succeeds by using electronic

¹⁰Alcatel 2033H, pumping speed 35 m³/h.

¹¹Alcatel 5100, pumping speed 50 l/s.

manometers for two ranges in order to increase accuracy ¹².

The temperature vapour pressure curve of ^3He is experimentally determined and is used to determine the temperature of the liquid ^3He from vapour pressure measurements. It also gives information about the temperature error of a pressure measurement from the uncertainty depending on the vapour pressure measurement in the different ranges. It amounts to about 1 mK in the high temperature range and 0.1 mK in the lower. Since both instruments were accurately calibrated, the vapour pressure thermometry for the dHvA experiments is well determined.

7.4 Experiment control softwares

The development of the AREDOS measurement method implied the development of special programs as well, covering functions of control and management of both the cryostat and the complex measurement routine. The main features are the real time control of the parameters and of the measurement results, thus enabling the experimentator to find the better setting for a precise measurement. The programs here described were written in LabVIEW 7.1.

CRYOSTAT^{ion}® for the cryostat control

Although the low temperature processes and the cryostat maintainance are manually regulated via a gas handling system of valves and pumps, their effects are monitored via sensors. The pre-cooling stage of the cryostat with liquid nitrogen is executed by contemporary employment of ^4He gas flow through the cold plate in-let capillar into the bath in order to prevent obstruction, thus the actual flow is controlled by a digital mass flow meter ¹³. Many resistive thermometers are also mounted at the important places of the cryostat and inside the insertion assembly at the coldplate. The pressure of the ^4He bath is controlled by a digital manometer ¹⁴. The reading of flux, temperatures and pressure is performed by a multichannel Digital Multimeter Keithley 2000 while the ^3He pressure sensors dispose of a CERACON indicator. The instruments are comfortably managed during the whole experimentation time by the program CRYOSTAT^{ion}®. Fig. 7.21 illustrates the window used for the last cooling stages. The upper section shows the virtual instrument controlling the coldplate temperature reading via the Keithley, which is reported in the adjacent diagram in dependence of the time. The lower section shows the virtual instrument controlling the pressure gauges via the CERACON and displays the ^3He temperature in the adjacent diagram. The curves displayed in Fig. 7.21 refer to the ^3He condensation process under the coldplate, after ^3He gas was let into the sample space. The program saves the data on demand.

MA-SAT 61® for inductive measurement

The program MA-SAT 61® is the assistant for the AREDOS measurement. Its function is to control the experimental temperature, to adjust the applied and the modulation magnetic fields and to execute the measurement of the magnetization with the detection system.

¹²CERAVAC CTR90 gauges of Leybold. They use capacitive sensors for absolute pressure measurement of gases. In the range 10 Torr to 160 Torr a CTR90 0 – 1000 Torr is used. The corresponding temperature interval is from 1.03 K to 2.03 K. For the range from 40 mTorr to 10 Torr, corresponding to a temperature interval between 0.42 K and 1.03 K, a CTR90 0 – 10 Torr model is used. The specifications give an accuracy with 0.2 % of reading and a resolution with 0.0015 % of full scale.

¹³Honeywell Mass flow sensor for gases AWM3100V, full scale 200 sccm.

¹⁴VRC 1 – 1500 Torr Integral Sensor Diaphragm Gauge.

Figure 7.21: Window of the control software for the cryostat during the ^3He condensation.

For the temperature measurements the Keithley 2000 and CERACon are used. The modulation field amplitude is directly determined from the applied alternate current measured with the Multimeter Keithley 2000 as well. The a.c. signal originates from the sine reference output of a lock-in amplifier, model SR 850 DSP. The sine signal has to be amplified with a Hewlett-Packard 467A Power Amplifier and stabilized resistively in order to avoid influences on the current from the magnetoresistance of the solenoid. The major magnetic field is produced with a Magnet Power Supply IPS 120-10 by the superconducting solenoid. The detection system is connected through a 500:1 transformer amplifier SR 554 to the input port of the lock-in amplifier. Here, the phase sensitive detection at the k -th harmonic of the modulation signal resolves the oscillating voltage signal expression (7.55) and all the q -th harmonics.

The instruments are comfortably managed during the whole experimentation time by the virtual instruments. The access to the instruments is regulated by a scrolling list on the left of the program window in figures 7.22 and 7.23. On the right the diagrams bar is displayed. In each panel a series of diagrams display the variables involved in the on-going measurement or execution procedure in dependence of time or magnetic field. One can choose among plotting the variables versus direct field scan B , reciprocal scan of $1/B$ or time by scrolling the list. The "Time&Control" and "Magnetic Field" modules constitute the measurement execution modules which manage the instruments and read the variables that the AREDOS experiment requests. In order to obtain dHvA oscillations, the detection voltage amplitude (7.55) has to be registered as the outer magnetic field is changed. Fast Fourier Transform (FFT) allows the correct computation of the dHvA frequencies from a discrete set of integer N voltage values in dependence of the reciprocal outer magnetic field $1/B$. Once the magnetic field interval and the N points (usually $N = 1024, 2048$) are determined, the magnetic field is swept and the voltage signal (7.55) is registered at constant successive intervals

$$\Delta \frac{1}{B} = \left(\frac{1}{B_{start}} - \frac{1}{B_{finish}} \right) / N \quad (7.65)$$

Figure 7.22: Measurement of the induction signal in the magnetic field dependent modus.

Figure 7.23: Measurement of the induction signal in the reciprocal magnetic field dependent modus.

from the starting magnetic field value. On the basis of this routine the execution module also gives the alternative of only setting the initial magnetic field value and the maximal frequency expected from the FFT. Before the start of the measurement the option "save" the data must be switched on. Fig. 7.22 shows a dHvA oscillation measurement versus magnetic field of a LaIrIn_5 sample. Fig. 7.23 illustrates a completed dHvA measurement of the same sample.

7.5 Data analysis softwares

The two analysis programs VIEWer[®] and DA-CER 54[®] were written in order to open and display the AREDOS field scan files and to apply the necessary mathematical analysis, respectively.

VIEWer[®] for data display

This program provides a files-opening tool bar that opens simultaneously up to six field scans and six reciprocal field scans, refer to the left side of the program windows in figures 7.24 and 7.25. The main field of the window is dedicated to display the opened data files. Two diagrams are available for the field and the reciprocal field scans respectively. Each selected file is automatically opened and displayed in the relative diagram with different colours and is labelled with the tilt θ -angle value. The multiple file opening feature is particularly useful in order to compare the measurements after changement of the AREDOS parameters, especially

Figure 7.24: Data control of a magnetic field scan.

Figure 7.25: Data control of reciprocal magnetic field scans.

Figure 7.26: Analysis software with the Fast Fourier Transform module.

the temperature, field modulation and field scan. Two reciprocal field scans at different temperatures are displayed together in the diagram of Fig. 7.25.

DA-CER 54[®] for Fast Fourier Transform

The program DA-CER 54[®] works together with the MA-SAT 61[®] and both constitute the analysis part for the AREDOS method. It consists of the spectrograph of the dHvA frequencies. The program window of the DA-CER 54[®] is illustrated in Fig. 7.26. Similarly to all the previous programs it presents a control panel on the left and display panels on the right side. The control panel is equipped with the Fast-Fourier-Transform calculation module and the FFT file opening module. A reciprocal field scan can be, also during the measurement, opened, FFT analysed and displayed. The diagrams directly give the values of the component amplitudes (7.57) versus the relative dHvA frequencies. Diagrams for low and high frequency ranges display the real time FFT together with additional four FFT curves, Fig. 7.27. This enables a direct, real time analysis of a measurement and its comparison with previous measurements, reference frequencies and theoretical data. In the diagrams panel a peak selector module helps to read the peak frequency values and to position reference marks at expected values one introduces. A second diagram focuses on the real time calculated curve in more detail. The program saves the calculated FFT data on demand.

Figure 7.27: Module for FFT-curves display and analysis.

Figure 7.28: Extremal orbits of the Fermi surface of LaIrIn₅ perpendicular to the direction [001].

7.6 De Haas-van Alphen effect in LaIrIn₅

7.6.1 Calculation of extremal areas and orbit integrals

The calculation of dHvA quantities goes back to the numerical determination of path contours on the Fermi surface and their areas. Extremal orbits of the Fermi surface of LaIrIn₅ for planes intersecting the irreducible Brillouin zone in the vertical $\mathbf{b}_3$ -direction are represented in the extended zone scheme in Fig. 7.28. The angular dependence of the extremal areas with the angle between the normal to the intersection plane and the reference reciprocal lattice axis displays the Fermi surface topology which is measured by the AREDOS method. Use of the Onsager relation (7.7) gives the respective dHvA frequencies, which can be directly compared to the measured quantities. Figure 7.29 represents the calculated angular dependence of the dHvA frequencies of LaIrIn₅ in planes delimiting the irreducible part of the Brillouin zone. Fig. 7.30 more extensively shows the Fermi surface anisotropy for directions in the plane (001). Calculated de Haas-van Alphen quantities for orbits perpendicular to direction [001] are listed

position	orbit Ω	RFPLO		
		band ν	Frequency [T]	m^* [m_e]
M	ϵ_1	131	13855	-0.985
M	β_1	133	9632	0.697
M	α_2	135	3259	0.473
M-A	α_1	135	3829	0.558
A	β_2	133	5259	0.628
A	α_3	135	3178	0.477
R	χ	133	263	0.149
Z	γ_1	131	695	0.235
Z	γ_2	131	142	—

Table 7.4: Calculated dHvA quantities from the full relativistic band structure of LaIrIn₅ perpendicular to the direction [001].

Figure 7.29: Calculated angular dependence of the dHvA frequencies between the high symmetry directions [100], [110] and [001].

Figure 7.30: Calculated angular dependence of the dHvA frequencies between the high symmetry directions [100] and [010] within the (001) plane.

in Tab. 7.4. From the angular dependence of the theoretical dHvA frequencies calculated with the RFPLO method, sets of main branches named ϵ_i ($i = 1, 2, 3$ and 4), β_i ($i = 1$ and 2) and α_i ($i = 1, 2$ and 3) are distinguished. Representing the related Fermi sheets separately in the extended zone scheme as in figures 7.31, 7.32 and 7.33, the branches can easily be addressed.

The branches ϵ_i belong to the main sheet of the 131-band Fermi surface. The ϵ -Fermi sheet builds a network-like lattice of not occupied states in the extended zone scheme of Fig. 7.31, since it originates from an hole band. Outside the sheet are the occupied states filling the Fermi body. The highest dHvA frequency ϵ_1 of nearly 14 kT is centered at the point M for the direction [001]. The existence of this frequency is limited to a few degrees about the [001] direction. Then ϵ_1 sharply dissolves into smaller frequencies ϵ_i , as represented with the dot lines in Fig. 7.29. ϵ_2 comes from the cushion body centered at Γ and has a minimum of 805 T in the [110] direction. ϵ_3 refers to the elongated ellipsoidal parts centered at points X and with major axis in the [100] directions. Thus [100] is also the direction of minimal frequency, compare to Fig. 7.30. The frequency branch ϵ_4 originates from the neck parts connecting the ellipsoids to the cushion and has its minimum also in the [100] direction but is centered at approximately 0.2 (in unit of the reciprocal lattice constant b_1). The neck-like restriction of the ϵ -sheet along $\Gamma - X$ is also shown in Fig. 7.28.

Branches β_i are due to the highly corrugated 133-band electron Fermi sheet. This Fermi surface has a convex part stretching along the [110] direction. Representation in the extended zone scheme shows the cylindrical symmetry of the β -sheet with a four-fold symmetry axis. Thus the β_i frequency branches show local maxima and minima at angles off the [001] direction. β_1 is centered at M and has its local maximum of 9632 T for $\theta = 0^\circ$ and minima for $\theta = 27.9^\circ$ and $\theta = 34.1^\circ$ by tilting inside the plane (110) and (100), respectively. β_2 has a cylindrical dependence $1/\cos \theta$ for tilting in a small angle range around [001]. At $\theta = 0^\circ$ the minimum amounts to 5259 T.

The branches α_i are due to the 135-band electron Fermi surface, which is nearly cylindrical but slightly corrugated. This causes several cross-sections. Three frequency branches are distinguished. All of them follow a rather cylindrical dependence with small angles. Thus their local minima are at $\theta = 0^\circ$ but centered at different points along [001] in the reciprocal space, refer to Fig. 7.33. α_1 with 3829 T is the largest, centered at point 0.34 from M and has a wider minimum. Branch α_2 has a minimum of 3259 T and is centered at the M point. α_3 is centered at the A point and its minimum frequency amounts to 3178 T. Due to the corrugation of the sheet, at increasing tilting the angular dependences develop nearby and with many intersections.

The electron-hole Fermi sheet of the 131-band appears in the extended representation of Fig. 7.34 like a strong anisotropic dumbbell with a hole along its vertical axis and appendices at its edges. The effect of the symmetry elements at its center Z is to produce a four-fold symmetrical object. The cavity has hole behaviour, as cut pictures in Fig. 7.34 illustrate. It has a minimum frequency of 142 T in the [001] direction. The outer sheet has electron behaviour, refer to Fig. 7.34 again, and minimum calculated frequency of 697 T in the same direction. The four-fold symmetry of the dumbbell sheet is observed for tilting angle in the (001) plane from the periodicity of the branch γ of 90° between [100] and [010]. Refer to the angular dependence in Fig. 7.30. Therefore the dumbbell extremities consist of four-cornered rosettes, elongating in the [110] directions. The frequency in the sagittal plane changes from 270 T for the [100] direction to 400 T for the [110] direction.

The Fermi surface of LaIrIn₅ is thus completed by the 133-band sheet centered at R, Fig. 7.35. It is an electron pocket with leaned elongations in the (100) planes. The symmetry elements of the R position produce a χ -like sheet, with the multiplicity of the R point in the Brillouin zone. This causes that, for the [100] direction, the smallest frequency of the waist and the frequency from around the total χ are simultaneously present, being 98 T and 2197 T respectively. By tilting the angle of 45° in the (001) plane these two frequencies merge together in the [110] direction. By further tilting they depart again to reach the values 2197 T and 98 T, respectively, in the [010] direction, thus showing the 90° periodicity. Compare Fig. 7.35 and Fig. 7.30. The other waist frequency is for the [001] direction and amounts to 263 T.

Figure 7.31: Hole Fermi sheet from the 131 band and extremal cross-sections.

Figure 7.32: Electron Fermi sheet from the 133 band and extremal cross-sections.

Figure 7.33: Electron Fermi sheet from the 135 band and extremal cross-sections.

Figure 7.34: Electron-hole Fermi sheet from the 131 band and extremal cross-sections.

Figure 7.35: Electron small pocket Fermi sheets from the 133 band and extremal cross-sections.

Figure 7.36: Set-up for sample orientation with Laue imaging (refer to Fig. 4.11). Configuration for cylindrical spark erosion.

7.6.2 Sample preparation

The space group of the crystal is also maintained in reciprocal space. Thus lattice directions and planes are consistent with high symmetry directions and planes of the Brillouin zone. To study the complete Fermi surface of LaIrIn_5 , three intersecting crystallographic planes are sufficient. Planes (100), (110) and (001) are conveniently chosen, since they delimitate the irreducible part of the Brillouin zone. The dHvA effect for magnetic field directions in these planes permits the definition of the Fermi surface in its asymmetrical and minimal range. For symmetry considerations, a complete study involves inclinations in the vertical planes (100) and (110) within 90° from [001], the four-fold axis, and in the horizontal plane perpendicular to the four-fold axis within 45° from [100] to [110] direction. The dHvA measurement employing the ARE-DOS technique (field modulation method with a rotating coil magnetometer, Sections 7.1 and 7.2) allows to rotate the sample in the magnetic field within the crystallographic plane. For a complete investigation one would have to rotate several differently oriented samples, but for symmetry considerations, only two samples with axis parallel to the [001] and [100] direction are needed to perform the scans. The sample filling the coil magnetometer should be cylindrical with dimensions $1.2 \times 1.2 \times 3$ mm. The two cylinders were cut with spark erosion from the crystals in Fig. 3.3 and Fig. 3.2, which will be labelled *EK1* and *EK2* respectively. The axis orientation was accurately determined by X-ray-diffraction analysis along the axis of the

Figure 7.37: Percentage erosion in the [001] and [100] crystal directions of LaIrIn_5 with wet etching.

Figure 7.38: Cylindrical samples of LaIrIn_5 with axis orientation $[001]$ and $[100]$ respectively.

goniometer, with the geometry illustrated in Fig. 7.36 to be mounted on the Laue system (Section 4.3.3). Vertical cutting along the axis with a rotating cylindrical electrode as performed in Fig. 7.36 showed a better accuracy. The samples were chemically polished in diluted acid solution to remove surface damages and to fit precisely within the sample holder. Both use of HCl or HNO_3 showed anisotropical behaviour of the etch rate for the directions $[001]$ and $[100]$ or $[010]$. A comparison of the percentage erosion is reported in Fig. 7.37 for the two solutions. Although the etch rate for the $[100]$ is much slower than in the $[001]$ direction, HNO_3 reduced the samples size more effectively. The results for *EK1* and *EK2* are shown in Fig. 7.38 separately. The samples were fixed with silicon glue on a Vespel® stick and easily introduced into the magnetometer. The stick is appropriately long enough to hold the sample in the middle of the coil magnetometer. The crystallographic plane to be studied was accurately selected by azimuthal rotation of the sample holder in the rotator and aligned to the rotation plane with the Laue photograph method. Fig. 7.39 reports the accurate orientation of the samples in the rotator before being mounted to the long probe and being introduced into the cryostat for the measurement. The vertical directive through the middle of the photographs corresponds to the rotation plane. The first picture from the left refers to the selection of the (110) plane for sample *EK1*. The second is the orientation into plane (100) after azimuthal rotation of 90° from the previous setting. The third photograph shows the selection of plane (001) of sample *EK2*.

Figure 7.39: Laue images of the samples mounted in the rotator are used to orient a crystal plane with adjustment of the ϕ -angle, refer to figures 7.14 and 7.15.

7.6.3 Experimental results

The results of the dHvA rotation experiment is a set of data giving the change in frequency, or Fermi surface extremal area, as a function of angle in the rotation plane with respect to some arbitrary reference direction, usually the start position. To convert this to information concerning the Fermi surface, the axis of the plane and the reference angle within the plane must be accurately known with respect to the crystalline axes. Thus the sample has to be accurately oriented. Otherwise it is necessary to use the symmetry of the data itself to determine the angular coordinate of the high-symmetry directions from the zero angle at start.

The dHvA rotation experiment was performed for tilting angles up to 70° in each plane. Such scans widely cover the contours of the asymmetric unit of the crystal structure as represented with the stereographic projection in Fig. 7.40 and as it is requested for an extended study. Conventional angle step is 2.5° – 5° . More accuracy needed the study of the ϵ_1 frequency in its restricted angular range, thus the step was as small as 0.5° . The existence of dHvA frequencies in the kilotesla range required the use of magnetic fields up to 9 T (as mentioned in Section 7.1.1). Wide scans from 6.5 T to 8 T were also necessary to improve the sensitivity of the FFT spectra with angular variation. The dHvA frequency spectrum of the signal amplitude (7.55) in the reciprocal field is a discrete map of $N/2$ points at intervals of the sampling frequency $f = 1/\Delta \frac{1}{B}$, refer to Section 7.4. Exceptionally strong medium frequency oscillations about 3 – 6 kT were very rich in harmonic content and combination tones due to the magnetic interaction effect (see Section 7.1.1). Fortunately it did not compromise the definition of the neighbour fundamental frequencies and closely spaced frequencies could be resolved.

dHvA frequency spectra from Fast Fourier Transform of the oscillating dHvA signal in reciprocal field $\frac{1}{B}$ were collected as a function of field direction for crystal rotation in the (110), (100) and (001) planes. The data set for each plane is represented as angular dispersion of the dHvA frequencies with amplitude maps that also give information about the amplitude of each frequency components.

Figure 7.40: Stereographic projection for the tetragonal structure of LaIrIn_5 . Directions of magnetic field for the rotation dHvA measurements of the asymmetric unit of the crystal are shown.

Topology of the Fermi surface

The measured angular dispersion of dHvA frequencies in the (110) plane from [001] to [110] direction is represented in Fig. 7.41. The amplitude map indicates the voltage amplitude $\mathcal{U}_k$ with which the relative dHvA frequencies participate in the oscillating dHvA voltage signal $\mathcal{V}_k$, refer to Section 7.2.3. (The amplitude information depends on the temperature, the modulation amplitude and field scan: for this set of measurements they amount to 1.46 K, 1.5 mT and 6.5 – 8 T, respectively. Modulation frequency $\omega = 117$ Hz and detection harmonic $k = 2$ are fixed). The calculated angular dependence of Fig. 7.29 for the related (110) plane is superimposed in Fig. 7.41. Here we find great agreement with the experimental results.

Following the calculated data (solid lines), the experimental angular dependence is easily withdrawn. The dotted lines give guidance to the eye. The experimental and calculated frequencies depart differently from each other for different Fermi sheets. Some frequencies agree quite completely, while discrepancies between 1 up to 10% are also observed.

For a quantitative analysis it is convenient to display a frequency spectrum at constant angles, as the two blue lines at $\theta = 0^\circ$ and $\theta = 24.25^\circ$ indicate. The spectrum and the relative dHvA oscillations for the [001] direction ($\theta = 0^\circ$) are represented in figures 7.43 and 7.42, respectively. Coloured bars indicate the calculated frequencies. The best agreement is noticed for frequencies ϵ_1 and β_1 . The other peaks lie next to the calculated ones, both conveniently separated from harmonic and combination tones, which remain thus unlabelled. Frequencies belonging to the Fermi sheets ϵ, β and α could be resolved. The very low frequencies of sheets γ and χ could not be resolved in the range up to 1 kT. The topology of the observed sheets can be recognized by the angular dependence in Fig. 7.41. The experimental β -sheet reproduces the calculated one. Thus branch β_1 and β_2 meet off the [001] direction and β_1 passes through a minimum at 24.25° . Both the minimum and all of the branch β_2 lie at slightly higher frequencies than the calculated

Figure 7.41: Amplitude map of the dHvA frequency spectra for rotations between the high symmetry directions [001] – [110] in the plane (110) of LaIrIn₅. Lines show the calculated angular dependence.

Figure 7.42: $dHvA$ oscillations at $\theta = 0^\circ$ from $[001]$ in the (110) plane measured with AREDOS.

Figure 7.43: FFT of the oscillations in Fig. 7.42. Calculated frequencies from RFPLO are indicated.

Figure 7.44: dHvA oscillations at $\theta = 24.25^\circ$ from [001] in the (110) plane measured with AREDOS.

Figure 7.45: FFT of the oscillations in Fig. 7.44. Calculated frequencies from RFPLO are indicated.

ones. The spectrum and the relative dHvA oscillations for $\theta = 24.25^\circ$ off the [001] direction, for which the minimum is observed, are represented in figures 7.45 and 7.44, respectively. The calculated peak for β_1 lies next to the experimental peak but it is not the calculated minimum, which appears for $\theta = 27.9^\circ$, refer to Fig. 7.41. The experimental α sheet develops its three frequencies with a smooth $1/\cos \theta$ -like dependence and then follows the stronger angular dependence very similar to the calculated curve.

Fig. 7.46 is the amplitude map of the dHvA frequency spectra in the (100) plane from [001] to [100] direction. The basic experimental settings are for the temperature 1.5 K, modulation amplitude 1.5 mT and the magnetic field scan 6.5 – 8 T. As for the preceding measurement, by superimposing the calculated angular dependence of Fig. 7.29 for the related (100) plane into Fig. 7.46, we find great agreement with the experimental results.

Again following the calculated data (solid lines), the experimental angular dependence is easily withdrawn (dotted lines). The experimental and calculated frequencies depart differently from each other for different Fermi sheets. The behaviour is consistent with the (110) plane. In fact, some frequencies agree quite completely, while discrepancies between 1 up to 10% are also observed.

Frequencies belonging to the Fermi sheets ϵ, β and α could be resolved. The very low frequencies of sheets γ and χ could not be resolved in the range up to 2 kT. The observed angular dependences reproduce the calculated topology. Thus, the experimental β -sheet produces branch β_1 and β_2 , which meet off the [001] direction. β_1 also passes through a minimum, estimated at 29.1° . Both the minimum and all of the branch β_2 lie at slightly higher frequencies than the calculated ones, as in the (110) plane. The spectrum and the relative dHvA oscillations for $\theta = 29.1^\circ$ off the [001] direction, for which the minimum is observed, are represented in figures 7.48 and 7.47, respectively. Notice that the calculated peak for β_1 lies next to the experimental peak but it is not the calculated minimum, which appears for $\theta = 34.1^\circ$, refer to Fig. 7.46. The peaks aggregation around 5 kT belongs to the α_i branches. Back to the Fig. 7.46, the experimen-

Figure 7.46: Amplitude map of the dHvA frequency spectra for rotations between the high symmetry directions [001] – [100] in the plane (100) of LaIrIn_5 . Lines show the calculated angular dependence.

Figure 7.47: dHvA oscillations at $\theta = 29.1^\circ$ from [001] in the (100) plane measured with AREDOS.

Figure 7.48: FFT of the oscillations in Fig. 7.47. Calculated frequencies from RFPLO are indicated.

tal α sheet develops its three frequencies with a smooth $1/\cos \theta$ -like dependence and then follows the stronger angular dependence very similar to the calculated curve. In order to follow the high frequency values, in the angular interval between 50° and 70° , the magnetic field scan was changed to 8 – 9 T, thus the frequency spectrum extends to 36 kT and widely covers the expected frequency range.

The dHvA frequencies in the [001] direction give the most information about the Fermi body in its highest symmetry direction and about its extension in the (001) plane. In this plane and within a narrow angle tilting, the highest frequency ϵ_1 is expected. Its existence is put into discussion, since it was not observed in the LaTMIn_5 compounds with $TM = \text{Co}, \text{Rh}$ [91]. The missing of the ϵ -sheet could not be explained properly.

The dHvA rotation study was thus focused into a range of approximately $\pm 10^\circ$ from the [001] direction, within the (100) plane. The basic experimental settings are for the temperature 1.55 K, modulation amplitude 2 mT and the magnetic field scan 7 – 8.5 T, while tilting the angle in steps of 0.5° . The measured angular dispersion is represented in Fig. 7.49. The calculated curves (coloured lines) match the measured frequencies in all the range. Particular interest should be put on the ϵ_1 branch. Its existence range can be followed clearly until nearly $\pm 5^\circ$, before being confused from a branch of summation frequency. At larger angles the frequency ϵ_1 is expected to disappear and decomposes into the small frequency branches from the long ellipsoids centered at X, refer to Fig. 7.31.

The best matching is shown by the branch β_1 in the complete observed range. The second branch of the β sheet shows slight departure from the calculated curve in the value but not in the angular dependence. As the amplitude map shows, β_2 is the strongest frequency of the spectrum. Second and third harmonics of this frequency, due to magnetic interactions are present at about 11600 T and 17500 T, respectively.

The peculiar results from the previous dHvA rotation experiments are summarized in the following table 7.5, together with the related dHvA frequencies from the RFPLD angular disper-

Figure 7.49: Amplitude map of the dHvA frequency spectra for rotations across the [001] direction in the plane (100) of LaIrIn_5 . Lines show the calculated angular dependence.

sion of figures Fig. 7.29 and Fig. 7.30.

The previous experiments were performed with settings able to resolve the main frequencies of the spectrum. The analysis of the small frequencies and thus of the small parts of the Fermi sheets is then integrated by the study of the angular dispersion of the dHvA frequencies in the (001) plane from [100] to [110] direction. For this set of measurements the temperature was held at 1.47 K, while a slightly larger field modulation of 2 mT and a field scan of 2 – 3 T were required. The spectrum dispersion is represented in Fig. 7.50. By superimposing the calculated angular dependence of Fig. 7.30 for the relative (001) plane we find a relative good agreement with the experimental results.

The experimental ϵ sheet produces the branch ϵ_2 referred to the cushion part centered at Γ . Its angular dependence has local minimum of 815 T at $\theta = 45^\circ$, in the [110] direction. The data (blue dotted line) practically coincide with the calculated curve (blue line). The spectrum and the relative dHvA oscillations for $\theta = 45^\circ$ off the [100] direction, for which the minimum is observed, are represented in figures 7.54 and 7.53, respectively. The peak appears clearly decoupled, although the cause is not clear. The effect of the presence of two very similar frequencies is the beat pattern of the dHvA oscillation illustrated in Fig. 7.53.

The inset in Fig. 7.50 shows the lower frequency range in more detail. The ϵ_3 and ϵ_4 branches are expected, coming from the ellipsoids and the neck parts of the ϵ sheet respectively (green lines). The experimental branch ϵ_3 can be recognized by the characteristic raising dependence being mirrored at $\theta = 45^\circ$, because of the four-fold multiplicity of these ellipsoids in the (001) plane. Although it is consistent with the calculated curve, its minimum at $\theta = 0^\circ$ departs nearly 20% from the expected value of 483 T. The small frequencies belonging to the ϵ_4 branch instead could not be resolved. The spectrum and the relative dHvA oscillations for $\theta = 0^\circ$ in the [100] direction are represented in figures 7.52 and 7.51, respectively. The χ sheet could be partly re-

Figure 7.50: Amplitude map of the dHvA frequency spectra for rotations between the high symmetry directions [100] – [010] in the plane (001) of LaIrIn₅. Lines show the calculated angular dependence.

Figure 7.51: $dHvA$ oscillations at $\theta = 0^\circ$ from $[100]$ in the (001) plane measured with AREDOS.

Figure 7.52: FFT of the oscillations in Fig. 7.51. Calculated frequencies from RFPLO are indicated.

Figure 7.53: dHvA oscillations at $\theta = 45^\circ$ from [100] in the (001) plane measured with AREDOS.

Figure 7.54: FFT of the oscillations in Fig. 7.53. Calculated frequencies from RFPLO are indicated.

solved following the red solid lines from the calculation. The smaller frequency from its waist and the raising angular dependence is reproduced by the red dotted lines, which do not complete to the expected maximum at 0° and 90° . Nevertheless, the data curves show the expected bisection at 45° due to the four-fold symmetry in the (001) plane. Experimentally, only the γ sheet could not be resolved, represented by the blue line. It is not unexpected that very small dHvA frequency could not be resolved. The additional results from the previous dHvA rotation experiment are summarized in Tab. 7.5, together with the relative dHvA frequencies from the RFPLO angular dispersion of figures 7.29 and 7.30.

orbit Ω	dHvA experiment		RFPLO calculation	
	direction sample	Frequency [T]	direction	Frequency [T]
scan 6.5 – 8 T @ 1.46 K				
ϵ_1	[001] $_{EK1}$	13955.2 ± 34.6	[001]	13855
β_1	[001] $_{EK1}$	9730.5 ± 34.6	[001]	9632
β_1	24.25° from [001] in (110) $_{EK1}$	8587.8 ± 34.6	62.1° from [001] in (110)	8361
β_1	29.1° from [001] in (100) $_{EK1}$	7896.3 ± 34.6	55.9° from [001] in (100)	7570
β_2	[001] $_{EK1}$	5817.5 ± 34.6	[001]	5259
α_1	[001] $_{EK1}$	4155.4 ± 34.6	[001]	3829
α_2	[001] $_{EK1}$	3601.3 ± 34.6	[001]	3259
α_3	[001] $_{EK1}$	3358.9 ± 34.6	[001]	3178
χ	[001] $_{EK1}$	-	[001]	263
γ_1	[001] $_{EK1}$	-	[001]	697
γ_2	[001] $_{EK1}$	-	[001]	142
scan 2 – 3 T @ 1.47 K				
ϵ_2	[110] $_{EK2}$	815.2 ± 5.9	[110]	805
ϵ	[110] $_{EK2}$	544.6 ± 5.9	[110]	643
ϵ_3	[100] $_{EK2}$	395.6 ± 5.9	[100]	483
ϵ_4	[100] $_{EK2}$	-	[100]	107
χ_1	[100] $_{EK2}$	-	[100]	2197
χ_2	[100] $_{EK2}$	209.8 ± 5.9	[100]	98
χ	[110] $_{EK2}$	327.7 ± 5.9	[100]	140
γ_1	[110] $_{EK2}$	-	[110]	400
γ_2	[100] $_{EK2}$	-	[100]	270

Table 7.5: High symmetry and non-central dHvA frequencies for LaIrIn_5 from the present rotation experiment in comparison with the recent calculations.

The effective masses at the Fermi surface

Orbit effective-masses are determined by measuring the temperature dependence of the amplitude of the dHvA oscillations at a constant field. From the extended Lifshitz-Kosevich theory (see Section 7.1) of the dHvA effect, the temperature dependence of the amplitude of the fundamental harmonic of a dHvA frequency F is

$$\mathcal{M}(B, \theta, \phi, T) = \mathcal{M}(B, \theta, \phi) R_D R_S \frac{b m^* T / B}{\sinh [b m^* T / B]}. \quad (7.66)$$

where $\mathcal{M}$, R_D and R_S are temperature independent. b is the constant factor with value 14.69 TK^{-1} . For the field modulation method, the measured fundamental amplitude for a dHvA frequency is, after expressions (7.57),

$$\mathcal{U}_2(F) = 4 \omega J_2(\delta\varphi) \mathcal{M}(B, \theta, \phi, T) \hat{\mathbf{M}} \cdot \mathbf{c} \quad \text{with} \quad \delta\varphi = \frac{2\pi F b}{B^2} \quad \text{for} \quad q = 1, \quad (7.67)$$

for detection at the second harmonic.

To determine the effective mass m^* , the usual procedure is to take field sweeps at different temperatures in constant intervals typically in the range from 0.5 K to 2 K¹⁵. The field sweeps are kept short in order to characterize the range by a single field value as the magnetic field enters into equation (7.67) only as a constant in the amplitude temperature dependence. The effective value used is

$$B_{eff} = 2 \left(\frac{1}{B_{start}} + \frac{1}{B_{stop}} \right)^{-1}, \quad (7.68)$$

¹⁵The successive sweeps are generally taken going down in temperature so that the convection from the boiling ³He liquid would help to minimize any thermal gradients. Typically, after pumping down to a new nominal temperature, about 5-10 min was allowed for thermal equilibrium to be attained before recording the field sweep. This was determined to be a satisfactory period since trial runs allowing longer equilibration times did not significantly affect the results.

Figure 7.55: dHvA frequency spectra (FFT) versus experimental temperature.

Figure 7.56: $dHvA$ oscillations in $[001]$ measured with AREDOS at two different temperatures.

Figure 7.57: FFT of the oscillations in Fig. 7.56. Calculated frequencies from RFPLO are indicated.

which is rigorously correct when the amplitude varies linearly over the range of data. For each field sweep, amplitudes are determined using the Fourier transform program, refer to Section 7.5. The amplitudes of any dHvA frequency are then fitted with the following procedure to obtain the effective mass specific of the dHvA frequency. By writing the hyperbolic sine in exponential form, expression (7.66) becomes a relation for the exponential arguments and reduces with use of relation (7.67) to

$$\ln \left[\frac{\mathcal{U}_2}{T} (1 - e^{-2m^*t}) \right] = \quad (7.69)$$

$$\ln(4 \omega J_2 \hat{\mathbf{M}} \cdot \mathbf{c}) + \ln[\mathcal{M}(B, \theta, \phi)] - m^*t. \quad (7.70)$$

Expression (7.69)-(7.70) shows that the function (7.69) is a straight line with slope $-m^*$ in the rescaled temperature t . $t = \frac{bT}{B_{eff}}$ is a dimensionless number. Temperature independent factors and experimental gain factors occur as constants which do not affect the estimation of the slope. Since m^* appears in both relations, the equation is a self consistent formula for m^* . For each frequency of the spectrum, formula (7.69) is plotted as function of t introducing the related dHvA amplitudes, the corresponding measurement temperatures, the effective field and a guess value $m^* = 0.5$ or 1 . Thus, from the slope, the m^* for the next iteration step is evaluated. The procedure is then repeated with the new calculated m^* until a converging value of m^* is reached.

Temperature dependent dHvA measurement of LaIrIn_5 were performed in both the directions [001] and [100]. The measurement set of dHvA spectra at different temperatures is illustrated in Fig. 7.55 for the [001] direction. The temperature dependence of the amplitudes is relatively strong. The effect of temperature on the amplitudes is precisely illustrated by comparing the dHvA oscillation at the high and low temperatures in Fig. 7.56. The related frequency spectra are shown in Fig. 7.57. The amplitude $\mathcal{U}_2(\epsilon_1)$ shows a very strong temperature dependence, thus hinting to a large effective mass, relative to the other frequencies.

By applying the self-consistent procedure, the effective masses of the observed frequencies were determined quantitatively. Expression (7.69)-(7.70) converges in all the cases within few iterations and follows the linear dependence very well. The results are represented in figures 7.58 and 7.59 for the [001] and in 7.60 for the [100] direction and listed in Tab. 7.6. The probable error for each m^* is estimated from the standard deviation of the slope. The mass values are very accurate, particularly in the direction [100], as the low scatter of the data demonstrate. Corresponding orbit masses were calculated in [001] with the RFPLO method and their values give the slopes of the dotted lines represented together with the respective experimental curves (coloured lines). In all the cases the experiments show larger slopes, thus larger orbit effective masses, as expected from electron-phonon interactions. Their values range from 0.5 for the α_2 to 1.2 for the ϵ_1 frequency in the [001] direction. For [100] values of 0.2 are found. All the masses are expressed in units of free electron mass m_e .

The Fermi velocities

Considering formula (2.59), the orbit velocity depends on the orbit area. The use of the Onsager relation (7.7) permits to deduce the extremal orbit areas of the Fermi surface from dHvA frequencies, thus introducing (7.7) into (2.59) follows the expression

$$v_\Omega = \frac{1}{m^* \cdot m_e} \cdot \sqrt{2 \hbar e F} \equiv v_F, \quad (7.71)$$

generally used to estimate orbit-averaged Fermi velocities from dHvA data. Into expression (7.71) one introduces the dHvA frequencies and the corresponding orbit effective masses to obtain effective values of the Fermi velocities, which are generally smaller than the related Fermi velocities from the band data, since electron-phonon interaction is considered.

Table 7.6 shows the Fermi velocities estimated with this procedure. The values range between $5.11 \cdot 10^5$ m/s and $7.65 \cdot 10^5$ m/s. If we consider normal metals from the second group, the

Figure 7.58: Amplitudes of dHvA frequencies in [001] versus reduced temperature. The slopes give the relative effective masses m^* . The dotted lines are the respective RFPLO curves.

Figure 7.59: Amplitudes of dHvA frequencies in [001] versus reduced temperature. The slopes give the relative effective masses m^* . The dotted lines are the respective RFPLO curves.

Figure 7.60: Amplitudes of dHvA frequencies in [100] versus reduced temperature. The slopes give the relative effective masses m^* .

orbit Ω	direction sample	dHvA				RFPLO	el.-ph.
		Frequency [T]	iter- ations	m^* [m_e]	v_F [10 ⁵ m/s]	m_Ω [m_e]	$\langle \lambda \rangle_\Omega$
scan 7 – 8.5 T @ 0.67 – 1.75 K							
ϵ_1	[001] _{EK1}	13909.4 ± 39.6	4	1.236(59)	6.09	−0.985	0.255(60)
β_1	[001] _{EK1}	9748.5 ± 39.6	3	1.050(83)	6.00	0.697	0.506(119)
β_2	[001] _{EK1}	5825.2 ± 39.6	5	0.772(45)	6.31	0.628	0.229(72)
α_1	[001] _{EK1}	4161.0 ± 39.6	4	0.806(42)	5.11	0.558	0.444(75)
α_2	[001] _{EK1}	3606.2 ± 39.6	4	0.501(54)	7.65	0.473	0.059(114)
α_3	[001] _{EK1}	3368.4 ± 39.6	2	0.526(54)	7.04	0.477	0.103(113)
scan 2 – 3 T @ 1 – 1.95 K							
ϵ_3	[100] _{EK2}	395.6 ± 5.9	4	0.229(4)	5.55	-	-
χ_2	[100] _{EK2}	209.8 ± 5.9	4	0.183(3)	6.95	-	-
coupling constant : $\lambda_{dHvA} = 0.266$							

Table 7.6: High-symmetry dHvA properties for LaIrIn₅ from the present temperature dependent experiment in comparison with the recent calculations.

literature [8] reports values ranging from $13 \cdot 10^5 \text{ m/s}$ for lithium to $7.3 \cdot 10^5 \text{ m/s}$ for cesium. A diboride intermetallic compound like ZrB₂, having smaller Fermi surface and effective masses, showed higher values between $7.913 \cdot 10^5 \text{ m/s}$ and $9.956 \cdot 10^5 \text{ m/s}$ in a previous work [31]. Thus, in comparison, LaIrIn₅ is a "heavier" intermetallic compound.

Averaged electron-phonon coupling constant

A local effective mass at one point of the reciprocal space is enhanced from the local band mass due to dispersive interactions that the calculation does not consider. Among these the electron-phonon coupling has major influence.

The averaged value $\langle \lambda \rangle$ from the local electron-phonon enhancement factor $1 + \lambda(\mathbf{k})$ on an extremal orbit Ω is obtained by comparing the calculated orbit band mass with the dHvA orbit mass, which is an effective mass including electron-phonon renormalization:

$$m^* = |m_\Omega| (1 + \langle \lambda \rangle_\Omega) . \quad (7.72)$$

The measured m^* are independent of sign and can only be compared to the absolute values of the corresponding RFPLO band masses.

The results are shown in table 7.6 for the extremal orbits in the (001) plane. We report values ranging from 0.059 to 0.506. The total mean value is the estimation of the dHvA coupling constant of 0.266.

Chapter 8

Conclusions

Metallic crystals constitute the convenient systems for the study of conductivity through the assumption of an electronic structure. Departures from ideal behaviours like in the intermetallic compounds requested many efforts in the development of the measurement technique and stimulated the evolution in the calculation models. The present work is a guide through the complexity of the topic explaining, in every chapter, first the actual state-of-the-art and the available skills, then the implementation to the material LaIrIn_5 , following a modern physical description.

8.1 Summary

The work describes the fundamental concepts and the modern approach in solving the model electronic structure specific of LaIrIn_5 . Results from the RFPLO scheme for the band structure calculation constitute the reference for electron-dynamics parameters that find direct relation with experimental phenomena: electrical resistivity, heat capacity and de Haas-van Alphen effect. Primarily the good quality of the samples makes the measured results reliable. Crystal structure analysis with diffraction methods permits to establish the geometrical structure and the composition, also assessment for the calculation, and to determine the quality. LaIrIn_5 is a stoichiometric compound with tetragonal symmetry and layered distributions of the atomic elements. Electrical transport measurements on single crystals revealed that LaIrIn_5 behaves like an intermetallic compound without anisotropy of the carrier states, in agreement with the expectations from the calculations. The measurement was performed accurately and analysed in the Bloch-Grüneisen approximation. But inadequacy in the traditional interpretation of the data was found and suggested an analysis beyond the Bloch-Grüneisen, with the additional Einstein term. The complex analysis gives information about the crystal vibrations

(phonons) through the Debye and Einstein temperatures and about the electron-phonon interactions through the transport coupling constant. This is the enhancing factor of the electron-dynamics properties from the band structure calculation and quantifies the discrepancy of the model from the experimental reality. Heat capacity measurements also provide results for the lattice dynamics and the electron-phonon coupling. Furthermore, the study of the de Haas-van Alphen effect implied the development of the AREDOS method, providing a complete and profound description of the electron properties, for qualitative and quantitative comparisons with the RFPLO model. From the deviations with the calculated results electron-phonon coupling is estimated as well.

Accuracy in the AREDOS method required the design and realization of a versatile sample holder and a sensitive magnetization sensor. The measurement apparatus is to be used in commercial cryostat systems.

8.2 The Fermi surface

The rotation AREDOS experiment has shown the power of the de Haas-van Alphen effect for precise statements about the Fermi surface. Symmetry considerations have reduced the experiment to the basic domain of the Brillouin zone. The angular dependence for the major dHvA frequencies is thus completely determined for magnetic field directions inside the planes (110), (100) and (001) of the tetragonal structure. Since the dHvA frequencies correspond to extremal cross sections of the Fermi surface, the angle dependence diagrams determine the Fermi surface topology. The uncertainty about the position of the different Fermi sheets in the Brillouin zone is resolved by the band structure. Centers are Γ , M, Z and R. The calculated Fermi surface could be confirmed with precision in all its characteristics. The highest frequency of nearly 14 kT belonging to the largest sheet could be resolved. The small angle range in which this frequency exists was not a difficulty for the high-resolution measurement system used.

8.3 Electronic interactions

The size of the total temperature coefficient of resistivity $\rho' + \rho'_E$ is directly proportional to the electron-phonon coupling constant. The resistivity in the [100] direction of LaIrIn₅ gives a representative value of $\lambda_{lr} = 0.34$ for the electrical transport. The specific coupling constant λ_D for acoustic and λ_E for optical phonons amount to 0.316 and 0.024, respectively. As another probe for the average electron-phonon coupling in LaIrIn₅, a λ can also be obtained from the experimental value of the electronic specific heat coefficient γ . The result is thus a $\lambda_{hc} = 0.26$. The effective masses for the dHvA frequencies of direction [001] (orbits in the (001) plane) are compared to the corresponding calculated band masses. The differences are small but not negligible so that the electron-phonon enhancement amounts in average to $\lambda_{dHvA} = 0.266$.

The first thing to be noted is that the three different experiments (resistivity, heat capacity and dHvA) are reliable procedures producing consistent results of a small electron-phonon coupling in LaIrIn₅. As announced in Section 5.1, these results can be used to predict superconductivity. Strong electron-phonon coupling is considered responsible for the electron-electron pairing at low temperatures, which is the classic superconducting state. Introducing the experimental estimations for λ and $\Theta_D = 223\text{K}$ in the Dynes-corrected expression of the McMillan formula (5.37)

$$T_c = \frac{\Theta_D}{1.45} \exp\left(-\frac{1 + \lambda}{\lambda - \mu^*(1 + \lambda)}\right), \quad (8.1)$$

we find, assuming a standard value of $\mu^* = 0.10$, an expected low superconducting transition temperature between 13 mK ($\lambda = 0.26$) and 122 mK ($\lambda = 0.316$), consider Fig. 8.1. A measurement of the magnetic susceptibility at a high quality sample down to this interval did not show superconductivity above 56 mK. A T_c is also suppressed by the small Debye temperature or equivalently in the Dynes correction by a small average phonon energy. Thus LaIrIn₅ behaves in this sense without anomalies, like a traditional intermetallic compound, in classical terms. On the contrary, the occurrence of superconductivity in the Ce-substituted ternary compounds has to be attributed to a higher effective density of states due to strong electron-electron interactions. This leads to larger coupling constants, thus, referring to Fig. 8.1, transition temperatures between 0.5–2 K.

Figure 8.1: Superconductivity transition temperature as a function of the coupling constant λ for the experimental Debye temperature of LaIrIn₅.

FS LaCoIn₅ FS LaRhIn₅ FS LaIrIn₅ **Figure 8.2:** *Fermi surfaces.*

8.4 Fermi surface crossing

LaIrIn₅ is the only compound in the series La*TM*In₅ (*TM* = Co, Rh and Ir) for which the high frequency ϵ_1 , relative to the largest and thus most important sheet completing the Fermi surface, is observed. The effective masses are similar and approximately between 0.3 – 1.0 m_e for all these compounds. The hypothesis that ϵ_1 in the Co or Rh compounds should have an extremely high mass preventing the experimental observation, due to the damping of the dHvA amplitude, is not acceptable. Rather topological considerations should have to be introduced. In this relation, previous works [40, 91, 43] proposed that the disappearing of the frequency ϵ_1 could be ascribed to the strong damping of the dHvA amplitude due to the large curvature factor of this orbit. In fact the damping amounts to

$$\frac{1}{\sqrt{|\mathcal{A}_{ext}''(\theta, \phi)|}}, \quad (8.2)$$

as extracted from the amplitude of the oscillating quantum magnetization (7.10). Thus the Fermi surfaces of LaCoIn₅ and LaRhIn₅ were calculated¹ with the RFPLO scheme and compared with LaIrIn₅. The result is illustrated in Fig. 8.2. The fact that the ϵ sheets are topologically very similar excludes an anomalous damping for the Co and Rh compounds and other considerations must be made. This statement is confirmed by interpreting the theoretical and experimental results for the series Pr*TM*In₅ (*TM* = Co, Rh and Ir) [24, 43]. Similarly to La*TM*In₅, in Pr*TM*In₅ the frequency ϵ_1 is not observed, except for the compound PrIrIn₅. Thus the responsible factor is rather the *TM* element Co and Rh, whose role is to change the electron content and the dimensions of the Fermi surface. In order to consider the effect of Co and Rh on the Fermi surface, we analysed the ϵ -sheet cut and that of its neighbour β along the [001] direction in the vicinity of the point Γ , where ϵ is extremal. The results for the series La*TM*In₅ are shown in figures 8.3, 8.4 and 8.5, reproducing the band structure and the orbits in the extended zone scheme. The most striking changes with the element substitution develop in the band structure along the Γ –M path. The change from Co, Rh to Ir causes an upward shift of the bands 131 and 133 referred to the Fermi energy, here taken as zero of energy. These two bands actually cross, and the cross point exceeds the Fermi level when Ir is present. The effect is that the β -sheet penetrates the ϵ one in the Co and Rh compound producing what we call a Fermi surface “crossing”. Fig. 8.6 represents the ϵ and β sheets of LaIrIn₅ in more detail. Along the Γ –M line the ϵ and β sheets of LaIrIn₅ are clearly separated by a gap in the k -space, while for LaCoIn₅ and LaRhIn₅ the ϵ and β sheets are crossing each other. At the crossing points, a hole orbit (ϵ_1) and an electron orbit (β_1) share their character.

Effects of crossing like disappearing of both or one of the crossing sheets is not known in literature. Nevertheless effects due to the vicinity of Fermi sheets are known. Provided the separations (gaps) are not too wide in view of the strength of the magnetic field, it accounts for the magnetic breakthrough occurring between electron and hole orbits yielding frequency mixing to be observed in the dHvA spectra. Magnetic breakthrough is especially observed in two dimensional electron systems like in the organic metals ([103] and references therein). Mixing due to magnetic interactions instead (refer to Section 7.1.1) is not a topological effect rather the result of vector sum of oscillating magnetizations.

We address the crossing as the responsible phenomenon for the damping of the ϵ_1 frequency and evoke efforts in theory and experiments for the analysis of the question in these terms.

¹The calculations in the RFPLO scheme were performed by S. Elgazzar.

Figure 8.3: Band structure and Fermi surface cuts along [001] direction at Γ for LaCoIn_5 .

Figure 8.4: Band structure and Fermi surface cuts along $[001]$ direction at Γ for LaRhIn_5 .

Figure 8.5: Band structure and Fermi surface cuts along [001] direction at Γ for LaIrIn_5 .

Figure 8.6: *Fermi sheets from the 131 and 133 bands of LaIrIn₅.*

Chapter 9

Outlook and development

SUMMARY

The high sensitive AREDOS technique can be developed further with the use of MEMS sensors, in particular of piezoresistive cantilever. Their development and introduction [101, 84, 105] was dictated by the usual availability of very small samples (typically $100\text{ }\mu\text{m}^3$ dimension), thus producing very small magnetic moments, which the conventional induction methods could not detect. In this Chapter we illustrate the efforts attempted in the development of the AREDOS assembly, in order to extend it to the use of high-sensitivity sensors for a wider spectrum of applications and experiments. Some hints at new experimental intents are also given.

9.1 Multi-functional rotator system

The insertion probe system has also been realized to accommodate a multi-functional rotator, Fig. 9.1. The rotating sensor illustrated in Section 7.2.5 for high sensitivity AREDOS measurements can be easily removed from the forc holder by detaching the connectors and extracting the Vespel® bushings. Then, the multi-functional rotator is mounted with the same procedure in the inverse way. It again consists of a cylindrical barrel machined from Vespel® with a side bore to contain the sample-sensor system and performs the θ -rotation using the rotating shaft in German Silver as well. The design permits to mount any sensor for low temperature and

Figure 9.1: Exploded view of the multi-functional rotator with some examples of sensor chips.

high field measurements on a Macor®¹ plate furnished of contact pads too. The plate is then inserted sideways into the rotator, where a double layer pin socket² catches it and closes the electrical contacts. The available free area is nearly $10 \times 5 \text{ mm}^2$. The plate can also function as a sample holder for magneto-resistivity measurements in the very low temperature and high magnetic field ranges of a cryostat, refer to Section 7.3. Additionally, one can take advantage of the θ -rotation that permits the tilting of the magnetic field relatively to current and crystal sample axes. Samples only have to be oriented with respect to the plate which is indirectly a precise orientation with respect to the rotator. The multi-functional insertion probe system is thus illustrated in Fig. 9.2.

The most proper application of the system is in connection with Micro-Electro-Mechanical Systems (MEMS). Their use as sensor for fields or forces helps in the measurement of very small samples, like micro single crystals.

¹Machinable Glas Ceramics (MGC) of Corning Incorporated.

²Adapted commercial socket: FCI 61082-101000, 0.8 mm board-to-board socket.

Figure 9.2: Detail of the multi-functional insertion probe system.

9.2 AREDOS using MEMS sensors

Microcrystals are conveniently characterized by single crystal X-ray diffractometry, refer to Section 4.2.4. But the measurement of their electronic structure with AREDOS, using the induction sensor, quickly goes beyond the sensitivity of the system.

9.2.1 Piezoresistive cantilevers

The development of the AREDOS method is achieved with the use of piezoresistive cantilevers as sensors. With or without the field modulation for additional selectivity, the overall moment sensitivity reaches a factor of many hundreds compared to the inductive method. The sensitivity in high magnetic fields, typically of the order of 10^{-14} Am^2 at 10 T, is also much higher than the sensitivity of superconducting quantum interference devices (SQUID). Limiting dimensions for the crystals are approximately $100 \text{ } \mu\text{m}^3$.

The principle of the cantilever magnetometry, refer to Section 7.2.1, is based on the torque resulting from the magnetic moment and the magnetic field

$$\boldsymbol{\tau} = V \mathbf{M} \times \mathbf{B}, \quad (9.1)$$

which produces the bending of the lever. $\mathbf{M}$ is the quantum-oscillatory magnetization as expressed in the extended Lifshitz-Kosevich equation (7.24) for the de Haas-van Alphen effect or any other intrinsic magnetic property in reference to a sample of volume V . The effect is then commutated in a voltage signal from the resistivity changement of the path of a Wheatstone bridge at the position of the highest deformation on the lever. Cantilevers are fabricated from silicon single crystals. The resistive paths are properly doped ranges.

Commercial cantilevers are usually mounted on chips with contacts, so that a supporting Macor® plate positions the chip inside the rotator as in Fig. 9.1. Actually, only a few models are available for the purpose of cantilever magnetometry at very low temperatures, which dispose of highly doped resistive paths. Piezolevers for atomic force microscopy are well suited like those of TM Microscopes distributed by Veeco and those fabricated by Seiko Instruments Inc. (SII) ³. The first disposes of only one piezolever on the chip, which constitutes one of the four paths of the Wheatstone bridge. A cantilever chip of this type is illustrated in Fig. 9.3. Those from SII dispose of a second lever, which constitutes the reference path of the sensing bridge, thus the background signal originating from the temperature and magnetic field dependence of the cantilever is effectively compensated [71]. Refer to Fig. 9.4.

³The author is grateful to Dr. C. Rossel and D.Sc. E. Ohmichi, who provided some test cantilevers.

Figure 9.3: TM microcantilever. Detail.

Figure 9.4: *SII microcantilever. Detail.*

Previous works [84, 13, 71] revealed how the use of microcantilevers was very helpful in low-temperature experiments. Now, in combination with the high accurate rotation system here developed, it promises the possibility to go beyond some sensitivity limits of modern available systems.

Because of the very reduced scale of both the sensor and the suitable samples, the handling and the orientation is made quite difficult. Micro-positioning systems are used to place some amount of epoxy glue or grease and then the sample on it. A single crystal, whose physical properties like electric transport and heat capacity were previously measured, has to be cleaved into suitable small pieces. One sample should be characterized with single crystal X-ray diffraction and then be mounted on the cantilever for the rotation dHvA measurement. A measurement relative to a known crystal orientation inside lattice planes is only assured when a sample, previously oriented with the Laue method, can be successfully transferred onto a cantilever. Actually, microcrystals grown with the flux method very often preserve the lattice symmetry in their geometry, thus the habitus constitutes the reference for the crystal orientation, which is helpful to orient the crystal on the cantilever.

The cantilever method is thus very promising in the study of the electronic structure of the non-stoichiometric compound $\text{Al}_{1-x}\text{B}_2$ at hexagonal plate-like microcrystals. One sample is shown in Fig. 9.5, as mounted for the crystal structure characterization with X-ray diffractometry ⁴ (refer to Section 4.2.4).

⁴The measurement was executed with the advice and co-work of Dr. M. Biadene, University of Göttingen, Dept. of Structural Chemistry, Prof. G. M. Sheldrick.

Figure 9.5: *Single crystal of $\text{Al}_{1-x}\text{B}_2$. Scale unit 20 μm .*

9.3 New experiments with AREDOS

Materials of high interest are the intermetallic ternary compounds $RE_5Ir_4Si_{10}$, showing collective phenomena of the electronic structure like charge density waves, local moment antiferromagnetism and conventional superconductivity within the same system [33], for which the study of the Fermi surface of single crystals ⁵ can be accurately performed by the AREDOS method with the induction sensor. In the non-magnetic compound $Lu_5Ir_4Si_{10}$ the charge density wave coexists with the superconductivity at low temperatures below the transition at $T_c = 3.8$ K [12].

The low dimensionality of the charge density wave is induced in three dimensional systems by the nesting of the Fermi surface, which can lead to electron instabilities depending on the band structure of the compound. Nesting is a phenomenon that, like crossing and magnetic breakthrough of the Fermi surface, depends on the topology of the Fermi surface. Thus it has to be analysed by accurate study with the AREDOS method in a future work, in companion with band structure calculations as presented in Section 8.4.

⁵The author is grateful to Dr. H. Rosner and Prof. Dr. J.A. Mydosh, who provided some single crystals of $Lu_5Ir_4Si_{10}$.

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