

MAGNETIC AND TRANSPORT PROPERTIES OF RARE-EARTH-BASED HEUSLER PHASES $REPdZ$ and $REPd_2Z$ ($Z = \text{Sb, Bi}$)

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Abstract

Four series of ternary compounds $REPdSb$ ($RE = \text{Y, Ho, Er}$), $REPdBi$ ($RE = \text{Nd, Y, Dy, Ho, Er}$), $REPd_2Sb$ ($RE = \text{Y, Gd-Er}$) and $REPd_2Bi$ ($RE = \text{Y, Dy-Er}$) were studied by means of magnetization, magnetic susceptibility, electrical resistivity, magnetoresistivity, thermoelectric power and Hall effect measurements, performed in the temperature range 1.5–300 K and in magnetic fields up to 12 T. All these ternaries, except for diamagnetic Y-based phases, exhibit localized magnetism of RE^{3+} ions, and a few of them order antiferromagnetically at low temperatures ($T_N = 2\text{--}14$ K). The equiatomic compounds show half-metallic conductivity due to formation of narrow gaps in their electronic band structures near the Fermi energy. Their Seebeck coefficient at room temperature is exceptionally high (S up to 200 $\mu\text{V/K}$), being promising for thermoelectric applications. In contrast, all the 1:2:1 phases are semimetals and their thermoelectric power is much lower (maximum S of 10–25 $\mu\text{V/K}$). The Hall effect in the compounds studied corroborates complex character of their electronic structure with multiple electron and hole bands with different temperature and magnetic variations of carrier concentrations and their mobilities.

Introduction

The phases of the general compositions XYZ and XY_2Z , where X and Y stand for d - or f -electron transition metals and Z denotes a p -electron element, continuously attract much attention due to their remarkable magnetic and electrical transport properties [1,2]. Equiatomic compounds crystallize with the MgAgAs type of structure (space group $F\bar{4}3m$) and exhibit semimetallic or semiconducting behaviour. In systems like $X\text{NiSn}$ ($X = \text{Ti, Hf, Zr}$) [3,4] the presence of a vacancies sublattice gives rise to the formation of a narrow gap near the Fermi level of the size of several tenth electron volts. This feature leads to high values of the Seebeck coefficient and thus the XYZ compounds are considered as attractive candidates for thermoelectrical applications [5–8].

In turn, the XY_2Z Heusler phases (AlCu_2Mn type, space group $Fm\bar{3}m$) usually show metallic-like conductivity. Interestingly, within this series of alloys several superconductors have been discovered, e.g. $REPd_2\text{Sn}$ ($RE = \text{Er, Tm, Yb, Lu, Y, Sc}$) [9–12] and $REPd_2\text{Pb}$ ($RE = \text{Tm, Yb, Lu, Y, Sc}$) [13]. Most spectacularly, in ErPd_2Sn [11] and YbPd_2Sn [12] the superconductivity was found to coexist with long-range magnetic ordering.

Isostructural phases $REPdZ$ and $REPd_2Z$ were reported to exist with $Z = \text{Sb}$ and Bi [14] but, to the best of our knowledge, no data on their physical properties have been published yet, except those for a heavy-fermion compound YbPd_2Sb [14] and short account on the magnetic behaviour in $REPdSb$ ($RE = \text{Dy, Ho, Er}$) [15–17]. Thus, in this paper we report some results of our systematic study on the structural, magnetic, thermal and electrical transport of the phases $REPdSb$ ($RE = \text{Y, Ho, Er}$), $REPdBi$ ($RE = \text{Nd, Y, Dy, Ho, Er}$), $REPd_2Sb$ ($RE = \text{Y, Gd-Er}$) and $REPd_2Bi$ ($RE = \text{Y, Dy-Er}$).

Experimental details

Polycrystalline samples of $REPdSb$ ($RE = \text{Y, Dy, Ho, Er}$), $REPdBi$ ($RE = \text{Y, Dy, Ho, Er}$), $REPd_2Sb$ ($RE = \text{Y, Gd, Tb, Dy, Ho, Er}$) and $REPd_2Bi$ ($RE = \text{Y, Dy, Ho, Er}$) were prepared by arc-melting the constituents (RE : 99.9 wt%, Pd : 99.999 wt%, Sb : 99.999 wt%, Bi : 99.999 wt%) under argon atmosphere. The ingots were then wrapped in tantalum foil, sealed in evacuated quartz tubes and annealed at temperatures ranging from 800 °C to 1000 °C for several weeks (in the case of the $REPdBi$ phases such a heat treatment led to multiphase products and therefore as-cast samples were used in physical measurements). Quality of the obtained materials was checked at room temperature by powder X-ray diffraction (Huber Guinier G670 image plate camera with $\text{CuK}\alpha_1$ radiation, $\lambda = 1.5406$ Å, and silicon as an internal standard, $a = 5.43119$ Å), EDX analysis (Philips XL30 scanning electron microscope with integrated EDXS system and S-UTW-Si(Li) detector) and optical metallography (Zeiss Axioplan 2 optical microscope with a CCD camera). The samples were found to be single-phase with the expected cubic structures of the MgAgAs or AlCu_2Mn type, and with the lattice parameters close to those given in the literature [15,17]. For HoPd_2Bi powder X-ray diffraction was extended to temperatures down to 50 K (Siemens D-5000 powder diffractometer with $\text{CuK}\alpha_1$ radiation equipped with a helium low-temperature attachment). This study revealed a phase transition from cubic to lower symmetry structure occurring at about 135 K.

Magnetic studies were carried out in the temperature range 1.7–300 K and in magnetic fields up to 5 T using a SQUID magnetometer (Quantum Design MPMS-5). The electrical resistivity was measured from 4.2 to 300 K by a four-point DC technique. Transverse magnetoresistivity and Hall effect measurements were performed within the temperature range 1.5–300 K and in applied fields up to 12 T (Oxford Instruments TESLATRON). The thermoelectric power was

measured from 6 to 300 K employing a differential method with copper as a reference material.

Magnetic behaviour

All the equiatomic compounds, but diamagnetic YPdSb and YPdBi, were found to exhibit localized magnetism of RE^{3+} ions. DyPdSb, HoPdSb, GdPdBi, DyPdBi and HoPdBi order antiferromagnetically at low temperatures ($T_N = 2.0 - 13.5$ K), whereas ErPdSb and ErPdBi remain paramagnetic down to the lowest temperature studied. It is worthwhile noting that the Néel temperature derived here for HoPdSb is slightly lower than that determined before by means of powder neutron diffraction ($T_N = 2.7$ K) [18]. In the paramagnetic region the susceptibility of all these compounds exhibits a Curie-Weiss behaviour with the effective magnetic moments, μ_{eff} , close to the theoretical values given by the Hund's rules for the respective RE^{3+} ions ($= g[J(J+1)]^{1/2}$), and with the paramagnetic Curie temperatures, θ_p , being negative, i.e. consistent with antiferromagnetic exchange interactions (see Table 1).

Table 1. Ordering temperatures and Curie-Weiss parameters for $REPdSb$, $REPdBi$, $REPd_2Sb$ and $REPd_2Bi$ alloys; P: paramagnetic behaviour, D: diamagnetic behaviour

Compound	T_N [K]	θ_p [K]	μ_{eff} [μ_B]
ErPdSb	P	-4.2	9.43
HoPdSb	2	-9	10.7
DyPdSb	3.3	-11.5	10.5
YPdSb	D	-	-
ErPdBi	P	-4.56	9.2
HoPdBi	2.2	-6.12	10.59
DyPdBi	3.5	-11.92	10.7
GdPdBi	13.5	-36.5	8
YPdBi	D	-	-
ErPd ₂ Sb	P	-2.7	9.4
HoPd ₂ Sb	P	-4.7	10.5
DyPd ₂ Sb	2.2	-6.1	10.4
TbPd ₂ Sb	3.1	-7.9	9.6
GdPd ₂ Sb	5.1	-9.8	7.9
YPd ₂ Sb	D	-	-
ErPd ₂ Bi	P	-5.1	9.58
HoPd ₂ Bi	5.2	-17.9	9.94
DyPd ₂ Bi	6.5	-14.7	10.8
YPd ₂ Bi	D	-	-

The magnetic studies on the novel compounds $REPd_2Sb$ and $REPd_2Bi$ revealed at low temperatures (2.2 – 6.5 K) the presence of fairly broad maxima in the magnetic susceptibility of the Dy-, Tb- and Gd-based antimonides and for the Ho- and Dy-based bismuthides. These features likely manifest the onsets of antiferromagnetic ordering. However it should be noted that the susceptibility decrease below T_N is quite small, and $\chi(T)$ is irreversible when measured in weak fields in zero-field-cooled (ZFC) and field-cooled (FC) conditions (as a typical example Fig. 1 displays the susceptibility of DyPd₂Sb). Similar behaviour was observed before e.g. for the $REPd_2Pb$

phases [13], and might be attributed to spin glass phenomena due to some structural disorder and/or topological frustration of magnetic interactions in the fcc lattice. Moreover, for TbPd₂Sb and DyPd₂Bi other phase transitions, possibly spin reorientations, were found to take place at $T_1 = 2.4$ K and 3 K, respectively. In contrast, ErPd₂Sb, HoPd₂Sb and ErPd₂Bi remain paramagnetic down to 1.7 K, while YPd₂Sb and YPd₂Bi exhibit a weak diamagnetism. In the paramagnetic region the susceptibility of each of the 1:2:1 compounds, except for the alloys with yttrium, follows a Curie-Weiss law with the parameters given in Table 1. Alike in the $REPdZ$ materials studied the local magnetic moments are carried here by RE^{3+} ions, while negative θ_p 's imply electronic correlations of antiferromagnetic character.

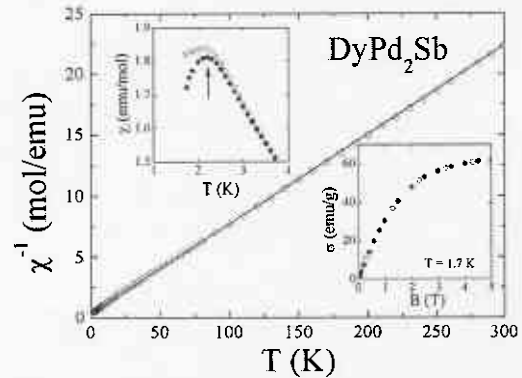


Fig. 1. Reciprocal molar magnetic susceptibility vs. temperature for DyPd₂Sb. The solid line is a Curie-Weiss fit. Upper inset: low-temperature susceptibility measured in $B = 0.01$ T in zero-field-cooled (full circles) and field-cooled (open circles) regimes. The arrow marks the magnetic phase transition. Lower inset: field dependence the magnetisation measured at $T = 1.7$ K with increasing (full circles) and decreasing (open circles) field.

Electrical transport properties

The electrical conductivities of the $REPdSb$ and $REPdBi$ compounds exhibit the magnitudes and overall temperature dependencies characteristic of semimetals or narrow-gap semiconductors. As typical examples there are shown in Fig. 2 the $\rho(T)$ curves measured for HoPdSb and ErPdBi. The electrical resistivity for both compounds is of the order of 1-10 m Ω cm. With decreasing temperature from 300 K it initially increases, goes through a broad maximum at $T_{\text{max}} = 70$ K and 150 K for HoPdSb for ErPdBi, respectively, and then decreases in a metallic-like manner at lower temperatures. Finally, below ca. 7 K for both compounds a rapid drop in $\rho(T)$ is observed.

The rise of the resistivity in the region 7 K – T_{max} is reminiscent to the behaviour of a doped semiconductor in its impurity range, where due to atomic disorder, defects or improper stoichiometry some donor or acceptor levels are formed, the presence of which governs the conduction at low temperatures. Above T_{max} the $\rho(T)$ variations have a semiconductor-like character and may be approximated by the formula:

$$1/\rho(T) = \sigma_0 + \sigma_a \exp\left(\frac{E_a}{k_B T}\right) \quad (1)$$

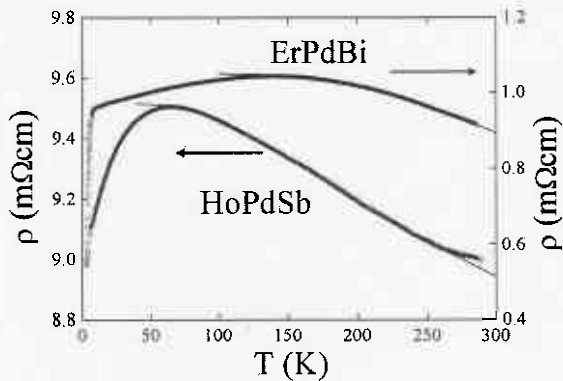


Fig. 2. Electrical resistivity vs. temperature for ErPdBi and HoPdSb. The solid lines are least-squares fits of Eq. (1) to the experimental data.

that accounts for scattering of the conduction electrons excited over the energy gap E_a . The values of E_a derived from the experimental data of HoPdSb and ErPdBi are equal to 31 and 87 meV, respectively. These numbers may be compared with those of about 200-500 meV calculated for the alloys $XNiSn$ and $XNiSb$ ($X = Ti, Zr, Hf$) [20,21]. Similarly, the gap calculated for a closely related antimonide LuPdSb is $E_a \sim 100$ meV [22]. Apparently, the values of E_a obtained for HoPdSb and ErPdBi are considerably smaller than those predicted theoretically and thus most probably the intrinsic regime is not reached in these compounds even at temperatures close to 300 K.

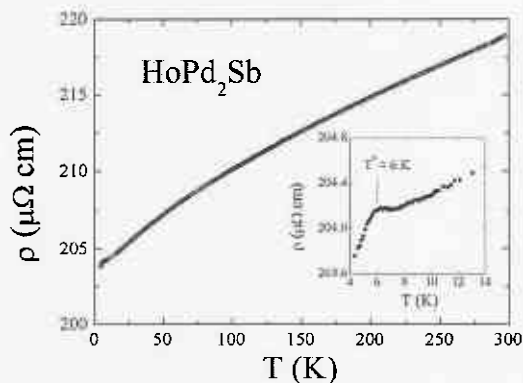


Fig. 3. Electrical resistivity vs. temperature for HoPd₂Sb. Inset: low-temperature resistivity. The arrow marks the anomaly at $T^* = 6$ K.

In contrast to the $REPdZ$ compounds studied all the $REPd_2Sb$ ternaries exhibit a metalli-like conductivity (see Fig. 3 for an example). However, the magnitude of the resistivity is relatively large (200 – 300 $\mu\Omega\text{cm}$) and the residual resistivity ratio is quite small (1 – 2), both findings being probably indicative of considerable atomic disorder. More complex behaviour of $\rho(T)$ was found for the $REPd_2Bi$ alloys. At high temperatures the resistivity linearly decreases with decreasing temperature as expected for simple metals. Then, below a temperature T_{tr} at which a structural phase transition takes place (see Experimental details), the resistivity shows a rapid

rise and saturates at low temperatures at values of about 300 $\mu\Omega\text{cm}$. As an example for such behaviour Fig. 4 presents $\rho(T)$ measured for HoPd₂Bi. For this compound a semiconducting-like region below 120 K may be described by Eq. (1) with $E_a = 15$ meV. As is apparent from the inset to Fig. 4, in the vicinity of $T_{tr} = 135$ K the resistivity exhibits a distinct hysteresis when measured on heating and cooling, which clearly manifests the first-order character of the structural phase transition. The T_{tr} temperatures for the other bismuthides are as follows: 170, 168 and 120 K for Er, Dy and Y-based phases, respectively.

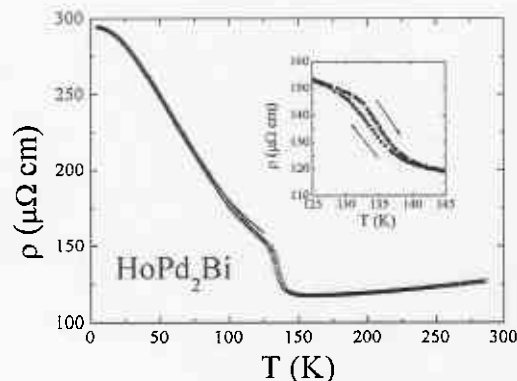


Fig. 4. Electrical resistivity vs. temperature for HoPd₂Bi. The solid line is a fit of Eq. (1) to the experimental data. Inset: electrical resistivity in the vicinity of the structural phase transition measured with decreasing and increasing temperature (as indicated by the arrows).

For the magnetically ordered $REPdZ$ and $REPd_2Z$ compounds one observes some weak anomalies in their $\rho(T)$ that may be associated with the magnetic phase transitions. Moreover, most unexpectedly, the resistivity of all the Er-based phases, HoPdSb and HoPd₂Sb (see Figs. 2 and 3) shows below a temperature $T^* = 6 - 7$ K a very rapid drop that can hardly be attributed to a magnetic phase transition because in this temperature region both the magnetic susceptibility and the specific heat [23] are featureless. This intriguing issue will be addressed in detail in our forthcoming paper.

Thermoelectric power measurement of $REPdSb$ and $REPdBi$ compounds revealed that the magnitude of the Seebeck coefficient at room temperature is as large as 150 – 200 $\mu\text{V/K}$ for the antimonides and 40 – 80 $\mu\text{V/K}$ for the bismuthides. All these materials show positive thermopower in the entire temperature range studied, which indicates that the dominant charge carriers are holes. The overall temperature dependencies of the Seebeck coefficient are similar to those observed before for the alloys $XNiSn$ ($X = Ti, Hf, Zr$) [24] and characteristic of low carrier density semimetals with parabolic electron and hole bands [25]. As examples, in Fig. 5 there are shown the $S(T)$ variations for a few compounds. A nearly linear-in- T behaviour at high temperatures is probably indicative of diffusion processes. The standard Mott's formula

$$S = \frac{k_B^2 \pi^2 T}{3eE_F} \quad (2)$$

applied to the experimental data yields the following values of the Fermi energy: $E_F = 32, 39, 132,$ and 144 meV for YPdSb, HoPdSb, HoPdBi and YPdBi, respectively. These values of E_F are considerably smaller than those characterising wide-band metals. For HoPdSb a hump below 50 K is observed that presumably comes from phonon drag or/and crystal field effect. The effective carrier concentrations estimated within a single-band model are of the order of 10^{19} cm⁻³ in REPdSb and 10^{20} cm⁻³ in REPdBi, being consistent with high magnitude of the electrical resistivity of these compounds.

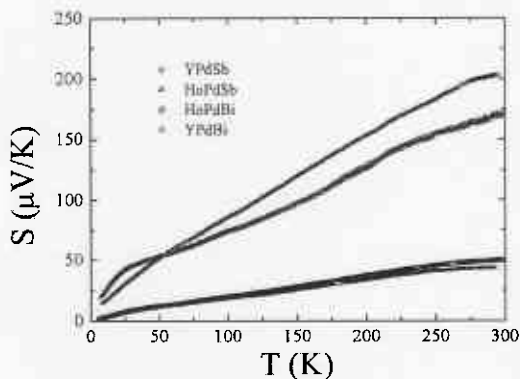


Fig. 5. Thermoelectric power vs. temperature for YPdSb, HoPdSb, HoPdBi and YPdBi.

The Seebeck coefficient is a sensitive probe of electronic band structure near the Fermi level. Its high magnitude is the main prerequisite for efficient thermoelectrical performance, the other factors being moderate electrical resistivity and small heat conductivity. In the case of ErPdSb the two first factors seem fairly appropriate ($S = 150$ $\mu\text{V/K}$ and $\rho = 1.8$ m Ωcm at room temperature) and hence measurements of the thermal conductivity, $\kappa(T)$, were performed in the temperature range 5–300 K. At room temperature the thermal conductivity is about 3 W/mK [26] that leads to a dimensionless figure of merit $ZT = S^2/\rho\kappa$ of about 0.15. The obtained value of ZT is comparable with those typical of 3d-electron transition metal – based XYZ phases, and materials like skutterudites or clathrates, which are being intensively studied in recent years. It is however much lower than the figure of merit achievable for alloys like Bi_xSb_{2-x}Te_{3-y}Se_y ($ZT \sim 1$; [27]), used in state-of-the-art commercial devices.

The thermoelectric power of the REPd₂Z compounds is generally much smaller than that found for the REPdZ alloys. It achieves maximum absolute values of about of 4–7 $\mu\text{V/K}$ for the antimonides and 10–25 $\mu\text{V/K}$ for the bismuthides. For all the REPd₂Sb phases the Seebeck coefficient is negative and that of the REPd₂Bi compounds is positive. These findings, together with complex temperature dependencies of the thermopower in both series, clearly indicate semimetallic character of the compounds with multiple bands of electrons and holes. As an example Fig. 6 presents the $S(T)$ variations for ErPd₂Sb and ErPd₂Bi. For both ternaries the thermopower is weakly temperature dependent just below room temperature. Below 170 K $S(T)$ of the antimonide shows a smooth curved variation towards zero, while that of ErPd₂Bi rapidly increases

at the structural phase transition and forms a broad maximum near 110 K. Interestingly, the overall temperature dependence of the thermopower of ErPd₂Bi is very similar to that of its electrical resistivity. In particular, around $T_{\text{tr}} = 170$ K $S(T)$ shows a pronounced hysteresis (see Fig. 6) closely resembling that observed in $\rho(T)$.

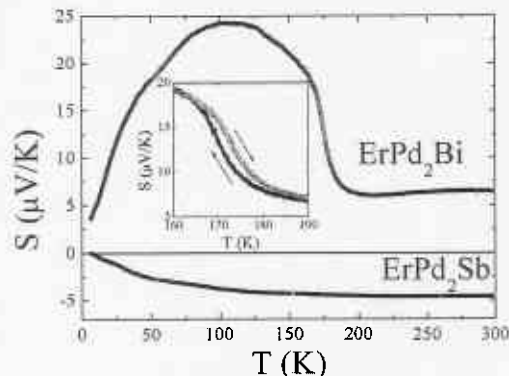


Fig. 6. Thermoelectric power vs. temperature for ErPd₂Sb and ErPd₂Bi. Inset: thermoelectric power in the vicinity of the structural phase transition in ErPd₂Bi, measured with decreasing and increasing temperature (as indicated by the arrows).

The Hall-effect measurements were performed for the Er-based phases only. For all the compounds the Hall coefficient measured in a field of 12 T is positive (see an example in Fig. 7), including the case of ErPd₂Sb that shows negative thermopower. Unlike in metals R_H is strongly temperature dependent, which implies complex underlying electronic structure with electron and hole bands containing carries with different temperature-dependent mobilities. Moreover, $R_H(T)$ shows a distinct magnetic field dependence at low temperatures, and the magnitude of the Hall coefficient is reduced with rising field. For ErPd₂Sb one observes a change in the sign of R_H to negative at low temperatures when the Hall effect is measured in weak fields. This latter feature hints at a reconstruction of the electronic structure in this compound upon applying magnetic field.

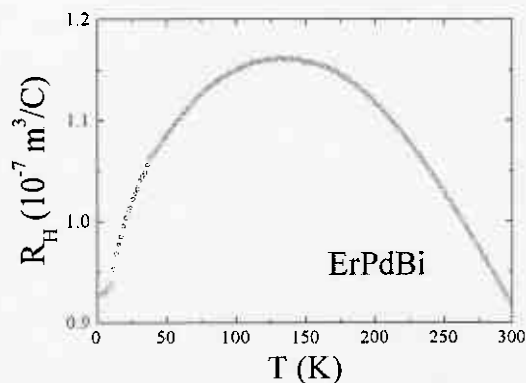


Fig.7. Hall coefficient vs. temperature for ErPdBi, measured in a magnetic field of 12 T.

At room temperature the magnitude of R_H is about 10^{-7} m^3/C for ErPdZ compounds, 10^{-9} m^3/C for ErPd₂Bi and 10^{-10} m^3/C for ErPd₂Sb. These values are $10^2 - 10^4$ times larger than the Hall coefficient of conventional metals, and $10^2 - 10^3$ times larger than that observed for heavy-fermion compounds [28] yet typical of semimetallic materials [29]. Considering a simple single-band model, the Hall carrier density is estimated to be of the order of 10^{19} cm^{-3} in ErPdSb and 10^{20} cm^{-3} in ErPdBi, in good agreement with the values obtained from the thermoelectric data. In turn, the Heusler alloys ErPd₂Sb and ErPd₂Bi exhibit much higher carrier density, of the order of 10^{23} cm^{-3} and 10^{21} cm^{-3} , respectively, in line with the metallic-like character of their electrical conductivity.

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References

1. P. J. Webster and K. R. A. Ziebeck, *J. Phys. Chem. Solids* **34** (1973) 1647.
2. J. Pierre, R. V. Skolozdra, J. Tobola, C. Hordequin, M. A. Kouacou, I. Karla, R. Currat and E. Lelievre-Berna, *J. Alloys Compd.* **262-263** (1997) 101.
3. R. A. de Groot, F. M. Mueller, P. G. Engen and K. H. J. Bushow, *Phys. Rev. Lett.* **50** (1983) 2024.
4. F. G. Aliev, N. B. Brandt, V. V. Moshchalkov, V. V. Kozyrkov, R. V. Skolozdra and A. I. Belogorokhov, *Z. Phys. B: Condens. Matter* **75** (1989) 167.
5. F. G. Aliev, V. V. Kozyrkov, V. V. Moshchalkov, R. V. Skolozdra and K. Durczewski, *Z. Phys. B: Condens. Matter* **80** (1990) 353.
6. Y. Xia, S. Bhattacharya, V. Ponnambalam, A. L. Pope, S. J. Poon and T. M. Tritt, *J. Appl. Phys.* **88** (2000) 1952.
7. B. A. Cook and J. L. Haringa, *J. Mat. Sciences* **34** (1999) 323.
8. Q. Shen and L. Zhang, *J. Mater. Sciences* **20** (2001) 2197.
9. M. Ishikawa, J. L. Jorda and A. Junod, in *Superconductivity in d- and f-Band Metals* (Kernforschungszentrum, Karlsruhe, 1982) p. 141.
10. M. J. Johnson and R. N. Shelton, *Solid State Commun.* **52** (1984) 839.
11. R. N. Shelton, L. S. Hausermann-Berg, M. J. Johnson, P. Klavins, and H. D. Yang, *Phys. Rev. B* **34** (1986) 199.
12. H. A. Kierstead, B. D. Dunlap, S. K. Malik, A. M. Umarji, and G. K. Shenoy, *Phys. Rev. B* **32** (1985) 135.
13. C. L. Seaman, N. R. Dilley, M. C. de Andrade, J. Herrmann, M. B. Maple and Z. Fisk, *Phys. Rev. B* **53** (1996) 2651.
14. D. Kaczorowski, A. Leithe-Jasper, T. Cichorek, K. Tenya, J. Custers, P. Gegenwart, Yu. Grin, *Acta Phys. Polon. B* **34** (2003) 1253.
15. S. K. Malik and D. T. Adroja, *J. Magn. Magn. Mater.* **102** (1991) 42.
16. A. Zygmunt and A. Szytula, *J. Alloys Compd.* **219** (1995) 185.
17. P. Riani, D. Mazzone, G. Zanocchi, R. Marazza and R. Ferro, *Z. Metallkd.* **86** (1995) 450.
18. G. André, F. Bouree, A. Oles, W. Sikora, S. Baran and A. Szytula, *Solid State Commun.* **104** (1997) 531.
19. I. Karla, J. Pierre and R. V. Skolozdra, *J. Alloys Compd.* **265** (1998) 42.
20. S. Ögüt and K. M. Rabe, *Phys. Rev. B* **51** (1995) 10443.
21. P. Larson, S. D. Mahanti, S. Sportouch and M. G. Kanatzidis, *Phys. Rev. B* **59** (1999) 15660.
22. K. Mastronardi, D. Young, C. C. Wang, P. Khalifah, R. J. Cava and A. P. Ramirez, *Appl. Phys. Lett.* **74** (1999) 1415.
23. W. Schnelle, private communication.
24. C. Uher, J. Yang, S. Hu, D. T. Morelli and G. P. Meisner, *Phys. Rev. B* **59** (1999) 8615.
25. K. Durczewski and M. Ausloos, *Z. Phys. B: Condens. Matter* **85** (1991) 59.
26. J. Mucha, private communication.
27. R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, *Nature* **413** (2001) 597.
28. A. Fert and P. M. Levy, *Phys. Rev. B* **36** (1987) 1907.
29. F. G. Aliev, *Physica B* **171** (1991) 199.