PHYSICAL REVIEW B, VOLUME 65, 132519

Nonmagnetic ground state of the superconductor $PrPt_2B_2C$ and magnetic pairbreaking in $La_{0.9}R_{0.1}Pt_2B_2C$ (R=Ce, Pr, Nd)

S. K. Dhar,[1] A. D. Chinchure,[1,*] R. Nagarajan,[1] S. M. Pattalwar,[1] L. C. Gupta,[1] E. Alleno,[2] and C. Godart[2]
[1]*Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India*
[2]*C.N.R.S. UPR 209, ISCSA, F-94320 Thiais, France*

(Received 28 October 2001; published 29 March 2002)

$PrPt_2B_2C$ is an unusual superconducting member ($T_c \sim 6$ K) of quaternary borocarbide family. At high temperatures, Pr ions are found to carry magnetic moment, but so far no magnetic order is reported. We have investigated the nature of the electronic ground state of this material (nominal composition $PrPt_{2.1}B_{2.4}C_{1.2}$) through magnetic and heat capacity studies. We confirm that $PrPt_2B_2C$ exhibits *bulk* superconductivity below 6 K. Our studies show that (non-Kramers) Pr ions at low temperatures are in the crystal field split singlet ground state (nonmagnetic) and there is no indication of an induced magnetic moment. In the nonmagnetic analogue superconductor $LaPt_2B_2C$ ($T_c \sim 10.5$ K), we have studied magnetic pairbreaking by magnetic ions Ce, Pr, and Nd. We find severe pair-breaking caused by Ce ions suggesting an enhanced Ce-4f-conduction electron hybridization.

DOI: 10.1103/PhysRevB.65.132519 PACS number(s): 74.70.Dd, 75.20.Hr, 75.30.Mb, 75.40.−s

I. INTRODUCTION

Following the discovery of superconductivity in Ni-based quaternary borocarbides RNi_2B_2C (R=rare earth),[1–3] Pt-based quaternary borocarbides RPt_2B_2C (R=La, Ce, Pr, Nd, and Y) were also found.[4] Although they are structurally similar to the extensively studied Ni-based quaternaries RNi_2B_2C ($LuNi_2B_2C$-type tetragonal structure[5]), there are significant differences between the two series. In RNi_2B_2C, superconductivity occurs in materials with R=Dy, Ho, Er, Tm, and Lu, belonging to the *latter half* of the rare earth series.[3,6] On the other hand, for RPt_2B_2C, superconductivity occurs in the *earlier half* of the rare earth series—in $LaPt_2B_2C$ ($T_c \sim 10.5$ K) (Ref. 4) and $PrPt_2B_2C$ ($T_c \sim 6$ K).[4] Interestingly, in both the series, for nonmagnetic Y, which from the size point of view is generally assumed to behave as a heavy rare earth ion, both the Ni and Pt members show superconductivity ($T_c \sim 15.5$ and ~ 10 K, respectively). Further, in the material aspect also there is a significant difference. Unlike Ni compounds, which readily form in the stoichiomentric ratio 1:2:2:1, the Pt compounds do not form in single phase when prepared in the same ratio.[4] In order to stabilize the $LuNi_2B_2C$-type phase, either one has to partially substitute Pt by Au, such as $LaPt_{1.5}Au_{0.6}B_2C$ (Ref. 7) or have off stoichiometry in Pt, B, and C, such as $LaPt_{2.1}B_{2.4}C_{1.2}$.[8]

Occurrence of superconductivity in $PrPt_2B_2C$ is one of the most fascinating features of the Pt-based borocarbides, as there are not many Pr-based superconducting compounds. For instance, among high-T_c cuprates, superconductivity is absent in $PrBa_2Cu_3O_7$. In addition, this material has anomalously high Pr-magnetic ordering temperature. Precise nature of the electronic state of Pr ions in this material is still under discussion.[9] More relevant in the present context, is the example of nonsuperconducting $PrNi_2B_2C$, where the absence of superconductivity may be primarily due to the effect of ionic size/band-structure effects[10] though presence of 4f-conduction electron hybridization has also been shown in this material.[9,11,12] $PrRh_4B_4$ (which forms under pressure) is a rare example of Pr compounds which exhibit superconductivity ($T_c \sim 4.6$ K). It also undergoes a magnetic transition at $T_N \sim 1.6$ K.[13]

As several other members of the borocarbide family exhibit coexistence of magnetism and superconductivity, it is of interest to know the nature of the crystal field split ground state of the Pr ions in $PrPt_2B_2C$. A crystal field split nonmagnetic singlet ground state, which is possible in Pr^{3+}, will not result in any magnetic ordering if a magnetic moment is not induced by exchange interaction.[12]

The above considerations motivated us to investigate the ground state of Pr ions in $PrPt_2B_2C$. We succeeded in preparing single phase material with the starting composition $PrPt_{2.1}B_{2.4}C_{1.2}$ and we present here the results of our measurements. For comparison, the corresponding nonmagnetic analog $LaPt_{2.1}B_{2.4}C_{1.2}$ was also prepared and studied. Further, we have also investigated the pair-breaking effect by dilute Ce, Pr, and Nd ions in $LaPt_2B_2C$.

II. EXPERIMENTAL

As mentioned above, we have used the off stoichiometry method[8] for preparing $LuNi_2B_2C$-type phase stabilized samples. Starting nominal composition of our samples was $RPt_{2.1}B_{2.4}C_{1.2}$ (R=La, Pr). This was also the case for the doped materials $La_{0.9}R_{0.1}Pt_{2.1}B_{2.4}C_{1.2}$ (R=rare earth). The constituents were taken in the desired atomic ratio and were arc melted under argon atmosphere. The samples were melted six times and were flipped over each time before the next melting. Loss in weight after the final melting was <1%. The ingots, wrapped in tantalum foils and sealed in evacuated quartz ampoules were annealed for seven days at ~1100 °C. Magnetization measurements at various fields and temperatures were carried out using a SQUID magnetometer (Quantum Design, USA). Resistivity measurements were made using the four-probe dc method. Heat capacity

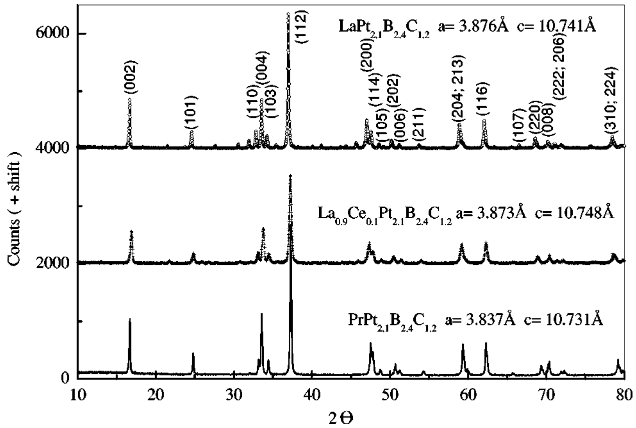

FIG. 1. The x-ray diffraction pattern of $PrPt_2B_2C$, $LaPt_2B_2C$, and $La_{0.9}Ce_{0.1}Pt_2B_2C$.

measurements were made using semi-adiabatic heat pulse method on a home built automated calorimeter.

III. RESULTS AND DISCUSSION

Powder x-ray diffraction data (XRD) for the samples confirmed the formation of the $LuNi_2B_2C$-type tetragonal phase in these alloys. For further discussion, we shall refer to our samples as RPt_2B_2C. Figure 1 shows XRD patterns for $LaPt_2B_2C$, $La_{0.9}Ce_{0.1}Pt_2B_2C$, and $PrPt_2B_2C$ (curves have been shifted up for clarity). Lattice parameters were refined using least squares fitting technique, values of the a and c parameters of the centered tetragonal structure are also given in the figure. The impurity phase was $<1\%$ in all the cases except for $LaPt_2B_2C$ where the most intense nonindexable peak was $\sim 5\%$ of the most intense peak of the main phase. $La_{0.9}R_{0.1}Pt_{2.1}B_{2.4}C_{1.2}$ with $R=$ Sm and Gd resulted in multiphase materials. This confirms that the phase formation in the series RPt_2B_2C critically depends upon the size of the rare earth ions.

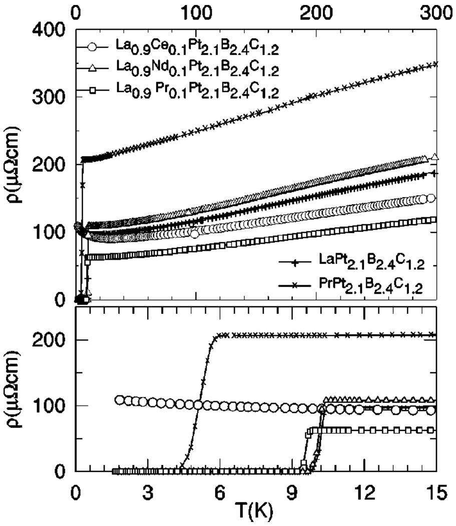

FIG. 2. The resistivity of RPt_2B_2C ($R=$La, Pr) and $La_{0.9}R_{0.1}Pt_2B_2C$ ($R=$Ce, Pr, Nd) from 2 to 300 K (top), and enlarged view of the same below 15 K (bottom).

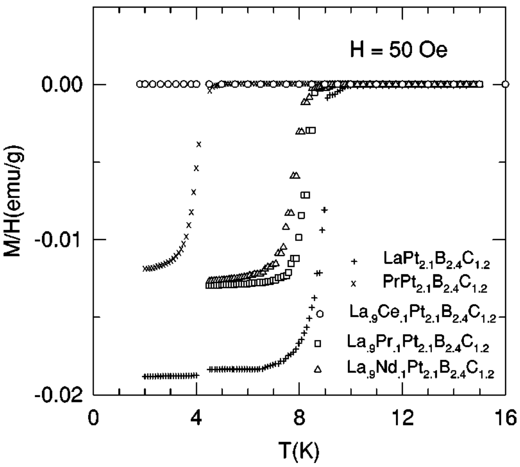

FIG. 3. The low field (50 Oe) magnetization M/H of RPt_2B_2C ($R=$La and Pr) and $La_{0.9}R_{0.1}Pt_2B_2C$ ($R=$Ce, Pr, and Nd).

A. Superconductivity and nature of the ground state of Pr ions in $PrPt_2B_2C$

Figure 2 (top) shows the resistivity of RPt_2B_2C ($R=$La, Pr) and $La_{0.9}R_{0.1}Pt_2B_2C$ ($R=$Ce, Pr, Nd) as a function of temperature from 300 K down to 2 K. An enlarged view of the resistivity below 15 K is shown in Fig. 2 (bottom). Room temperature resistivity of $PrPt_2B_2C$ (~ 350 $\mu\Omega$ cm) is rather high compared to that of other materials studied here and so is the residual resistivity ~ 200 $\mu\Omega$ cm (the resistivity just above the onset temperature, $T_{c,\mathrm{on}}$ in the case of superconducting Pr compound). We believe that high value of resistivity may have appreciable contribution from the sample dependent microstructure. The low-temperature resistivity data of $PrPt_2B_2C$ show clearly the occurrence of superconductivity with $T_{c,\mathrm{on}}\sim 6$ K ($T_{c,0}\sim 4.4$ K). Evidence for bulk superconductivity in Pr compound is further confirmed by our zero-field-cooled low field magnetization data (Fig. 3). The T_c observed by us in $PrPt_2B_2C$ and in $LaPt_2B_2C$ ($T_c\sim 10.5$ K) are in reasonable agreement with those reported in the literature.[4]

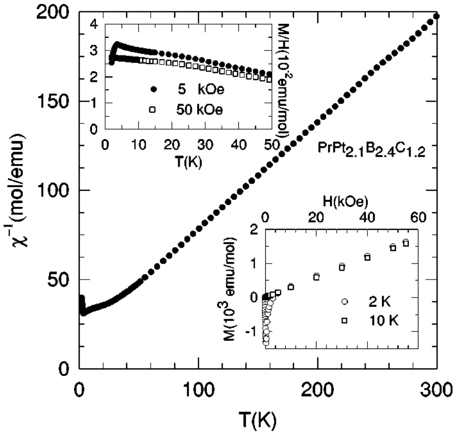

FIG. 4. The inverse susceptibility of $PrPt_2B_2C$ in 5 kOe between 1.8 and 300 K. The upper inset shows M/H in fields of 5 and 50 kOe. The lower inset shows the magnetization at 2 and 10 K in fields up to 55 kOe.

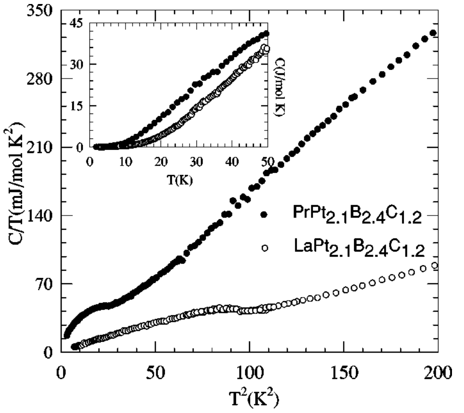

FIG. 5. The heat capacity C of PrPt$_2$B$_2$C and LaPt$_2$B$_2$C as C/T versus T^2. The inset shows the heat capacity of the two compounds up to 50 K.

Figure 4 shows inverse susceptibility versus temperature of PrPt$_2$B$_2$C measured in a field of 5 kOe. Above 100 K, the susceptibility χ follows a Curie-Weiss behavior. The data were least squares fit to the expression $\chi = C/(T-\theta_p)$. The effective moment μ_{eff} derived from C, is 3.63 μ_B/Pr ion, and the paramagnetic Curie temperature θ_p is -33 K. The value of μ_{eff} is close to the value of the magnetic moment of free Pr^{3+} ion ($3.58\mu_B$). The large negative θ_p indicates dominant antiferromagnetic exchange interaction between the Pr ions but we do not observe any magnetic ordering down to 1.7 K in this compound. The relatively large value of θ_p may therefore be due to crystal field effects. The sharp upturn in the inverse susceptibility below 3 K (seen as a corresponding sharp drop in M/H in the upper inset of Fig. 4) is due to superconductivity. At 2 K, the sample is diamagnetic up to nearly 5 kOe and attains paramagnetic nature at higher fields (lower inset, Fig. 4). Considering that there may be some paramagnetic contribution due to Pr ions, H_{c2} at 2 K may be >5 kOe. The nearly temperature independent M at low temperatures in 50 kOe ($>H_{c2}$ at 2 K) (upper inset Fig. 4) indicates that the crystal field split ground state is a nonmagnetic singlet. We note that the observed low temperature value of susceptibility is comparable to that reported in singlet ground state system PrIn$_3$.[14]

Heat capacity C of PrPt$_2$B$_2$C and LaPt$_2$B$_2$C is shown in Fig. 5 as C/T versus T^2. The inset in Fig. 5 shows C versus T up to 50 K in both LaPt$_2$B$_2$C and PrPt$_2$B$_2$C. The anomaly in the form of a broad hump, beginning at 5 and 10 K for PrPt$_2$B$_2$C and LaPt$_2$B$_2$C, respectively, corresponds to the superconducting transitions in these compounds and confirms the bulk nature of superconductivity. The jump in the heat capacity is not sharp at the transitions and the anomaly is broad reflecting the width of broad superconducting transition as seen in the resistivity and magnetization data discussed above. The heat capacity data of PrPt$_2$B$_2$C is consistent with the nonmagnetic ground state of the Pr ions. At a magnetic transition the heat capacity typically shows a huge peak with a magnitude of several J/mol K. Such a feature is not seen in our data taken between 1.8 and 60 K. The heat capacity decreases monotonically with temperature and has a low value of 32 mJ/mol K at 1.8 K. This low value of C indicates that Pr ions are not likely to order even at lower temperatures. If Pr ions were to order magnetically below 1.8 K, an upturn would have been seen in the heat capacity precursor to the magnetic transition. This conclusion receives further support from a comparison of the heat capacity of PrPt$_2$B$_2$C with that of the nonmagnetic reference analog LaPt$_2$B$_2$C (Fig. 5). At low temperatures, though the heat capacity of PrPt$_2$B$_2$C is higher than that of the nonmagnetic La analog, they have comparable values, clearly pointing out the nonmagnetic nature of Pr ions at low temperature. We, thus, conclude from our magnetization and heat capacity data that Pr ions are in the nonmagnetic singlet ground state in PrPt$_2$B$_2$C. The difference in the heat capacity of the Pr and La compounds becomes appreciable above 10 K. The excess heat capacity in the Pr compound that persists up to at least 50 K is the Schottky contribution to the heat capacity from the excited crystal field levels.

B. Pair breaking in LaPt$_2$B$_2$C

It is of general interest to study Cooper pair breaking by magnetic ions in a superconductor. Such a study in La$_{0.9}R_{0.1}$Pt$_2$B$_2$C is appealing as LaPt$_2$B$_2$C has a rather high T_c and because Ce and Pr ions exhibit anomalous behavior in their respective RPt$_2$B$_2$C ($R=$Ce and Pr) compounds. Our investigation here is limited to only $R=$Ce, Pr, and Nd, since, as mentioned above, we could get single-phase materials for these substitutions only. Figure 3 shows the results of our low field magnetization data in these samples.

The depression of T_c due to 10% substitution of La by Pr and Nd ions in LaPt$_2$B$_2$C, as deduced from the susceptibility data, is 1 and 1.5 K ($\Delta T_c/T_c \sim 0.1$ and 0.15), respectively. The magnitude of the depression is less than that observed in the RNi$_2$B$_2$C series; corresponding $\Delta T_c/T_c$ by 10% Pr and Nd substitution in YNi$_2$B$_2$C ($T_c=16.5$ K) is 0.35 and 0.25, respectively.[15] In the context of suppression of T_c by Pr and Nd, we should mention that the band-structure effects have been cited to be responsible for the nonoccurrence of superconductivity in RNi$_2$B$_2$C with R as light rare earth elements, including Pr.[10] The peak in the density of electronic states at the Fermi level [$\rho(E_f)$], which is a characteristic feature of the superconducting RNi$_2$B$_2$C ($R=$Dy, Er, Ho, Tm, Lu, and also Y), does not exist amongst the light rare earth members. However, in the case of PrNi$_2$B$_2$C, the effect of $4f$-conduction electron hybridization also exists,[12] which may further contribute to the suppression of superconductivity.

The depression of T_c in Ce doped sample is dramatic. As can be seen from Figs. 2 and 3, superconductivity is suppressed by 10% Ce ions at least down to 1.8 K. For normal trivalent Ce ions, the pair-breaking effect in La$_{0.9}$Ce$_{0.1}$Pt$_2$B$_2$C would have been smaller than that induced by Pr and Nd ions in La$_{0.9}R_{0.1}$Pt$_2$B$_2$C ($R=$ Pr, Nd). The large depression of T_c by Ce ions in LaPt$_2$B$_2$C is indeed surprising considering that Ce ions are trivalent in CePt$_2$B$_2$C, as inferred from our L_{III} edge[16] and magnetic susceptibility measurements[16] and they have effective magnetic moment ($\sim 2.58\mu_B$) which is very close to that in the free ionic state. However, we should point out that $CePt_2B_2C$ does exhibit an unusual behavior: Its magnetic susceptibility over a wide range of temperature follows a Curie-Weiss behavior but it does not order magnetically at least down to 2 K. Rather high (~ -60 K) paramagnetic Curie temperature suggests the presence of spin fluctuations in $CePt_2B_2C$. Further, resistivity of $La_{0.9}Ce_{0.1}Pt_2B_2C$ sample shows a rise below 20 K (Fig. 2) suggesting occurrence of Kondo effect, possibly with rather low Kondo temperature ($T_K \sim 10$ K). We suggest that spin fluctuation effects arising from $4f$-electron hybridization with conduction electrons are responsible for the suppression of superconductivity in $La_{0.9}Ce_{0.1}Pt_2B_2C$.

The anomalous nature of the suppression of superconductivity by Ce in the Pt system is further emphatically seen from the fact that 10% Ce ions in YNi_2B_2C depress T_c by only about 6 K, even though Ce ions in $CeNi_2B_2C$ are in mixed valent state. The absence of superconductivity in $CePt_2B_2C$ and suppression of superconductivity by Ce in $LaPt_2B_2C$ is almost identical to the case of $YbNi_2B_2C$.[17] Yb ions are almost trivalent in $YbNi_2B_2C$ and considering the T_c of its neighboring members, superconductivity is expected with a T_c of ~ 12 K but the material does not superconduct down to 300 mK. The moderate heavy fermion behavior ($\gamma \sim 300$ mJ/mol K^2) of $YbNi_2B_2C$ indicates that the $4f$ level in this case is close to the Fermi level and is believed to be responsible for the absence of superconductivity in it. We note that γ of $CePt_2B_2C$ is also high ~ 180 mJ/mol K^2.[18] Further, a strong depression of T_c is found in YNi_2B_2C when doped with Yb ions. Substitution of 0.1 Yb in YNi_2B_2C depresses T_c by 12 K.[15]

With the condition that T_K is comparable or smaller than T_c, one may see a reentrance of superconductivity due to the Kondo effect in $La_{1-x}Ce_xPt_2B_2C$ as has been seen, for example, in $La_{1-x}Ce_xAl_2$.[19] It would be therefore very interesting to carry out a systematic study of this system to look for the possible reentrant superconductivity.

IV. CONCLUSION

Superconductivity in $PrPt_2B_2C$ is indeed quite remarkable considering that only a few Pr-based materials are known to be superconducting. From magnetization and heat capacity measurements, we have shown that superconductivity in $PrPt_2B_2C$ is *bulk* in nature. Our results indicate a crystal field split singlet ground state with no indication of induced magnetic moment and therefore magnetic order is unlikely. As the $4f$ conduction electron hybridization has been suggested to be one of the reasons for the nonexistence of superconductivity in $PrNi_2B_2C$ and because the same phenomenon is responsible for the drastic suppression of T_c by Ce ions in $LaPt_2B_2C$, we conclude that $4f$-conduction electron hybridization is negligible in $PrPt_2B_2C$.

The depression of T_c by Ce ions is anomalously large even though Ce ions appear to be in 3+ state in $CePt_2B_2C$. We interpret this as due to the hybridization of Ce-$4f^1$ conduction electrons. We have pointed out the striking similarity of $CePt_2B_2C$ with $YbNi_2B_2C$.

ACKNOWLEDGMENTS

Part of this work was carried out under Project No. 1808 of Indo-French Center for Promotion of Advanced Research, New Delhi. We acknowledge valuable technical help of S.K. Paghdar, in some of the sample preparations and measurements.

---

*Present address: Kammerlingh Onnes Laboratory, Leiden, Netherlands.

[1] Chandan Mazumdar *et al.*, Solid State Commun. **87**, 413 (1993).

[2] R. Nagarajan *et al.*, Phys. Rev. Lett. **72**, 274 (1994).

[3] R. J. Cava *et al.*, Nature (London) **367**, 252 (1994).

[4] R. J. Cava *et al.*, Phys. Rev. B **49**, 12 384 (1994).

[5] T. Siegrist *et al.*, Nature (London) **367**, 254 (1994).

[6] Z. Hossain *et al.*, IEEE Trans. Magn. **31**, 4133 (1995); B. K. Cho *et al.*, Phys. Rev. B **52**, R3844 (1995); C. V. Tomy *et al.*, Physica C **248**, 349 (1995).

[7] R. J. Cava *et al.*, Physica C **226**, 170 (1994).

[8] M. Buchgeister *et al.*, Physica C **255**, 19 (1995).

[9] V. N. Narozhnyi *et al.*, in *Proceedings of the NATO-ARW*, Rare Earth Transition Metal Borocarbides (Nitrides): Superconducting, Magnetic and Normal State Properties, Dresden, Germany 2000, edited by K.-H. Muller and V. Narozhnyi, Vol. 14 of *NATO Science Series II: Mathematics, Physics and Chemistry* (Kluwer Academic Publishers, Dordrecht, 2001), p. 171, and references therein.

[10] M. Divis *et al.*, Phys. Rev. B **62**, 6774 (2000).

[11] V. N. Narozhnyi and K.-H. Muller, Rep. Prog. Phys. **64**, 943 (2001).

[12] V. N. Narozhnyi *et al.*, Physica C **364-365**, 571 (2001).

[13] K. Kumugai *et al.*, Physica B **148**, 133 (1987).

[14] K. H. J. Buschow *et al.*, J. Chem. Phys. **50**, 137 (1969).

[15] Z. Hossain *et al.*, Physica B **230-232**, 865 (1997).

[16] Chandan Mazumdar, E. Alleno, O. Sologub, P. Salamakha, H. Noel, M. Potel, Arvind. D. Chinchure, R. Nagarajan, L. C. Gupta, and C. Godart, J. Alloys Compd. (to be published).

[17] S. K. Dhar *et al.*, Solid State Commun. **98**, 985 (1996).

[18] S. A. Carter *et al.*, Phys. Rev. B **51**, 12 829 (1995).

[19] M. B. Maple *et al.*, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Chap. 11.