Doctoral Thesis

Influence of superconductivity and magnetism on transport properties of rare earth rhodium boride compounds

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INFLUENCE OF SUPERCONDUCTIVITY AND MAGNETISM ON TRANSPORT PROPERTIES OF RARE EARTH RHODIUM BORIDE COMPOUNDS

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1 INTRODUCTION

The rare earth rhodium borides have only been known since 1977, nevertheless they attracted a widespread interest in the short period since then. The reason for the special attention is the broad variety of magnetic and superconducting properties of these compounds which stimulated the research on the old question of coexistence of long range magnetic order and superconductivity (Ginsburg 1956). In the past this problem was studied in systems like La$_{1-x}$Gd$_x$ (Hein, Falge, Matthias and Corenzwit 1959) but all these systems had the disadvantage of inhomogeneous distribution of the magnetic ions in the sample (for a review see Roth 1977). In the rare earth rhodium borides the magnetic ions form a regular lattice. Therefore the problem of inhomogenity is avoided but the problem of single phased samples remains.

For a discussion of superconductivity and magnetism it is essential to measure real bulk properties. A small amount of an impurity phase which becomes or remains superconducting profoundly affects the electrical conductivity whereas the measurements of the thermal conductivity probes genuine bulk properties.

When a material transforms from the normal to the superconducting state conduction electrons condense in a ground state with no entropy and consequently they do not contribute to the thermal conduction. The electronic thermal conductivity in the superconducting phase will be reduced. Phonons are no more scattered at the condensed electrons, therefore the lattice contribution to the thermal conductivity is enhanced. Thus measurements of the thermal conductivity give information on superconductivity.
When a material undergoes a magnetic phase transition it changes from a disordered to a magnetically ordered state. This transition also influences the mean free path of the electrons and with this the electrical resistance and the thermal conductivity. Therefore, measurements of the electrical resistivity and the thermal conductivity provide complementary information on superconductivity and magnetism.

In this thesis we discuss the thermal conductivity and the electrical resistivity of four rare earth rhodium borides, namely LuRh$_4$B$_4$, HoRh$_4$B$_4$, ErRh$_4$B$_4$ and SmRh$_4$B$_4$, each of them showing different behaviour.

LuRh$_4$B$_4$ shows superconductivity, HoRh$_4$B$_4$ exhibits ferromagnetic order. A study of these two compounds gave us the "background information" for the compounds where both phenomena occur.

ErRh$_4$B$_4$ becomes superconducting at 8.7 K (Matthias, Corenzwit, Vandenberg and Barz 1977) and returns to a normal magnetically ordered state at 0.9 K (Fertig, Johnston, DeLong, McCallum, Maple and Matthias 1977). Of special interest is the temperature range between 1.2 and 0.87 K where magnetic order sets in but the electrical resistivity still remains zero (Moncton, McWhan, Eckert, Shirane and Thomlinson 1977). With thermal conductivity measurements we hope to gain more information about the order parameter in this temperature range.

SmRh$_4$B$_4$ shows superconductivity below 2.68 K down to at least 50 mK. A lambda-type anomaly in the specific heat indicates a magnetic phase transition at 0.8 K without destruction of superconductivity. The interaction of the normal electrons with the localized magnetic Sm$^{3+}$ ions cannot be seen in the electrical resistivity because of the superconduc-
tivity but according to the theory of thermal conductivity in the superconductor containing magnetic impurities by Ambegaokar and Griffin (1964) this interaction should affect the thermal conductivity due to a pair-breaking effect of the Cooper pairs by localized magnetic moments. The thermal conductivity therefore provides a tool to study this pairbreaking effect.
2. EXPERIMENTAL METHODS

The results reported in this thesis were taken in either a $^3$He-$^4$He dilution refrigerator or in a conventional $^4$He pumping cryostat. A longitudinal or a transverse magnetic field could be applied on the sample space. The longitudinal field was provided by a small superconducting selenoid for fields up to 8 kOe. A circular bent head superconducting coil (Harris 1934) was used to produce a transverse magnetic field with a maximum strength of 5 kOe. The rather complicated form of a circular bent head coil instead of a pair of rectangular coils was chosen in order to improve the homogeneity over a typical sample length. The optimised parameters, taking into account the small space for a coil in our refrigerator, were finally chosen so that the homogeneity of the magnetic field over 2 cm was better than 1%.

2.1 $^3$He-$^4$HE DILUTION REFRIGERATOR

The $^3$He-$^4$He dilution refrigerator used in this work is self constructed and covers the temperature range from 35 mK to 4 K. This technique of cooling substantially below 0.3 K has the advantage, in comparison to other known methods, that it works continually. An excellent description of this technique is found in Lounasmaa's book "Experimental Principles and Methods Below 1 K" (1974) or in papers by Wheatley, Vilches and Able (1968) or Wheatley, Rapp and Johnson (1971).

As can be seen from figure 2.1 our design is conventional. There is a single continuous heat exchanger. To prevent the superfluid $^3$He
Figure 2.1
1 Impedance for continuous filling of the 1 K plate; 2 pumping tube for 1 K plate; 3 $^3$He condensing line; 4 still pumping line; 5 vacuum chamber; 6 1 K plate; 7 heat shield; 8 flow impedance; 9 still; 10 inlet of $^4$He rich mixture; 11 continuous heat exchanger; 12 graphite support; 13 mixing chamber; 14 heat shield; 15 sample holder; 16 experiment.
film flow through the pumping tube in the still, we used an idea of Wheatley et al (1971) by pumping the still through a heated tube whereby the film on the outside of the tube is evaporated. With this construction one improves the $^3$He/$^4$He ratio and reduces the danger of thermal conduction shorts between still and 1 K plate. The surface of the bottom in the mixing chamber was increased by cutting thin grooves into the copper bottom to improve the thermal contact to the outside. A copper extension is connected to the mixing chamber and reaches into the tail of the vacuum chamber around which the magnet is fixed. There are two heat shields surrounding the sample. The inner shield is fixed at the mixing chamber and mainly prevents residual $^4$He exchange gas from reaching the sample. The radiation shields are made out of copper coil foils i.e. of tightly packed insulated thin parallel copper wires which are reinforced by a thin layer of epoxy (Anderson, Salinger and Wheatley 1961). The advantage of such a foil is the good heat conduction in one direction and the suppression of eddy currents perpendicular to the direction of heat conduction.

Six carbon resistor thermometers (see below) are mounted at strategical points of the dilution unit to monitor the cooling. Heaters in the still, on the mixing chamber and on the sample holder served to establish the desired temperatures. All heaters are supplied by a dc current taken from a battery to avoid any ripple. An electronic feedback system (SHE temperature controller) allowed us to stabilise the sample holder on a fixed temperature within 0.0005 K. The performance of the whole cryostat depended strongly on the correct $^3$He-$^4$He mixture. With the optimised mixture we reached an ultimate temperature of 35 mK. The cooling power in the low temperature region is then a function of the still heater power which
defines the $^3$He circulation rate. Figure 2.2 shows the temperature dependent cooling power with the still heater power as a parameter.

The appropriate temperature region for the use of a dilution refrigerator is below 1 K. Measurements above 1 K often suffered of instabilities of the temperature.

![Figure 2.2](image)

**Figure 2.2**

Cooling power of the dilution refrigerator as a function of the heat input in the still.

---

### 2.2 $^4$He Cryostat

To extend the temperature region beyond the easily accessible range of a dilution refrigerator we designed a $^4$He cryostat suitable for thermal and electrical conductivity measurements up to 50 K. The design is shown in
2.3 THERMAL AND ELECTRICAL CONDUCTIVITY MEASUREMENTS

For the thermal conductivity measurement we used the method of a steady heat flow through the sample (c.f. fig. 2.4). In this case, a known rate of heat $Q$ is supplied at one end of the sample and removed at
Experimental arrangement

Figure 2.4
1 Sample holder; 2 thermally anchored leads; 3 copper camps; 4 thermometer 2; 5 thermometer 1; 6 sample; 7 Sample heater.
the other end. Two thermometers separated by a distance \( L \) on the sample determine the temperature difference \( \Delta T \) between them. The thermal conductivity is then given by the relation

\[
\lambda(T) = \frac{L}{F} \frac{1}{\Delta T} \dot{Q}
\]

(2.1)

where \( F \) is the (uniform) cross section of the sample. Assuming \( \Delta T \) is small compared to the mean temperature \( \bar{T} \) of the thermometers this value of the thermal conductivity \( \lambda \) corresponds to the temperature \( \bar{T} \). In our measurements \( \Delta T \) was normally \( \sim 2-3\% \) of the mean temperature and never exceeded 7\%. Only thermometer 1 was calibrated. The resistances of the two thermometers were first measured in the absence of a heat current. Then with a heat current present, the temperature of the sample holder was regulated to give the same reading of thermometer 2 as before. The two values of thermometer 1 then defined \( \Delta T \) and \( \bar{T} \). This procedure reduced the error in \( \Delta T \) by using only one resistance versus temperature fit.

2.4 THERMOMETRY

For the calibration of the sample thermometers we used a CMN thermometer in connection with a calibrated germanium resistor. The experimental arrangement is shown in figure 2.5. Powdered CMN sits in one of two balanced pick-up coils. Thermal contact to the sample holder is provided through a coil foil slab which is pressed into a copper block. A superconducting primary coil produces an alternating field of 87 Hz and maximal amplitude of 0.7 Oe. The primary can be moved relatively to the pick-up coils so as to balance the signals coming from the two secondaries. The difference of the induced pick-up coil signals is proportional to the
susceptibility of the CMN and therefore inversely proportional to the temperature. The CMN thermometer was calibrated against a Ge thermometer (Lake Shore model no. GR-200A-50, calibrated between 0.3 and 1.4 K). The superconducting critical temperature $T_c$ of Ir served as a check point for the reliability of the calibration. We estimate our absolute temperature error below 1 K to about 2%. For higher temperatures a carbon glass resistor was used (Lake Shore model CGR-1-500, calibration range 1.4-80 K).

![CMN thermometer diagram](image)

Figure 2.5
CMN thermometer: 1 coil foil slab; 2 primary coil; 3 pick-up coil; 4 CMN; 5 epoxy block; 6 screw for balancing.

The sample thermometers were made out of Allen Bradley carbon resistors for the high temperature range or of Matsushita resistors for the temperature below 1 K. They were carefully ground down to slices of approximate 0.2 mm thickness. This reduces the heat capacity, improves the thermal contact and makes it possible to glue them to the flat surface of copper clamps which were pressed onto the sample. The calibration points were fitted to a polynomial in logR (Clement and Quinell 1952). The whole temperature range was divided into several overlapping fit regions with different coefficients.
3. THEORETICAL BACKGROUND

The thermal conductivity is defined by

\[ h_{ij} = - \lambda_{ij} \frac{\delta T}{\delta x_j} \]  

(3.1)

where the \( h_{ij} \)'s are the components of a vector \( \vec{h} \). \( \vec{h} \) is the heat flow across unit cross section perpendicular to \( \vec{h} \), \( T \) is the temperature and the \( \lambda_{ij} \) are the components of a second rank tensor of the thermal conductivity. For an isotropic solid or a crystal with cubic symmetry this equation reduces to the simpler form

\[ \vec{h} = - \lambda \nabla T. \]  

(3.2)

The heat current therefore can be described in these materials by a single value \( \lambda \) which is temperature and material dependent.

In the following sections we give a short description of the main mechanisms which determine \( \lambda \) in the temperature range of our measurements.

3.1 THERMAL CONDUCTION BY PHONONS

The heat current \( \vec{h} \) due to phonons can be written as (Berman 1976)

\[ \vec{h} = \sum N(q) \ h_\omega(q) \ \vec{v}_g(q) \]  

(3.3)

where \( N(q) \) is the phonon density, \( q \) the wave vector, \( h_\omega \) the energy of a phonon with frequency \( \omega \) and \( \vec{v}_g(q) \) the group velocity of propagation. The sum includes all phonon modes. In the relaxation time approach of the thermal conductivity and with the simplifying assumption of the Debye
model of specific heat (Kittel 1971) (3.3) yields

$$\lambda = \frac{k_B}{2\pi v g} \left(\frac{k_B}{\hbar}\right)^3 \int_0^{\Theta/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} \, dx$$

(3.4)

for the lattice thermal conductivity $\lambda$ where $x = \frac{\theta}{k_B T}$, $\Theta =$ Debye temperature and $\tau(x) =$ effective relaxation time for a phonon with energy $\hbar \omega$.

Equation (3.4) can be generalised by adding different scattering rates $\tau_{i-1}$ to a total scattering rate $\tau_{\text{tot}}^{-1}(x)$ (Klemens 1951)

$$\tau_{\text{tot}}^{-1}(x) = \sum_i \tau_{i-1}(x).$$

(3.5)

The mean free path $l(x)$ of the heat carriers is related to the relaxation time $\tau(x)$ by

$$l(x) = v(x) \tau(x).$$

(3.6)

The problem of calculating $\lambda$ is to find the appropriate relaxation rate for different scattering mechanisms.

At the lowest temperatures the phonons are mainly scattered by crystal boundaries including internal grain boundaries. In this case the scattering is independent of frequency (see e.g. Berman 1976) and given by $\tau_b^{-1} = v/k$ where $k$ is the mean free path of the phonons due to boundary scattering and typically of grain size of the crystal. Using (3.4) this yields a $T^3$ dependence of the thermal conductivity:

$$\lambda_{\text{boundary}} = 7.2 \frac{k_B k}{2\pi^2 v^2 \hbar} \left(\frac{k_B}{\hbar}\right)^3 T^3.$$
At higher temperatures, depending on the actual mean free path $k$, scattering by electrons will become predominant. The relaxation rate $\tau_{\text{ge}}^{-1}$ of this process, assuming a spherical Fermi surface, is proportional to $\omega$ (see e.g. Klemens 1956) and, if phonon-electron scattering is the only scattering mechanism one gets

$$\lambda_{\text{ge}} = \frac{T^2}{A}$$

again using (3.4). $A$ is a constant, given by inserting $\tau_{\text{ge}}$ into (3.4).

Still higher temperatures will make the impurities and finally the umklapp processes of importance (see e.g. Olsen and Rosenberg 1953). We do not consider this scattering here because our temperature range is too limited to see these interactions.

3.2 THERMAL CONDUCTION BY ELECTRONS

The main contribution to the thermal conductivity in a metal is normally given by the electrons and we can write the total thermal conductivity $\lambda_{\text{tot}}$ by

$$\lambda_{\text{tot}} = \lambda_{\text{l}} + \lambda_{\text{e}}$$

(3.9)

where $\lambda_{\text{l}}$ is the lattice part of the thermal conductivity and $\lambda_{\text{e}}$ the electronic contribution.

In a discussion of the electronic thermal conductivity $\lambda_{\text{e}}$, one follows similar lines of reasoning as in section 3.1. The important scattering mechanisms at intermediate and low temperatures are the electron-phonon and the electron-defect scattering described by relaxation times $\tau_{\text{eg}}$ and $\tau_{\text{ed}}$ respectively. If one assumes Matthiessen's rule (1862), that is the
additivity of the thermal resistivities, the electronic part of the thermal conductivity $\lambda_e$ may be written

$$\lambda_e^{-1} = \frac{\beta}{T} + \alpha T^2$$  \hspace{1cm} (3.10)

at low temperature (Ziman 1960). The first term on the right side is related to the defect and impurity scattering and is connected with the residual resistivity $\rho_0$ through

$$\beta = \frac{\rho_0}{L_0}$$  \hspace{1cm} (3.11)

with the Lorenz number $L_0 = 24.5 \text{ nWatt}\Omega/K^2$. The second term describes the scattering of electrons by phonons.

3.3 THERMAL CONDUCTION IN A SUPERCONDUCTOR

The thermal conduction in a superconductor is governed by the same processes as in the normal metal. Due to the rearrangement of the density of states of the electrons $N(E)$ in the superconducting state and the development of a temperature dependent energy gap $\Delta(T)$ these processes are different in strength in the superconductor compared to the normal metal. The occurrence of a gap reduces the number of excitations which are responsible for the thermal conduction of the electrons. Therefore the electronic part of the thermal conductivity is reduced. The lattice part on the other hand is increased on account of the reduced phonon-electron scattering. Below about $t = 0.2$, $t$ being the reduced temperature $T/T_c$, the thermal conductivity is comparable to an insulator.
The temperature variation in the superconducting state depends strongly on the specific dominant scattering mechanisms at $T_c$ and the relative amount of electronic and lattice contributions to the thermal conductivity as was demonstrated in measurements of Olsen (1952) on lead and lead-bismuth alloys.

The first quantitative description of the behaviour of the electronic and lattice thermal conductivity in the superconducting state on the basis of the BCS theory of superconductivity (Bardeen, Cooper and Schrieffer 1957) was given by Geilikman and Kresin (1958) and Geilikman (1958). Their calculations were restricted to the case where the impurity scattering of the electrons is dominant and the phonon-electron scattering is the limiting process for the lattice thermal conductivity. In the same year Bardeen, Rickayzen and Tewordt (1958) published a theory on the thermal conductivity of superconductors. We refer to it as the BRT-theory. They deal with the electronic contributions when the dominant scatterers are impurities or phonons. BRT also calculated the effect of the electrons on the lattice conductivity. Although BRT cannot explain the strong depression of the thermal conductivity in the case of lead (Olsen 1952) where electron-phonon scattering is dominant they explain the other mechanisms quite well (Sousa 1969).

For a dominant electron-defect scattering BRT give an equation for the electronic thermal conductivity in the superconducting state $\lambda_e^S$

$$\lambda_e^S = - \frac{2N(E_F)v_0}{3T} \int_{\Delta(T)}^{\infty} \frac{dE}{E^2} \frac{\delta f}{\delta E}.$$  \hspace{1cm} (3.12)

$f$ is the Fermi function $f = (e^{E/k_BT} + 1)^{-1}$, $v_0$ the electron velocity on the
Fermi surface and \( l \) the mean free path of the electrons. Wyder (1965) showed that the mean free paths in the normal and superconducting state are the same. \( E \) is the excitation energy of the BCS quasiparticles, that is

\[
E = (\varepsilon^2 + \Delta^2)^{\frac{1}{2}}
\]

where \( \varepsilon \) is the energy of the normal electrons measured from the Fermi surface and \( 2\Delta(T) \) is the superconducting energy gap. For \( \Delta(T) \equiv 0 \) (3.12) describes the normal state electronic conductivity. The ratio of the two electronic conductivities \( \lambda^s_e / \lambda^n_e \) in the superconducting state and \( \lambda^n_e \) in the normal state can be written as

\[
\frac{\lambda^s_e}{\lambda^n_e} = \frac{2F_1(-y) + 2y\ln(1 - e^{-y}) + y^2(1 + e^y)^{-1}}{2F_1(0)}
\]

with \( y = \Delta(T)/k_BT \) and

\[
F_1(-y) = \int_0^\infty z(1 - e^{(z+y)})^{-1}dz.
\]

\( F(-y) \) is tabulated by Rhodes (1950). A more convenient form for the calculation of (3.14) is given by Geilikman (1958)

\[
\frac{\lambda^s_e}{\lambda^n_e} = \frac{6}{\pi^2 k_BT} \left[ \exp(\Delta(T)/k_BT) + 1 \right]^{-1} \left[ 2\Delta(T) \ln \left[ 1 + \exp(-\Delta(T)/k_BT) \right] \right]
\]

\( \Delta(T) \) was calculated by Mühlschlegel (1959) for \( 1 > t > 0.2 \).

We evaluated (3.16) numerically and show the results in figure 3.1. Although the ratio \( 2\Delta(0)/k_BT \) in the BCS theory for weak coupling supercon-
Figure 3.1

Ratio of the electronic thermal conductivity in the superconducting state $\lambda^s_e$ to the electronic thermal conductivity in the normal state $\lambda^n_e$ if impurity and defect scattering is dominant.

The value of 3.53 for $2\Delta(0)/k_B T_c$ in the superconductor is often cited, but this ratio may be different in a real superconductor. We included values for $2\Delta(0)/k_B T_c$ between 3.0 and 4.5.

If not only impurity scattering but also electron-phonon processes are important, Kadanoff and Martin (1961) deduced a formula for the ratio $\lambda^s_e/\lambda^n_e$ as a function of a single parameter $a$ which gives the ratio of the...
phonon resistance to the impurity resistance at the critical temperature $T_c$. $\lambda^s_e/\lambda^e$ is then given by

$$\frac{\lambda^s_e}{\lambda^e} = \frac{3}{2\pi^2} \int_0^\infty \frac{e^{-\gamma e^2 \text{sech}^2 \left[ \sqrt{2} \left( e^2 + (\gamma \Delta)^2 \right) \right]}}{\sqrt{1 + a(T/T_c)^3 \left( \gamma e \right) \left( \gamma e \right) \left( \gamma e \right)}} \, dx$$

(3.17)

with $\gamma = \nu k_BT$ and $a$ taken from (3.10)

$$a = \frac{\alpha T_c^3}{\beta}.$$  

(3.18)

For $a = 0$ (impurity scattering dominant) (3.17) is equivalent to (3.14).

BRT also discussed the lattice thermal conductivity in a superconductor. Assuming that the phonons are scattered only by electrons BRT give a formula for the lattice thermal conductivity $\lambda^s_g$ in the superconducting state

$$\lambda^s_g = D(T/\Theta)^2 \int_0^\infty \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})g(x)}$$

(3.19)

where $D$ is a constant independent of temperature, $\Theta$ the Debye temperature and $g(x)$ the ultrasonic attenuation coefficient in the superconducting state (for longitudinal phonon modes) normalized to the attenuation coefficient in the normal state:

$$g(x) = \frac{\alpha^s}{\alpha^e} = \frac{1^{-1}}{1^{-1}} = \frac{r^{-1}}{r^{-1}}$$

(3.20)

$\alpha$ is the attenuation coefficient, the indices $n$ and $s$ refer to the normal and superconducting state. $g(x)$ can be written as
\[ g(x) = \frac{1-e^x}{x} (2J_1 + J_2) \]  
(3.22)

with

\[ J_1(x) = \int_{\Delta(T)}^{\infty} \frac{e^{2 + E x k_B T}}{\epsilon \epsilon'} f(E)f(-E') \]  
(3.23)

and

\[ J_2(x) = \int_{-\Delta(T)}^{-\Delta(T)-xk_B T} \frac{E E'}{\epsilon \epsilon'} \left[ 1 - \frac{\Delta^2}{\epsilon \epsilon'} \right] f(E)f(-E') \]  
(3.24)

where \( E' = E + x k_B T \). The second integral is nonzero only if \( x > 2\Delta(T)/k_B T \). This corresponds to the creation of a pair of quasiparticles which is only possible when the phonon energy is higher than the energy gap.

Because no tabulated values of (3.23) and (3.24) were available we integrated \( J_1 \) and \( J_2 \) numerically. The singular points in the integral are eliminated by appropriate substitutions following the procedure given by Bobetic (1964). The results are shown in figure 3.2 for various reduced temperatures \( t \) as a function of \( x \). \( t \) is calculated assuming the BCS value \( 2\Delta(0)/k_B T_c = 3.53 \).

The ratio \( \lambda^s/\lambda^l \) describing the relative increase of the lattice thermal conductivity in the phonon-electron scattering regime is shown in figure 3.3 for different values of \( 2\Delta(0)/k_B T_c \). Numerical values of this ratio can be found in a paper by Lindefeld and Rohrer (1965) as a function of \( \Delta(T)/k_B T \).

The enormous enhancement of the lattice thermal conductivity in the superconducting state is damped down at low temperatures by different
Figure 3.2
Ratio of the relaxation rates due to phonon-electron scattering in the superconducting state to that in the normal state as a function of the frequency.

scattering mechanisms. As Klemens and Tewordt (1964) pointed out, point defect scattering can have a pronounced effect on the lattice thermal conductivity in the superconducting state because the phonon-electron scattering is highly reduced. They took this into account by adding to the BRT equation an additional point defect scattering term with $\tau = \omega^4$. 
Figure 3.3
Ratio of the lattice thermal conductivity in the superconducting state to that in the normal state if electron scattering is dominant.

At the lowest temperatures the boundary scattering term takes over and we expect a $T^3$ dependence of the lattice thermal conductivity.
In 1977 Matthias, Corenzwit, Vandenberg and Barz presented a new system of rare earth ternary compounds. This system with the formula RERh$_4$B$_4$ where RE stands for rare earth exhibits either superconductivity or magnetic ordering or both phenomena. A survey of the magnetic $T_m$ as well as the superconducting transition temperatures $T_c$ is presented in figure 4.1. In addition we included a third temperature $T_\lambda$ where a lambda-type anomaly in the specific heat is observed that points to a phase transition at low temperature.

The compounds with RE = Gd, Tb, Dy and Ho were originally found to order ferromagnetically whereas for RE = Nd, Sm, Er, Tm and Lu superconductivity was found (Matthias et al 1977). The compound ErRh$_4$B$_4$ was later found to exhibit reentrant superconductivity, wherein ferromagnetic ordering of the Er$^{3+}$ magnetic moments around $T_m$ destroys superconductivity (Fertig, Johnston, DeLong, McCallum and Maple 1977). The isostructural compounds with Nd (Hamaker, Woolf, MacKay, Fisk and Maple 1979) and Sm (Hamaker, Woolf, MacKay, Fisk and Maple 1979) revealed in further investigations the possible coexistence of long-range magnetic order and superconductivity. This broad variety of superconductivity and magnetism in a system with a regular sublattice of magnetic ions stimulated an extensive study on the interaction of superconductivity and magnetism.

Since electrical resistivity measurements sometimes simulate superconductivity even with only a small fraction of a superconducting phase
in a sample, we have chosen thermal conductivity measurements as a probe for the bulk properties of these compounds.

In the following sections we present electrical and thermal conductivity measurements of four different members of the group of RERh$_4$B$_4$ compounds each of them showing quite different behaviour. Starting with LuRh$_4$B$_4$ as a representative of a superconductor with no magnetic interference we proceed to the other extreme to HoRh$_4$B$_4$ which only orders magnetically. ErRh$_4$B$_4$ shows both phenomena but in an exclusive way whereas in SmRh$_4$B$_4$ there is strong evidence for the coexistence of superconductivity and magnetic order.

4.1 SAMPLES

All the samples were made available by Profs. B.T. Matthias and M.B. Maple and their groups at the UCSD, La Jolla. A description of sample preparation is found e.g. in the thesis of L.D. Woolf (1980). The structure is shown in figure 4.2. To clarify the regular sublattice of the RE ions the interatomic distances are not drawn to scale. This structure was found by Vandenbergh and Matthias in 1977. The unit cell is primitive tetragonal and contains two formula units with a pronounced clustering of Rh and B atoms. As the above authors pointed out, this clustering behaviour is a general feature of some high transition temperature superconductors.
Figure 4.1
Survey of ferromagnetic $T_m$ and superconducting $T_c$ critical temperatures of $\text{RERh}_4\text{B}_4$; $T_\lambda$ indicates a lambda-type anomaly in the specific heat. In $T_m$, the specific heat is not measured through the whole anomaly.

Figure 4.2
Crystal structure of $\text{RERh}_4\text{B}_4$ compounds. Dashed lines indicate the tetragonal unit cell. For clarity the cubes representing $\text{Rh}_4\text{B}_4$ clusters are not drawn to scale (MacKay 1979).
The nonmagnetic LuRh$_4$B$_4$ shows only superconductivity. This enables us to study the effect of superconductivity on the thermal conductivity in this series without any interference with magnetic ordering. LuRh$_4$B$_4$ becomes superconducting at 11.45K. Specific heat measurements by Woolf, Johnston, McKay, McCallum and Maple (1979) as well as magnetisation measurements by Ott, Cambell, Rudigier, Hamaker and Maple (1981) indicate that LuRh$_4$B$_4$ is a type II superconductor. The lattice specific heat data revealed a complicated phonon spectrum which could be explained by assuming a molecular crystal model with Lu and Rh$_4$B$_4$ clusters as a "diatomic" crystal (Woolf et al 1979). Below about 15 K an extended Debye model of the specific heat can fit the data equally well. The Debye temperature of this fit turns out to be $\Theta_D = 444$ K which is in reasonable agreement with sound velocity measurements of Schneider, Levy, Johnston and Matthias (1980) who found for the sound velocity of longitudinal waves $v_s = 6$ km/s.

The thermal conductivity data of LuRh$_4$B$_4$ in the range of 2 to 25 K are given in figure 4.3. Also shown in this graph is the thermal conductivity in an applied magnetic field parallel to the heat current $\dot{Q}$. From electrical resistivity measurements $T_C$ is found to be 9.5 K in our sample. Unfortunately it was not possible in our apparatus to restore the normal state below 9 K. The thermal conductivity above the critical temperature $T_C$ cannot be described by a linear temperature dependence. Below $T_C$ we observe a substantial increase above the roughly extrapolated values of the normal state. These two features are typical for metals in which the normal state conductivity of the electrons is not governed completely by
impurity scattering. A similar behaviour is found e.g. in a lead-bismuth alloy with 0.5% bismuth (Olsen 1952). Additionally, the lattice thermal conductivity must be considerable.

\[ \lambda_{\text{thermal}} \]

\text{Lu Rh}_4\text{B}_4

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.3.png}
\caption{Figure 4.3}
\end{figure}

Thermal conductivity of \text{LuRh}_4\text{B}_4 in zero magnetic field and in an applied field of 5 kOe parallel to the heat current.

In order to analyse our data we separate the total thermal conductivity in a lattice and an electronic part (c.f. (3.9)). For the electronic thermal conductivity in the normal state \( \lambda_e^n \) we use the additive resistance approximation (c.f. (3.10) and (3.11))
The residual resistivity $\rho_0$ of our sample is 9.9x10^{-8} \, \Omega\,cm, the residual resistivity ratio $RRR = 16.4$. The resistance starts to deviate from $\rho_0$ around 13 K due to electron-phonon interactions, therefore we have to allow for a small value of $\alpha$ which is related to the same interactions. The electron-phonon scattering is responsible for the downward curvature of $\lambda^e_n$ with increasing temperature. For the lattice part we use (3.4). Considering the scattering mechanisms which are important in the superconducting state and may have some influence on the normal state lattice conductivity we write the overall relaxation rate $(\tau^p_R)^{-1}$ of the normal state as a sum of a boundary, a phonon-electron and a phonon-impurity rate.

(3.4) can then be written as (Gupta and Wolf 1972)

$$\lambda^p_n = \frac{k_B}{2\pi \nu_2} \left[ \frac{k_B}{\hbar} \right]^3 T^3 \int_0^{\theta/T} \frac{x^4 e^x dx}{(e^x-1)^2(1/k + CTx + GT^4x^4)}.$$  \hspace{1cm} (4.2)

$k$ is the boundary mean free path. $C$ and $G$ are related to the phonon mean free path due to the conduction electrons and point defects. In the superconducting state, only the phonon-electron scattering rate will be changed, $\lambda^s_g$ is thus given by

$$\lambda^s_g = \frac{k_B}{2\pi \nu_2} \left[ \frac{x_B}{\hbar} \right]^3 T^3 \int_0^{\theta/T} \frac{x^4 e^x dx}{(e^x-1)^2(1/k + CTxg(x) + GT^4x^4)}.$$  \hspace{1cm} (4.3)

Below $t = 0.2$ according to the BRT theory (c.f. fig. 3.1) the electronic thermal conductivity can be ignored and the lattice thermal conductivity is mainly limited by boundary scattering. $\lambda^s_g / T^3$ therefore should be a
constant. The lowest points of the thermal conductivity \( \lambda^S \) indeed tend to a \( T^3 \) dependence. Taking this value we can write for the low temperature thermal conductivity \( \lambda^S = \lambda^S \) for \( t < 0.2 \)

\[
\lambda^S = 4 \times 10^{-2} T^3 \frac{W}{K^4 m} \quad (4.4)
\]

The mean free path \( k \) in the integral (4.3) is therefore given by

\[
k^{-1} = 650 \frac{k_B}{2 \pi v^2} \left( \frac{k_B}{h} \right)^3 \quad (4.5)
\]

We introduced (4.5) into (4.4) and used \( \rho_o / L_o \) in (4.1). The energy gap relation \( 2\Delta(0)/k_B T_c = 4.1 \) was taken from the specific heat measurements by Woolf et al (1979). There was no combination of the remaining parameters which reproduced the experimental results over the whole temperature range. The energy gap relation therefore was used as an additional unknown parameter. The best fit to our data is shown in figure 4.4. The parameters used for this fit are

\[
2\Delta(0)/k_B T_c = 3.5 \\
\alpha = 2.5 \times 10^{-6} m/KWatt \\
\beta = 4.05 mK^2/Watt \\
(Yk)^{-1} = 650 K^6 m/Watt \\
G/Y = 3.9 \times 10^{-3} m/Watt \quad (4.6)
\]

with

\[
Y = \frac{k_B}{2 \pi^2 h^3 v^2}
\]

The electron-phonon scattering term described by \( \alpha \) is small compared to the electron-defect scattering term \( \beta \). The use of the BRT theory for pure electron-defect scattering is therefore justified.
Figure 4.4
Thermal conductivity of LuRh$_4$B$_4$ with calculated lattice and electronic contribution. Lower indices e and g refer to electronic and lattice contribution, upper indices n and s to normal and superconducting state respectively (Odoni, Keller, Ott, Hamaker, Johnston and Maple 1981).

At $T_c = 11.45$ K the lattice part of the thermal conductivity $\lambda^g_n$ is about 23% of the total thermal conductivity. Below $T_c$ $\lambda^s_g$ increases rapidly but the increase is reduced due to the point defect scattering. Below about 4 K the thermal conductivity is mainly limited by boundary scattering of the phonons.
In the Debye approximation of specific heat a Debye temperature of 444 K corresponds to a velocity of sound of 3.4 km/s (assuming $8.7 \times 10^{28}$ atoms/m$^3$). With (4.5) we deduce a phonon mean free path in the superconducting state due to boundary scattering of about 10 μ. There exist no grain size measurements of our sample which can confirm this estimate.
4.3 Ferromagnetism in a Rare Earth Rhodium Compound: HoRh₄B₄

HoRh₄B₄, whose low temperature physical properties have recently been investigated in some details (Ott, Woolf, Maple and Johnston 1980; Maple Hamaker, Johnston, McKay and Woolf 1978) orders ferromagnetically at \( T_m = 6.7 \text{ K} \) (Matthias et al 1977) due to a spontaneous alignment of the localized 4f electron magnetic moments of the Ho³⁺ ions. Ott, Keller, Odoni, Woolf, Maple, Johnston and Mook (1981) showed that the magnetic contribution to the specific heat, zero field magnetisation, electrical resistivity and thermal expansion measurements can be described very accurately by using mean field theory and assuming an effective spin \( \frac{\sqrt{2}}{2} \).

We do not repeat the details of this discussion. The aim of this section is to show qualitatively the influence of the magnetic ordering on electrical conductivity and thermal conductivity. We hope to find some features in these transport properties which are characteristic for magnetic ordering and may give a hint on magnetic ordering in other ternary compounds of this type where the situation is not at all so clear (see e.g. SmRh₄B₄).

We measured the electrical resistivity \( \rho \) of our sample in the temperature range between 1.5 K and 15 K with a low frequency four probe technique. Assuming Matthiessen's rule of the additivity of the different resistive processes (for a review of deviations of Matthiessen's rule see e.g. J. Bass 1972) we can write the total resistivity \( \rho(T) \) at any temperature as (Taylor and Darby 1972)

\[
\rho(T) = \rho_{\text{res}} + \rho_{\text{ph}}(T) + \rho_{\text{m}}(T)
\]  (4.7)
where $\rho_{\text{res}}$ is the residual resistivity which is independent of temperature and depends only on crystalline imperfections and impurities in the sample. The scattering of conduction electrons by phonons leads to a temperature dependent resistivity $\rho_{\text{ph}}(T)$. The third term $\rho_{\text{m}}(T)$ finally is due to the magnetic contribution caused by the disorder of the spin system. Experimentally it is often difficult to separate the different temperature dependent terms but in the case of HoRh$_4$B$_4$ this is easier because the magnetic contribution $\rho_{\text{m}}$ is not masked by the phonon term.

Figure 4.5 shows the electrical resistivity of HoRh$_4$B$_4$ between 1.5 K and 10 K. The resistivity $\rho$ is constant below 2.5 K with the value $\rho_{\text{res}}$ and also between $T_m$ and 10 K. Hence, the temperature dependence of $\rho$ below 10 K is due only to a magnetic scattering term $\rho_{\text{m}}(T)$ which is constant in the paramagnetic state and tends to a constant value well below $T_m$. One can show (Ott et al 1981) that the temperature dependent term below $T_m$ is...
proportional to $1 - (M/M_o)^2$ where $M$ is the magnetisation at the temperature $T$ and $M_o$ the magnetisation at $T = 0$.

Figure 4.6 shows the thermal conductivity of the same sample in the temperature range of 100 mK up to 12 K. As may be seen, the data above and well below $T_m$ depend linearly on temperature. The steepening in the slope of the thermal conductivity versus temperature below the ordering temperature $T_m$ is interpreted as an increase of the mean free path of the electrons due to the reduced scattering on magnetic moments and is consistent with the behaviour of the reduced electrical resistivity. There is too much scattering in these data to detect a sharp edge at $T_m$ as found in the electrical resistivity.
4.4 REENTRANT SUPERCONDUCTIVITY: ErRh$_4$B$_4$

Among the RERh$_4$B$_4$ compounds, ErRh$_4$B$_4$ is probably the best known member because of its peculiar superconducting and magnetic properties. ErRh$_4$B$_4$ shows a superconducting transition at $T_{c1} = 8.9$ K on zero external magnetic field (Matthias et al 1977). At a second lower temperature $T_{c2} \sim 0.9$ K the electrical resistivity appears again (Fertig et al 1977). Susceptibility and specific heat measurements indicated that around $T_{c2}$ a long range magnetic order appears. Neutron scattering experiments have confirmed ferromagnetic order below $T_{c2}$ with a considerable precursor scattering starting at about 1.2 K (Moncton, McWhan, Eckert, Shirane and Thomlinson 1977).

These data showed an ordered magnetic moment of 5.6 $\mu_B$ per Er$^{3+}$ ion in the ferromagnetic phase consistent with the value of $\sim 6$ $\mu_B$ from magnetisation measurements. This value is well below the Hund's rule value of 9.59 $\mu_B$ per Er$^{3+}$ ion. Ott, Fertig, Johnston, Maple and Matthias (1978) suggested that crystalline electric fields lift the degeneracy of the Er$^{3+}$ Hund's rule ground state.

The ac electrical resistance and the susceptibility showed a thermal hysteresis in a range of about 50 mK around $T_{c2}$ in disagreement with the first neutron scattering experiments. Similar hysteretic behaviour is found in the thermal conductivity measurements by Odoni and Ott (1979). Subsequently, hysteresis was found in the neutron scattering as well (Moncton, McWhan, Schmidt, Shirane, Thomlinson, Maple, MacKay, Woolf, Fisk and Johnston 1980).

The specific heat near $T_{c2}$ (Woolf, Johnston, MacKay, McCallum and Maple 1979) shows a rather unusual behaviour. A broad specific heat maxi-
mum is found around 1 K. Superimposed on it is a lambda-type anomaly with a width of about 70 mK which peaks at a temperature $T = 0.93$ K. In addition to this special feature around $T_{c2}$, the calorimetric study provided strong evidence for the partially lifted degeneracy of the Hund's rule ground state by the crystalline electric field as proposed by Ott et al (1978). The precursor scattering together with the specific heat anomaly and the electrical resistivity measurements lead to the speculation that there exists a limited region where long range magnetic order and superconductivity coexist. In a discussion of these problems it is essential to know more about real bulk properties in order to confirm that the observed effects are not just spurious.

In the following sections we discuss thermal conductivity measurements on ErRh$_4$B$_4$ in a temperature range between 0.05 K and 50 K and in an external magnetic field up to 3 kOe with the field direction parallel or perpendicular to the heat flow. Our sample was a prism of polycrystalline material with dimension of 7x1.5x1.5 mm$^3$ and in previous work it was denoted as sample A (see Ott et al 1978).

The thermal conductivity of ErRh$_4$B$_4$ in zero applied field is shown in figure 4.7. There are four clearly distinguishable regions. The thermal conductivity above $T_{c1}$ is mainly due to electronic conduction. The deviation from a nearly linear temperature dependence at higher temperature is due to the increasing importance of electron-phonon scattering. Between $T_{c1}$ and \( \sim 1.2 \) K the thermal conductivity behaves as in a superconductor with a small contribution from the lattice thermal conduction. Between 1.2 K and \( \sim 0.9 \) K the thermal conductivity increases again and reaches a local maximum around 0.9 K. In this temperature range we observe a thermal hysteresis of about
Figure 4.7
Thermal conductivity of ErRh$_4$B$_4$ in zero applied field in the temperature range of 50 mK to 50 K.

60 mK (see below). Below 0.87 K the thermal conductivity shows a linear temperature dependence as one expects for a normal metal with almost exclusive electronic conduction. In figure 4.8 we give the thermal conductivity data together with the variation due to an applied external field parallel to the heat current $\dot{Q}$. Figure 4.9 demonstrates the effect of a parallel and a perpendicular external magnetic field around 1 K. In the parallel case we expect that a magnetic field in a type II superconductor induces normal cores and reduces the average order parameter. The thermal conductivity is increased. In the perpendicular field the normal cores are much more effective in scattering the normal electrons, therefore the in-
Figure 4.8
Thermal conductivity of \( \text{ErRh}_4\text{B}_4 \) for different applied magnetic fields parallel to the heat current.
Figure 4.9
Thermal conductivity of ErRh$_4$B$_4$ around 1 K in an applied magnetic field of 0.5 kOe parallel and perpendicular to the heat current $\dot{Q}$ (Ott and Odoni 1980).
crease of the thermal conductivity at a given field is less pronounced (Ott and Odoni 1980). Figure 4.10 demonstrates the hysteretic behaviour around $T_{c2}$.

In comparing the thermal conductivity with the electrical resistance of a similar sample of ErRh$_4$B$_4$ investigated by Ott et al (1978) (c.f. fig. 4.11) we find some equivalent features but there are several differences. The electrical resistance at $T_{c2}$ shows a narrow although hysteretic transition from the superconducting to the normal state. In contrast to this, the thermal conductivity slowly increases towards lower temperatures over a temperature region of $\sim 0.5$ K. The value of the electrical resistance below $T_{c2}$ in zero external magnetic field is about 85 % of the normal state value to which it saturates in fields greater than 2 kOe. No such saturation is found in the thermal conductivity. The thermal conductivity between $T_{c1}$ and $T_{c2}$ saturates to a linear temperature dependent value in a field of 3 kOe whereas one uses 12 kOe to suppress any reduction in the electrical resistance. This difference in the two transport properties suggests that a small amount of a second phase is present in the sample which remains superconducting at temperatures below $T_{c2}$ in zero external magnetic field. These superconducting phases are too small to affect the thermal conductivity but may be extended enough to electrically shorten parts of the sample. We interpret the slow increase of the thermal conductivity below 1.2 K as a reduction of the superconducting order parameter due to the onset of magnetic ordering. In this temperature range superconductivity is still present as can be seen from the electrical resistance measurements.

In analysing our data between $T_{c1}$ and 50 K we separate the total thermal conductivity into a lattice and an electronic contribution using (3.9),
Figure 4.10
Influence of the phase transition from the superconducting (T > 1 K) to the magnetically ordered normal state (T < 1 K) on the thermal conductivity of ErRh$_4$B$_4$. Full dots denote values when warming up, open circles denote values when cooling (Odoni and Ott 1979).

Figure 4.11
The ac electrical resistance versus temperature for a rod-shaped specimen of ErRh$_4$B$_4$ in various applied magnetic fields between 0 and 12 kOe (from Ott, Fertig, Johnston, Maple and Matthias 1978).
(3.10) and (3.11)

\[
\lambda = \frac{T}{\alpha T^3 + \rho_0/L_0} + \frac{T^2}{A}
\]  

(4.8)

To verify the assumption that the electronic contribution to the thermal conductivity is given by the ratio of the residual resistivity \(\rho_0\) and the Lorenz number \(L_0\) when electron-impurity scattering is considered, we check this relation below \(T_{c2}\) where the lattice contribution can be neglected. The residual resistivity of our sample is \(3.35 \times 10^{-8} \Omega m\). According to Ott et al. (1978) the saturation value below \(T_{c2}\) is \(\approx 95\%\) of the value above \(T_{c1}\). Using the same reduction in our sample, we have a residual resistivity of \(3.2 \times 10^{-8} \Omega m\) below \(T_{c2}\). Together with the Lorenz number \(L_0\), \(L_0/\rho_0\) yields 0.77 Watt/K²m. The measured value \(\lambda/T\) is 0.76 Watt/K²m and therefore justifies the above mentioned procedure. We used the following parameters to fit the thermal conductivity above \(T_{c1}\) up to 50 K:

\[
\alpha = 5.6 \times 10^{-5} m/(Watt K)
\]

\[
\beta = \rho_0'/L_0 = 1.37 (mK^2)/Watt
\]  

(4.9)

\[
\Lambda = 500 (K^3 m)/Watt.
\]

\(\rho_0'\) is the constant resistivity above \(T_{c1}\). Figure 4.12 shows the fit with these parameters.

In analysing the behaviour of the thermal conductivity in the superconducting state, we first have to discuss the influence of the magnetic \(Er^{3+}\) ions on the superconducting properties. The depression of the superconducting critical temperature \(T_c\) in presence of impurities with localized magnetic moments is treated by Abrikosov and Gor'kov (1960). They consider the additional scattering of the conduction electrons due to the exchange interaction. This theory is limited to systems with non-interacting magnetic
Figure 4.12
Theoretical fit to the normal state thermal conductivity of ErRh₄B₄. The fit includes electron-impurity and electron-phonon scattering for the electrons and phonon-electron scattering for the phonons.

Figure 4.13
Rate of depression of Tₜ vs RE in (Lu₁₋ₓREₓ)Rh₄B₄. The dashed lines are the limits of the assumed depression due to nonmagnetic effects of the substitution of Lu (MacKay, Woolf, Maple and Johnston 1980).
moments. The depression of $T_c$ by adding to the superconductor localized magnetic moments with a concentration $n_i$ can be described by a universal function $n_i/n_{cri}$. $n_{cri}$ is the critical concentration where the superconductivity is totally suppressed. In an attempt to distinguish between the magnetic and the nonmagnetic influence of a RE on $T_c$ of these compounds, MacKay, Woolf, Maple and Johnston (1980) measured the $T_c$ of compounds of the form Lu$_{1-x}$RE$_x$Rh$_2$B$_4$. The results are shown in figure 4.13. Because the depression rate for the nonmagnetic RE = La should be zero according to the Abrikosov-Gor'kov theory, a straightline has been drawn to display the assumed nonmagnetic effect of the substitution of Lu. For ErRh$_2$B$_4$, the depression due to nonmagnetic effects is about 1.5 K, a "nonmagnetic" ErRh$_2$B$_4$ compound therefore would have a $T_c$ of 9.9 K. The actual $T_c$ is 8.7 K. This corresponds to a ratio $T_c/T_{cp} = 0.88$ where $T_{cp}$ is the superconducting critical temperature without magnetic interactions and $T_c$ the superconducting critical temperature in the presence of magnetic moments. Using the tabulated values of the Abrikosov-Gor'kov function (Ramos and Sanchez 1974) this reduction of the critical temperature would be caused by an impurity concentration $n_i/n_{cri} = 0.17$.

In the framework of the Abrikosov-Gor'kov theory, Ambegaokar and Griffin (1964) calculated the ratio of the normal electronic thermal conductivity to the electronic thermal conductivity in the superconducting state in terms of the parameter $n_i/n_{cri}$. For $n_i/n_{cri} = 0.17$ they find an increase at $t = 0.6$ of $\lambda_e^n/\lambda_e^0$ of 3% above the BRT value which is within the errorbars of our measurements. We have therefore analysed the thermal conductivity data of ErRh$_2$B$_4$ neglecting the (small) magnetic influence of the Er$^{3+}$ ions.

The BRT theory gives an equation for the increase of the lattice thermal conductivity due to the reduced probability of phonon-electron scattering
in the superconducting state. Clearly this increase is damped at low temperatures by other scattering mechanisms. At the lowest temperatures the dominant scattering mechanism for phonons is boundary scattering, leading to a constant mean free path which is characterized by a $T^3$ dependence. Indeed between 1.4 K and 2 K we find such a $T^3$ dependence as can be seen from figure 4.14. We extracted the parameter which describes the phonon-boundary scattering and applied then the BRT theory using the parameters given in (4.9). The result of our fit is shown in figure 4.15 where we used for $2\Delta(0)/k_B T_c$ a value of 3.5. Below 1.4 K the measured thermal conductivity starts to increase again and deviates from the theoretical curve. At this temperature magnetic ordering sets in. With the onset of long range magnetic order, the assumption of non-interacting magnetic moments breaks down. Fisher(1979)

![Figure 4.14](image)

Figure 4.14

$T^3$ dependence of the thermal conductivity of ErRh$_4$B$_4$ in the temperature range of 1.2 K to 1.9 K.
Figure 4.15
Thermal conductivity of ErRh₄B₄. Solid lines are the lattice \( \lambda_\text{lat} \) and electronic \( \lambda_\text{e} \) contributions, calculated on the base of the BRT theory, including a boundary scattering term (Odoni, Keller, Ott, Hamaker, Johnston and Maple 1981).

points out that although the pairbreaking effect of the magnetic impurities may be very small in the paramagnetic state it may become very large in the magnetically ordered phase and thus lead to a decrease of the numbers of superconducting electrons or to a quenching of superconductivity.

From the increase of the thermal conductivity in this temperature range we can estimate the order parameter \( W(T) = 1 - \frac{n_n(T)}{n_o} \) within the framework of the two fluid model (Gorter and Casimir 1934). \( n_n \) is the number...
of normal electrons in the superconducting state at a temperature \( T \) and \( n_o \) the total number of conduction electrons. From figure 4.15 we see that the calculated electronic conductivity at 1.2 K is negligible. To calculate the ratio \( n(T)/n_o \) we assumed that the increase of the thermal conductivity between 1.2 K and 0.87 K is totally due to the creation of normal electrons and therefore this ratio is given by the ratio of the electronic thermal conductivity in the normal state \( \lambda_e^n \), given by \( \lambda_e^n = 0.76 \text{ Watt/(mK}^2) \), to that in the superconducting state \( \lambda_e^s = \lambda_e^\exp - \lambda_e^g \). As a rough estimate we assume that the lattice thermal conductivity at 1.2 K decreases linearly to zero at 0.87 K, taking into account that the occurrence of normal electrons quickly reduces the mean free path of the phonons. Therefore we calculated \( W(T) \) by

\[
W(T) = 1 - \left\{ 0.76T(\text{W/mK}^2)/(\lambda_e^\exp - \lambda_e^g) \right\}^{-1} \tag{4.10}
\]

The calculated behaviour of the order parameter \( W \) is shown in figure 4.16 as a function of the temperature. For (4.10) we used the cooling curve of the thermal conductivity.

The two fluid model is a rough description of superconductivity and the consequences have to be considered critically. In reality, magnetic interactions in a superconductor do not only change the number of "normal electrons" but also modify the energy gap and the density of states of the electrons.

The above defined superconducting order parameter \( W \) changes over a temperature range of about 0.5 K. We can compare this behaviour with the Bragg intensity of neutron scattering experiments on a similar sample of
Figure 4.16
Calculated order parameter in the two fluid model of Gorter and Casimir.
The order parameter $W(T)$ is defined in the text.

ErRh$_4$B$_4$ by Moncton et al (1980). At 0.97 K the superconducting order parameter $W$ is 0.6 whereas the normalized magnetisation $M/M_0$ is $\sim 0.66$. At this temperature magnetic order exists although 40% of the electrons are still in the superconducting state.

There are various theoretical attempts to explain the peculiar magnetic and superconducting properties in this temperature range. Blount and Varma (1979) found in their model that with decreasing temperature the superconducting state can transform over a narrow temperature range by a second order transition into a coexistent state of superconductivity with a spiral structure magnetisation followed by a first order transition to a uniform
magnetic state. Matsumoto, Umezawa and Tachiki (1979) and Bulaevski Rusinov and Kulič (1979,1980) come to similar conclusions in their model. In the light of these models, one can interpret the experimental facts. The thermal hysteresis in resistance, ac magnetic susceptibility, thermal conductivity and neutron diffraction and the lambda-type anomaly in the specific heat around 0.9 K indicate a first order transition from a superconducting to a normal ferromagnetically ordered state. Small-angle neutron scattering results near $T_{c2}$ indicate an oscillatory magnetisation with a wavelength of $\sim 100 \ \AA$ (Moncton et al 1980). Above $\sim 1.1 \ \text{K}$ the small angle scattering peak disappears and the thermal conductivity shows bulk superconductivity.
4.5 POSSIBLE COEXISTENCE OF SUPERCONDUCTIVITY AND MAGNETIC ORDER: SmRh$_4$B$_4$

In the foregoing sections we discussed how the thermal conductivity is affected when a material orders ferromagnetically (HoRh$_4$B$_4$), when it becomes superconducting (LuRh$_4$B$_4$) or when it loses its superconductivity upon magnetic ordering as the temperature is decreased (ErRh$_4$B$_4$). In this section we discuss the case where a substance becomes superconducting and where superconductivity persists below the magnetic ordering temperature.

Previous work (McCallum, Johnston, Maple and Shelton 1977, Ishikawa and Fischer 1977, Azevedo, Clark, Murayama, McCallum, Johnston, Maple and Shelton 1978, Moncton, Shirane, Thomlinson, Ishikawa and Fischer 1978) on rare earth Chevrel-phase compounds has shown that superconductivity may coexist with magnetic order if the magnetic order is antiferromagnetic in nature. Similar behaviour has recently been found in NdRh$_4$B$_4$ (Hamaker, Woolf, MacKay, Fisk and Maple 1979) and in SmRh$_4$B$_4$ (Hamaker, Woolf, MacKay, Fisk and Maple 1979, Ott, Odoni, Hamaker and Maple 1980). Both these boride compounds exhibit pronounced anomalies in specific heat and upper critical field, indicating the occurrence of magnetic ordering without destruction of superconductivity.

Reliable confirmation of the persistence of bulk superconductivity with magnetic ordering may be obtained from measurements of the thermal conductivity $\lambda$. Therefore we have measured the thermal conductivity of SmRh$_4$B$_4$ between 0.05 K and 4 K in zero external magnetic field and in external fields up to a value exceeding the critical field. The sample was a parallelepiped of polycrystalline material with dimensions 5.5x1.1x1 mm$^3$. 

In addition we measured the electrical resistivity $\rho$ on this specimen in the same temperature and magnetic field range. The residual resistance ratio of this sample is 22.3, the resistivity just above $T_c$ is $3.4 \times 10^{-6}$ $\Omega$ m. The resistively determined critical temperature $T_c$ of our sample is 2.68 K.

In figure 4.17 we show the temperature dependence of the electrical resistance of SmRh$_4$B$_4$ in zero magnetic field and in a supercritical magnetic field. In zero magnetic field the sample remains superconducting down to 100 mK. In a field of 2 kOe the sample remains normal down to the same temperature. The resistance data of SmRh$_4$B$_4$ in the normal state are simi-

![Graph showing electrical resistance of SmRh$_4$B$_4$ for magnetic field H = 0 and H = 2 kOe](image)

**Figure 4.17**

Electrical resistance of SmRh$_4$B$_4$ for magnetic field $H = 0$ and $H = 2$ kOe (Ott, Odoni, Hamaker and Maple 1980).
lar to those found in HoRh$_{4}$B$_{4}$ where the drop of the resistance is associated with magnetic ordering. Together with the thermal conductivity data (see below) these results confirm the conclusions obtained by Hamaker et al (1979) who suggested that the drop below 1 K may be due to a magnetic phase transition.

In contrast to ErRh$_{4}$B$_{4}$, where the residual resistance above $T_{c1}$ and below $T_{c2}$ differs about 5%, the resistance drop in SmRh$_{4}$B$_{4}$ amounts to 20%. This is an indication of a strong interaction of the conduction electrons with the localized magnetic moments.

Figure 4.18 shows the temperature dependence of the thermal conductivity $\lambda$ of SmRh$_{4}$B$_{4}$ in zero magnetic field and in a field of 2 kOe. In zero magnetic field and above $T_{c}$ we find a linear temperature dependence for $\lambda$. Below $T_{c}$ the thermal conductivity falls below the linear temperature dependence. No marked anomaly is found around 0.87 K where the specific heat shows a lambda-type anomaly. Below this magnetic ordering temperature (probably antiferromagnetic, according to the work of Hamaker et al (1979)), $\lambda$ continues to decrease with decreasing temperature, contrary to the steep rise back to the normal state thermal conductivity observed in ErRh$_{4}$B$_{4}$ as mentioned before. However, the temperature dependence of $\lambda$ below $T_{c}$ is not that of an ordinary superconductor. The reduction below the linear temperature dependence at the lowest temperatures is much less than what one would expect from the Bardeen-Rickayzen-Tewordt theory (see also figure 4.18). In a field of 2 kOe, SmRh$_{4}$B$_{4}$ remains normal. The thermal conductivity $\lambda$ can be divided into two distinct temperature regions with linear temperature dependence. Above $\sim 0.9$ K $\lambda$ can be written as $\lambda = 0.95T$ W/K$^2$m; below about 0.7 K $\lambda = 1.15T$ W/K$^2$m. The increase of $\lambda$ and the con-
Figure 4.18
Thermal conductivity of SmRh$_4$B$_4$ between 0.05 K and 4 K for magnetic field $H = 0$ and $H = 2$ kOe (Ott, Odoni, Hamaker and Maple 1980).
comitant drop in $\rho$ on the same sample indicate that one is not dealing with spurious superconducting phases but with a magnetic phase transition instead (Ott et al 1980). The difference in the coefficients of the linear thermal conductivity in the normal state is about 20% and corresponds in magnitude to the drop in the electrical resistance.

The magnetic moments have a strong influence on the electrical resistivity and the thermal conductivity in the normal state and we expect that they influence the thermal conductivity in the superconducting state as well. This situation is discussed in the theory of Ambegaokar and Griffin (1964) (AG theory). The AG theory is based on the Abrikosov-Gor'kov theory on the depression of $T_c$ due to magnetic interactions between localized magnetic moments and conduction electrons and gives the ratio of the electronic thermal conductivity in the superconducting state $\lambda_e^s$ to that in the normal state $\lambda_e^n$. The AG theory has the same limitations as the Abrikosov-Gor'kov theory in that it neglects the correlation between the impurity spins and assumes a random distribution of the magnetic impurities. Below the magnetic ordering temperature the assumption of noninteracting magnetic moments is no more fullfilled and we expect a deviation from the theoretical predictions. On the other hand we assume that the regular distribution of the magnetic moments is no obstacle to the applicability of the AG theory.

The ratio of the electronic thermal conductivities in the superconducting state $\lambda_e^s$ and in the normal state $\lambda_e^n$ is given in the AG theory by

$$\frac{\lambda_e^s}{\lambda_e^n} = \frac{3}{2\pi^2} \gamma^3 \int_0^\infty E^2 \text{sech}^2(\sqrt{2}yE) h(E/\Delta, \alpha) dE \quad (4.11)$$

where $\gamma = (k_B T)^{-1}$, $E$ is the excitation energy measured from the Fermi energy and $\Delta(T)$ the Abrikosov-Gor'kov order parameter. The pair breaking
parameter $\alpha$ is defined by

$$\alpha = \frac{n_i/n_{\text{cri}}}{2\Delta(T)/\Delta_o(0)}.$$  \hspace{1cm} (4.12)

$\Delta_o(0)$ is the order parameter at $T = 0$ for the pure superconductor without magnetic impurities. $h(E/\Delta, \alpha)$ is a function defined by

$$h(E/\Delta, \alpha) = \sqrt{2} \left[ 1 + \frac{|u^2| - 1}{|u^2 - 1|} \right]$$  \hspace{1cm} (4.13)

where $u$ is given by the equation

$$E/\Delta = u \left[ 1 - \frac{i\alpha}{\{u^2 - 1\}^{1/2}} \right].$$  \hspace{1cm} (4.14)

We evaluated (4.11), (4.13), and (4.14) numerically for different ratios $n_i/n_{\text{cri}}$. The ratio $\Delta(T, n_i/n_{\text{cri}})/\Delta_o(0)$ was taken from figure 4 of the paper of Ambegaokar and Griffin (1964). In absence of magnetic impurities, the ratio $\Delta(T)/\Delta_o(0)$ reduces to the BCS relation of the temperature dependence of the energy gap. In this case $h(E/\Delta, \alpha = 0)$ is zero for $E < \Delta(T)$. Therefore (4.11) reduces to the BRT curve for $\lambda^S/\lambda^N$.

Figure 4.19 shows the calculated ratio (4.11) using a value $n_i/n_{\text{cri}}$ of 0.85 together with the experimental results of $\lambda^S/\lambda^N$. Here we assumed that the thermal conductivity in the normal and superconducting state is totally due to electrons. This figure also shows the BRT curve for the pure limit $\alpha = 0$. As one can see, the Ambegaokar-Griffin curve with $n_i/n_{\text{cri}} = 0.85$ describes the experimental data above the magnetic ordering temperature $T_\lambda$ correctly. For lower temperatures the experimental points

1) I thank Dr. W Joss for the calculation of (4.11).
Figure 4.19
Experimental ratio of the electronic thermal conductivity in the superconducting state to that in the normal state assuming that the thermal conductivity is totally due to the electrons. The solid curves are the theoretical predictions of Ambegaokar and Griffin (AG) with $n_1/n_{cri} = 0.85$ and of Bardeen, Rickayzen and Tewordt (BRT). $T_\lambda$ indicates where a lambda-type anomaly in the specific heat is found. $T_G$ is described in the text.
the experimental points fall below the theoretical curve of Ambegaokar and Griffin indicating that the assumption of noninteracting magnetic moments is not fulfilled anymore. The decrease below the theoretical curve can be interpreted as a reduction of the pair breaking parameter $\alpha$ and is consistent with $H_{c2}$ measurements of Hamaker (1981) where an additional increase of the critical field $H_{c2}$ below $T_A$ is found. At the lowest temperatures the ratio of the thermal conductivity in the superconducting state to that in the normal state flattens out, that is, the thermal conductivity in the superconducting state tends to a linear temperature dependence.

There are different possibilities to explain this behaviour (Ott et al 1980). A small fraction of normal material extending over the sample length can dominate the thermal conductivity in this low temperature range and therefore lead to a nearly linear temperature dependence. The second possible explanation is the lattice contribution to the thermal conductivity in the superconducting state. In the discussion, we neglected this contribution. This is not justified anymore for the lowest temperatures where the enhancement of the lattice thermal conductivity due to reduced phonon-electron scattering can be appreciable. It also cannot be ruled out that we observe a contribution to the thermal conductivity other than those from electrons and phonons. In the antiferromagnetically ordered state, heat may be carried by spin waves (Lüthi 1962). This effect is usually not observed in metals because of the dominant electronic contribution. However, as far as thermal conductivity is concerned, a superconductor well below its transition temperature can be regarded as an insulator in the sense that only phonons contribute to $\lambda$ and the spin wave contribution to $\lambda$ may indeed become observable. The temperature dependence is then given by the dispersion relation of the spins. None of these possibilities can be confirmed with these data.
The effective concentration ratio \( n_i/n_{\text{cri}} \) found by fitting the experimental \( \lambda^S/\lambda^n \) to the AG theory is 0.85. There is another way to determine this ratio. An estimate can be gained from the depression of the superconducting critical temperature \( T_c \) due to localized magnetic moments compared to the nonmagnetic \( \text{LuRh}_4B_4 \) using the above mentioned Abrikosov-Gor'kov theory. A depression of 3.5 K must be attributed to the nonmagnetic effects by replacing Lu\(^{3+}\) ions by Sm\(^{3+}\) ions if we assume the validity of a linear interpolation of \( T_{\text{co}} \) between the \( \text{LuRh}_4B_4 \) and \( \text{Lu}_{1-x}\text{La}_x\text{Rh}_4B_4 \) (c.f. figure 4.13). (The compound \( \text{LaRh}_4B_4 \) does not exist.) A "nonmagnetic" \( \text{SmRh}_4B_4 \) therefore would have a \( T_{\text{co}} \) of 8.95 K. The actual critical temperature \( T_c \) of \( \text{SmRh}_4B_4 \) is 2.68 K. The estimated ratio \( T_c/T_{\text{co}} \) is 0.3 which, according to the theory of Abrikosov and Gor'kov on the depression of \( T_c \) due to magnetic interactions between localized magnetic moments and conduction electrons, corresponds to a normalized impurity concentration of \( n_i/n_{\text{cri}} = 0.85 \) in agreement with our value from the thermal conductivity.

Hamaker (1981) interpreted the temperature dependence of the critical field \( H_{c2} \) in the framework of a theory by Machida which extends the Abrikosov-Gor'kov theory to correlated spin systems. In fitting this theory to the \( H_{c2} \) data, Hamaker obtains \( T_c/T_{\text{co}} = 0.55 \).

In the Abrikosov-Gor'kov theory, a depression of \( T_c \) by magnetic impurities is accompanied by a change in the excitation spectrum of the superconductor and always leads to a temperature region below \( T_c \) where gapless superconductivity occurs. The extent of this temperature range is given by the condition \( \alpha = 1 \). In the case of \( T_c/T_{\text{co}} = 0.3 \) the creation of a gap takes place below \( T/T_{\text{co}} = 0.2 \). This temperature is marked by the arrow labelled with \( T_c \). For the direct observation of the predicted
gapless region we have to perform tunneling experiments on SmRh$_4$B$_4$
around and below 1 K.
5 CONCLUSIONS

The variety of magnetic and superconducting properties in the system of rare earth rhodium borides are also reflected in the electrical and the thermal conductivity. The measurements of these transport properties therefore provided valuable information on superconductivity and magnetism.

To study the influence of superconductivity on a compound of this system, we have measured the electrical resistivity and the thermal conductivity of LuRh$_4$B$_4$ where superconductivity is not influenced by a magnetic phase transition. The detailed analysis of these data showed that the lattice contribute about one third of the total thermal conductivity at the superconducting critical temperature $T_c$. The electronic thermal conductivity in the superconducting state could be described with the theory of Bardeen, Rickayzen and Tewordt (1958) (BRT). For the lattice thermal conductivity in the superconducting state, we had to include, besides the phonon-electron scattering, a phonon-impurity and a phonon-boundary term. From a fit to our data, the ratio of the energy gap to the superconducting critical temperature was found to be that of a weak coupling superconductor: $\frac{2\Delta(0)}{k_B T_c} = 3.5$.

The compound HoRh$_4$B$_4$ was chosen to study ferromagnetic order without interference of superconductivity. The behaviour of the thermal conductivity and the electrical resistivity was discussed only qualitatively. The increase in the electrical conductivity and the concomitant enhancement of the thermal conductivity could be interpreted as a mean free path effect of the conduction electrons. The magnetic ordering enhances the mean free path of the electrons due to the reduced spin disorder scattering in the ferromagnetic phase.
The reentrant superconductor $\text{ErRh}_4\text{B}_4$ shows both phenomena. Between 8.7 K and 1.2 K the compound was found to exhibit superconductivity. We successfully applied the BRT theory of thermal conductivity in this temperature range. Here, the influence of the localized noninteracting magnetic $\text{Er}^{3+}$ ions was found to be small. Below 1.2 K we found a gradual increase of the thermal conductivity over a temperature range of about 0.5 K, simultaneously with the onset of magnetic order. Below 0.87 K, the thermal conductivity displayed a linear temperature dependence indicating that the whole sample is in the normal state. The thermal hysteresis found in other physical properties was confirmed by the thermal conductivity measurements.

In $\text{SmRh}_4\text{B}_4$, the thermal conductivity data showed convincingly that superconductivity remains a bulk property below the magnetic ordering temperature $T_N$. In contrast to $\text{ErRh}_4\text{B}_4$, the localized magnetic moments of $\text{Sm}^{3+}$ ions seem to have a strong influence on the thermal conductivity of the superconducting state. We were able to interpret our results in terms of the theory of Ambegaokar and Griffin (1964) on thermal conductivity in a superconductor containing magnetic impurities. From a fit to our data we derived a pair-breaking parameter which is consistent with an estimated value deduced from the reduction of the superconducting critical temperature due to magnetic interactions.
We have measured the thermal conductivity and the electrical resistivity of \( \text{LuRh}_2\text{B}_4 \), \( \text{HoRh}_2\text{B}_4 \), \( \text{ErRh}_2\text{B}_4 \) and \( \text{SmRh}_2\text{B}_4 \) between 0.05 K and 50 K. The properties of these four compounds are characteristic for the whole series of the rare earth rhodium borides.

\( \text{LuRh}_2\text{B}_4 \) shows superconductivity. A detailed analysis shows that the lattice contributes about one third of the total thermal conductivity at the critical temperature \( T_c \). The thermal conductivity in the superconducting state can be described with the theory of Bardeen, Rickayzen and Tewordt (BRT). From a fit to our data, the ratio of the energy gap to the superconducting critical temperature is found to be that of a weak coupling superconductor: \( \frac{2\Delta(0)}{k_B T_c} = 3.5 \).

\( \text{HoRh}_2\text{B}_4 \) orders ferromagnetically. The behaviour of the thermal conductivity and the electrical resistivity below the ordering temperature can be explained in terms of an enhanced mean free path due to the decrease of spin disorder scattering in the ferromagnetic phase.

The reentrant superconductor \( \text{ErRh}_2\text{B}_4 \) shows superconductivity and ferromagnetic order. The effect of the noninteracting localized magnetic moments of the \( \text{Er}^{3+} \) ions on the superconductivity is weak and the BRT theory may be applied. The thermal conductivity data show a gradual destruction of superconductivity over a temperature range of 0.5 K with the onset of magnetic order. Below 0.87 K, the thermal conductivity displays a linear temperature dependence indicating that the whole sample is in the normal state. The thermal hysteresis around 0.9 K found in other physical properties was confirmed.
by the thermal conductivity measurements.

Superconductivity and possibly antiferromagnetic ordering persists in SmRh$_4$B$_4$. In contrast to ErRh$_4$B$_4$, the localized magnetic moments of Sm$^{3+}$ ions seem to have a strong influence on the thermal conductivity in the superconducting state. Our results can be interpreted in terms of the Ambegaokar and Griffin theory of the thermal conductivity in a superconductor containing magnetic impurities. In particular we derive a pairbreaking parameter which is consistent with the value deduced from the reduction of the superconducting critical temperature due to magnetic interactions. From the value of this parameter and following the Abrikosov and Gor'kov theory of magnetic impurities in superconductors we expect a gapless superconducting region for $T/T_C > 0.65$. 
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ZUSAMMENFASSUNG

Wir haben thermische und elektrische Leitfähigkeiten von LuRh\(_4\)\(_B\), HoRh\(_4\)\(_B\), ErRh\(_4\)\(_B\) und SmRh\(_4\)\(_B\) im Temperaturbereich von 0.05 K bis 50 K gemessen. Diese vier Verbindungen charakterisieren die magnetischen und supraleitenden Eigenschaften des ganzen Systems der Seltenen Erd Rhodium Boride.

LuRh\(_4\)\(_B\) ist ein Supraleiter. Eine detaillierte Analyse zeigt, dass an der kritischen Temperatur der Supraleitung ein Drittel der gesamten Wärmeleitung von den Phononen herrührt. Die Wärmeleitung im supraleitenden Zustand kann mit der Theorie von Bardeen, Rickayzen und Tewordt (BRT) beschrieben werden. Aus einem Fit auf unsere Wärmeleitungsdaten wurde das Verhältnis der Energielücke bei T = 0 zur kritischen Temperatur T\(_c\) bestimmt. Danach ist dieses Verhältnis das eines schwach koppelnden Supraleiters: \(2\Delta(0)/k_B T_c = 3.5\).

HoRh\(_4\)\(_B\) ordnet ferromagnetisch. Das Verhalten der thermischen Leitfähigkeit und des elektrischen Widerstandes kann auf einen Freie Weglängeeffekt zurückgeführt werden. Durch das Wegfallen der Spinunordnungstreueung vergrößert sich die Freie Weglänge der Elektronen.

ErRh\(_4\)\(_B\) zeigt Supraleitung und Ferromagnetismus. Da der Einfluss der nichtkoppelnden lokализierten magnetischen Momente der Er\(^{3+}\) Ionen schwach ist, kann man die BRT Theorie anwenden. Die Wärmeleitung zeigt, dass mit dem Einsetzen der langreichweitigen magnetischen Ordnung die Supraleitung langsam zerstört wird. Der Bereich dieses Überganges erstreckt sich auf ungefähr 0.5 K. Unterhalb 0.87 K weist die Wärmeleitung eine lineare Temperaturabhängigkeit auf wie wir sie von einem normalen Metall bei tiefen...
Temperaturen erwarten. Um 0.9 K zeigt auch die Wärmeleitung eine thermische Hysterese wie sie in anderen physikalischen Eigenschaften gefunden wurde.

In SmRh$_4$B$_4$ sind Supraleitung und antiferromagnetische Ordnung gleichzeitig vorhanden. Die magnetischen Sm$^{3+}$ Ionen scheinen hier einen viel stärkeren Einfluss auf die Supraleitung zu haben. Wir analysierten unsere Resultate im Rahmen einer Theorie von Ambegaokar und Griffin die die Wärmeleitung eines Supraleiters mit magnetischen Verunreinigungen beschreibt. Die Übereinstimmung oberhalb der magnetischen Ordnungstemperatur ist gut. Im speziellen haben wir einen Paarbrechungsparameter für Cooperpaare abgeleitet, der mit dem Wert aus einer Abschätzung mit Hilfe der Reduktion der kritischen Temperatur aufgrund von magnetischen Verunreinigungen übereinstimmt. Aufgrund des Wertes dieses Parameters erwarten wir einen Temperaturbereich $T > T_c/T_c > 0.65$ wo Supraleitung ohne Energielücke auftreten sollte.
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