Anisotropic giant magnetoresistance, magnetocaloric effect, and magnetic anomalies in single crystalline Tb_2PdSi_3

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(Received 16 June 2000)

The results of magnetization, electrical resistivity, and magnetoresistance measurements for two different directions on single crystalline Tb_2PdSi_3 are presented. The magnetic properties including magnetoresistance and the magnetic coupling are found to be strongly anisotropic with features attributable to more than one magnetic transition and the results reveal that this compound is presumably characterized by an interesting magnetic-field/temperature phase diagram. An unusual finding is that there is a broad peak around 50 K in the plot of magnetic susceptibility versus temperature, which appears to be magnetic in origin, for the data measured along the *c* direction, whereas Curie–Weiss behavior is observed down to (T_N=) 23 K for $[10\bar{1}0]$ direction. We also emphasize on the anisotropy in observing magnetocaloric effect in the sense that this effect is rather large over a wide low temperature range for $[10\bar{1}0]$ direction, in sharp contrast to relatively smaller values for [0001] direction.

Investigation of anisotropy of the physical characteristics of materials has considerably improved the understanding of different types of phenomena in condensed matter physics during the last 10 years. In particular, among rare-earth (R) systems, such studies are generally restricted to those cases in which R ions have been known to exhibit moment instablities; those with stable moment are usually ignored and it is our opinion that this avenue should be fully exploited to look for novel aspects of magnetism. In recent years, there has been considerable interest[1–6] in ternary rare-earth compounds of the type, R_2TX_3, crystallizing in a AlB_2-derived hexagonal structure.[6] Among these, the compounds Gd_2PdSi_3 and Tb_2PdSi_3 are of special importance due to their novel transport and magnetotransport anomalies relevant to the fields of heavy-fermion and giant magnetoresistance (GMR) even in polycrystalline form. The single crystals of Gd_2PdSi_3 and Ce_2PdSi_3 have been found to exhibit interesting features in many measured physical properties due to anisotropic nature of the chemical environment around the R ion.[4,5] In view of this, we considered it worthwhile to extend the studies to Tb_2PdSi_3 in its single crystalline form to gain better knowledge of its magnetic characteristics. The results presented in this paper reveal that this compound exhibits many interesting anisotropic magnetic properties, with some unusual features.

The single crystalline Tb_2PdSi_3 of 25 to 50 mm in length and 7 mm in diameter were grown by the floating zone method by rf inductive heating from stoichiometric polycrystalline feed rods.[7] Growth rate was 5 to 10 mm/h and asymmetric rotation of seed and feed rod was also given. The orientation of the single crystals was determined by the x-ray Laue backscattering method. Oriented rods with a few mm in length were cut from the grown crystal with a diamond-coated wire saw with the rod axis parallel to the crystallographic directions $[10\bar{1}0]$ and [0001]. The electrical resistivity (ρ) as a function of temperature (T) and also as a function of applied magnetic field (H) at selected temperatures and magnetization (M) measurements were carried out along these two directions. The ρ (T=2–300 K) and MR measurements (5–50 K) were performed with a conventional four-probe method employing silver paint for making electrical contacts of the leads with the samples; the MR measurements were carried out in the longitudinal mode ($I \| H$); though we measured in the transverse ($I \perp H$) mode as well, the data are not satisfactory for presentation here due to the rotation of sample by the applied field in this mode. The M data were collected by a commercial vibrating sample magnetometer (Oxford Instruments) with H parallel to the rod directions specified above.

The results of ρ measurements are shown in Fig. 1 for two rod directions. It appears that, in the paramagnetic state,

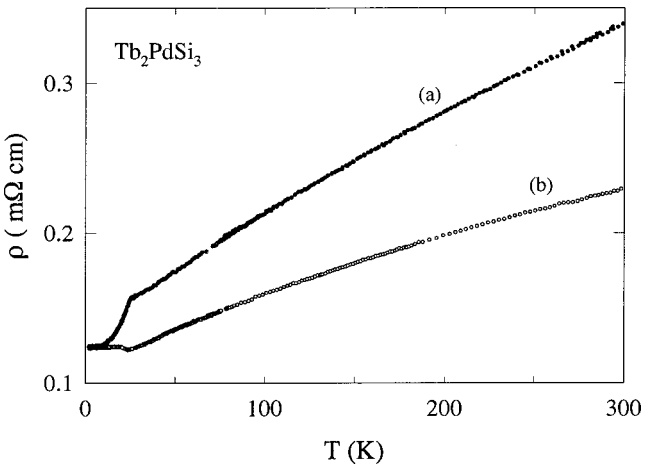

FIG. 1. Electrical resistivity as a function of temperature for (a) $[10\bar{1}0]$ and (b) [0001] in Tb_2PdSi_3.

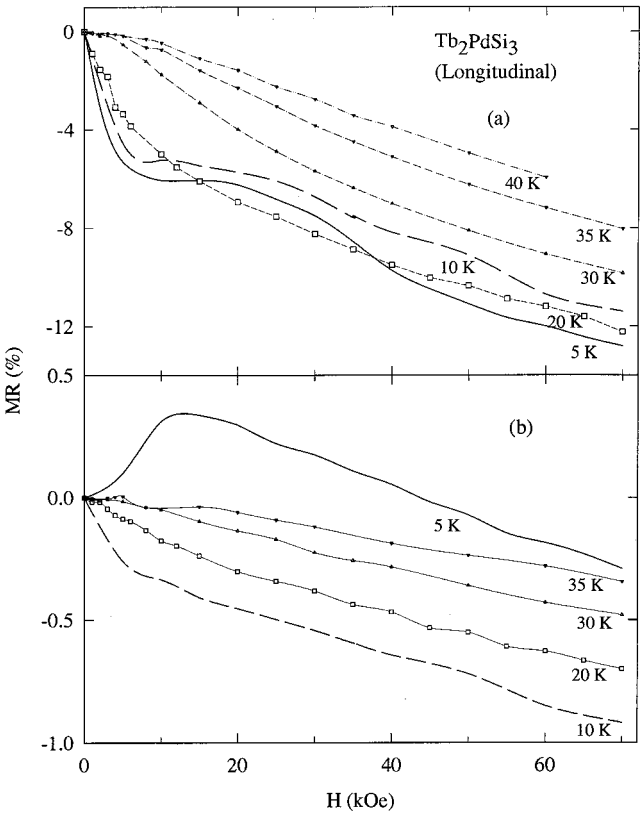

FIG. 2. Longitudinal magnetoresistance as a function of magnetic field at selected temperatures (mentioned at the bottom of the plots) for (a) $[10\bar{1}0]$ and (b) [0001] directions of Tb_2PdSi_3. The lines have been drawn through the data points.

the plots of ρ versus T look similar for both the directions, with comparable values of ρ at low temperatures. The features below 25 K are distinctly different. For $[10\bar{1}0]$ direction, there is a distinct drop of ρ at 23 K as the T is lowered, similar to be behavior in polycrystalline samples,[2] due to the onset of long range magnetic order. However, along [0001] direction, there is an upturn just below (T_N=)23 K, presumably due to the formation of magnetic Brillouin-zone boundary gaps. These findings may imply that the magnetic coupling along [0001] could be of an antiferromagnetic type, whereas it could be of a ferromagnetic type along $[10\bar{1}0]$ direction.

The ρ data were also obtained as a function of H at many temperatures and, for the sake of clarity, we show the data in the form of MR, defined as $[\rho(H)-\rho(0)]/\rho(0)]$, versus T in Fig. 2 at selected temperatures. The distinctly notable features for $[10\bar{1}0]$ direction are (i) MR is similar to that observed in polycrystalline form, in sign and magnitude as well as in the shape of the plot of MR versus H, the significance of which has been discussed in Ref. 2; (ii) the negative sign of MR throughout the measured range of H (and T) is in conformity with ferromagnetic coupling along this direction inferred from the ρ data above. The most interesting observation to be noted is that the magnitude of MR is very large; thus, for instance, for a H of 60 kOe, the MR as high as about -12% at 5 K is observed, and the magnitude remains large (about -6%) even at temperatures as high as 40 K attributable to magnetic precursor effects.[8] On the other

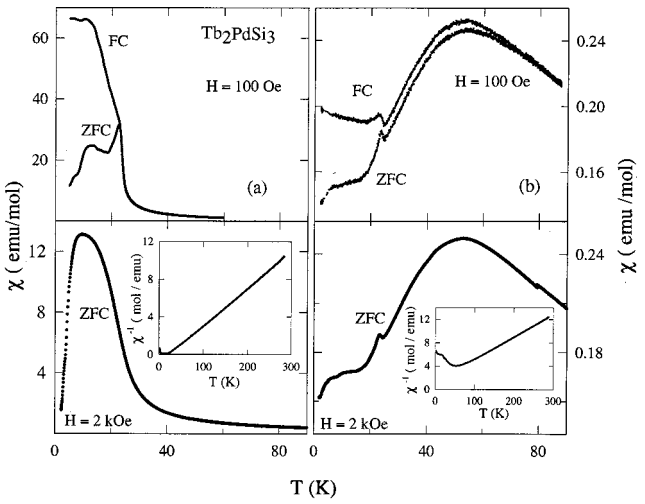

FIG. 3. Magnetic susceptibility (H=100 Oe and 2 kOe) as a function of temperature for (a) $[10\bar{1}0]$ and (b) [0001] in Tb_2PdSi_3. The insets show inverse χ as a function of temperature.

hand, MR for [0001] direction is small in magnitude. These findings establish that this material is an anisotropic GMR system; it is also important to note that the longitudinal MR for [0001] shows a distinct positive sign (until 30 kOe) at 5 K, as if antiferromagnetism dominates at low fields and at low temperatures; at higher temperatures or at higher fields, the sign of MR turns negative, implying thereby temperature/field induced changes in the magnetic structure.

We now discuss salient features in the magnetization data. The data were obtained both at 100 Oe and 2 kOe as a function of T. The most notable observations are (i) the values of χ are small and about two orders of magnitude smaller for [0001] direction compared to that for $[10\bar{1}0]$ direction [Fig. 3(a) and 3(b)]; this implies dominant antiferromagnetic coupling along the former direction. This conclusion is however different from the magnetic structure derived from the neutron diffraction data.[3] The present conclusion is further endorsed by the following experimental observations. For [0001], there is a sluggish variation (almost linear dependence) of isothermal M with H; also the tendency for saturation even in the magnetically ordered state [Fig. 4(b)] is absent; this behavior qualitatively differs from that for $[10\bar{1}0]$ [Fig. 4(a)], in which case there is a sharp rise at low fields in the magnetically ordered state followed by nearly linear variation, as though there is a superimposition of a ferromagnetic component (with a saturation magnetization of about 5 μ_B per formula unit) and a nonsaturating component (which is attributed to the occupation of higher lying Zeeman-split electronic levels). A careful look at the isothermal M data (below 20 K) reveals that the plots for [0001] direction are not perfectly linear and there appears to be a tendency for a spin–flip transition beyond 20 kOe, which can only arise due to zero-field antiferromagnetic coupling; interestingly, there is also a weak hysterisis [Fig. 4(b)] for intermediate field range, which reveals complexities in the magnetic structure at high fields. Further evidence for our conclusions on anisotropic magnetic interaction comes from the signs of paramagnetic Curie temperature, Θ_p, which is negative for [0001] and positive for $[10\bar{1}0]$ direction (-30 and 23 K, respectively), obtained from the plots of inverse χ

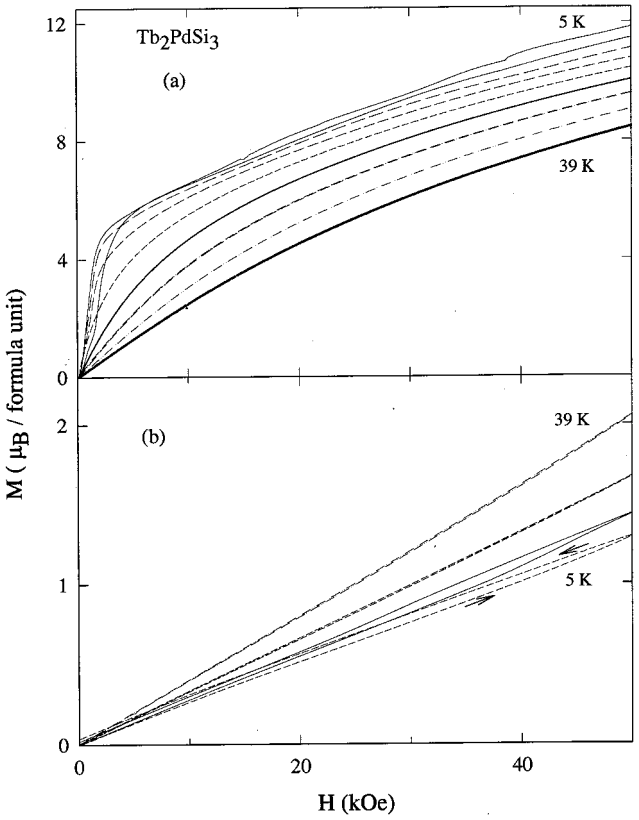

FIG. 4. Isothermal magnetization at selected temperatures for (a) $[10\bar{1}0]$ and (b) [0001] in Tb_2PdSi_3. The T sequence for the curves are 5, 11, 15, 19, 23, 27, 31, 35, 39 K for (a) and 5, 15, 27, and 39 for (b). In the case of (b) the data while decreasing H are also included to show hysterisis effects at higher fields and the arrows indicate the direction of the change of the magnetic field. For the sake of clarity, the lines through the (closed spaced) data points are drawn, omitting the data points.

versus T in the temperature interval 80–300 K (Fig. 3, insets). It is worthwhile to perform neutron diffraction studies on single crystals to confirm this proposal.

(ii) The χ data taken with $H=100$ Oe for the zero-field-cooled (ZFC) state of the specimen deviate from that of field-cooled (FC) state below ($T_N=$) 23 K for $[10\bar{1}0]$ direction, whereas the deviation begins at a somewhat higher temperature (at about 60 K) for [0001] direction, which may signal the onset of strong magnetic correlations well above T_N for this direction. Though the divergence in ZFC–FC χ is not surprising as this has been known in other magnetic systems with long range magnetic order, the onset of divergence at a temperature higher than T_N for [0001] is surprising.

(iii) There is also a peak in the plot of χ versus T (measured with both $H=100$ and 2 kOe) at about 50 K for [0001] direction; in sharp contrast to this, there is a monotonic increase of χ down to 23 K for direction $[10\bar{1}0]$. The origin of the above peak in the former case is not clear at present. In this regard, it is worthwhile to note that the upward curvature (deviation from the linearity) at high fields, typical of antiferromagnetic coupling, in the plots of M versus H persists (though weakly) even above 23 K for [0001] [see Fig. 4(b)]. Therefore, we speculate that this peak is also magnetic in its origin (rather than a crystal-field effect), which is further

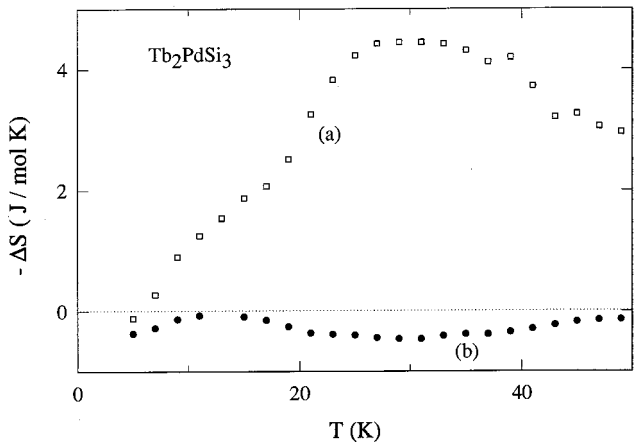

FIG. 5. Entropy change for an application of 50 kOe magnetic field with the initial field being zero, as derived from magnetization data, as a function of temperature for Tb_2PdSi_3.

endorsed by the divergence in ZFC–FC χ described above. It is of interest to explore whether this broad maximum arises[9] from possible quasi-one-dimensional character of a fraction (25%) of Tb ions along c direction expected for an ordered arrangement of Tb ions in $2(b)$ and $6(h)$ sites of this structure.[10] (We however continue to assign T_N to the 23 K feature only, until one completely understands the origin of the above peak.)

(iv) The plot of χ versus T below 23 K for the ZFC state for $[10\bar{1}0]$ direction, in addition to the feature at T_N, exhibits multiple shoulders for $H=100$ Oe, which transforms into a well-defined drop below 8 K if measured with $H=2$ kOe; there is a similar drop for the ZFC data for [0001] direction as well below 5 K; these features indicate interesting T–H magnetic phase diagram for this material.

Considering that there is a large anisotropy in the magnetization behavior, one would naively expect that there is also a corresponding anisotropy in magnetocaloric effect (MCE). MCE is measured in terms of the entropy change $[\Delta S=S(H)-S(0)]$, when the material is exposed to a magnetic field and ΔS is related to M via Maxwell's thermodynamic relation.[11] We have actually collected isothermal M data at 2 K interval below 50 K, though we present the data at few temperatures only in Fig. 4 for the sake of clarity. The T dependence of ΔS derived from the present M data is plotted in Fig. 5. The values thus obtained peak in the vicinity of T_N for $[10\bar{1}0]$ direction. What is interesting is that the values are large compared to that for [0001] direction. Thus there is a large anisotropy in magnetocaloric effect over a wide T range in the vicinity of T_N. Another noteworthy point is that the sign of $-\Delta S$ is essentially positive for the former direction, whereas it is negative for the latter, which also endorses the anisotropy in the magnetic coupling along these directions, proposed here.

Finally, it is of interest to explore whether MR depends on M, in view of the fact that, in GMR materials,[12] one generally finds that MR varies quadratically with M. For this purpose, we plot in Fig. 6 the data for $[10\bar{1}0]$ direction alone (with H as an intrinsic parameter) considering that the MR value for the other direction is negligible. It is apparent that the plots are nearly linear in the paramagnetic state (25 K

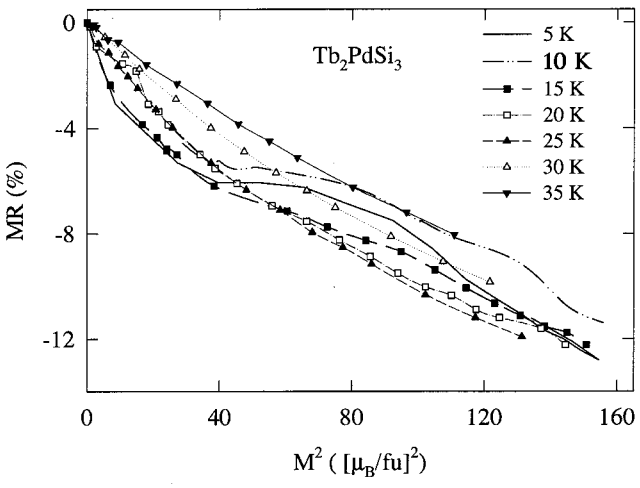

FIG. 6. Magnetoresistance as a function of square of magnetization with the field as an intrinsic parameter, at various temperatures for $[10\bar{1}0]$ in Tb_2PdSi_3. While only a line through the data points are shown omitting the data points in some cases, the lines through the data points in other cases are shown as a guide to the eyes.

and above) over a wide region and the field range (in other words M^2 range) over which the linearity holds increases with increasing T. In the magnetically ordered state, the linearity holds only at low fields (below 5 kOe), followed by a flat region and then another linear region in the plots. The plots in the magnetically ordered state can also be viewed differently in the sense that, if extrapolated from the linear region at the high field side, there is a much more rapid increase in the magnitude of MR for initial applications of H, mimicking grain boundary effects in $Tl_2Mn_2O_7$ (see Ref. 12). If so, it is interesting that this observation is made in the single crystalline form of an alloy, in which the grain boundary effects are less significant. We hope this observation will be helpful in global understanding of GMR phenomenon.

Summarizing, the results of magnetization, electrical resistivity, and magnetoresistance measurements for two different directions on single crystalline Tb_2PdSi_3 are presented. We observe many anisotropic magnetic anomalies. The isothermal M behavior and the signs of Θ_p, MR, and ΔS suggest that there are ferromagnetic correlations along $[10\bar{1}0]$ direction, whereas antiferromagnetic interaction prevails along [0001] direction; the M data indicate the existence of at least one more magnetic phase transition well below T_N. There are qualitative differences in the temperature dependent ρ data as well in the vicinity of magnetic ordering temperature, suggestive of the existence of highly anisotropic magnetic Brillouin-zone boundary gap effects. MR is rather large over a wide temperature range below 60 K for $[10\bar{1}0]$ direction, in sharp contrast to relatively smaller values for [0001] direction. It should be noted that the reports on anisotropic GMR, particularly at such high temperatures, in stable-moment rare-earth intermetallic compounds are generally scarce in the literature, barring our own report on Gd_2PdSi_3 (Ref. 4). In addition, we emphasize further here on two other major observations: (i) there is an unusual broad *peak* in the plot of χ vs T around 50 K for [0001] direction which appears to be magnetic in its origin, whereas the plot of inverse χ versus T is *linear* down to T_N for $[10\bar{1}0]$ direction. While a better understanding of this peak requires further work, such a sharp contrast in anisotropic magnetism (magnetic along one direction resulting in a peak in χ, but paramagneticlike behavior in a perpendicular direction) has not been known in a magnetic rare-earth compound to the best of our knowledge. (ii) This compound is characterized by relatively large magnetocaloric effect along $[10\bar{1}0]$, compared to that along [0001] direction; to our knowledge, anisotropic magnetocaloric effect has not been reported for an alloy in the past and in this sense this work gains importance; this implies that, if a material could be used for magnetic refrigeration at low temperatures, one may have a relatively better cooling power if the H is applied along a specific direction, for instance along $[10\bar{1}0]$ relative to [0001] in the present material. The results thus reveal that this compound exhibits interesting anisotropic behavior in its properties.

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[1] R. Mallik, E.V. Sampathkumaran, M. Strecker, and G. Wortmann, Europhys. Lett. **41**, 315 (1998); R. Mallik, E.V. Sampathkumaran, M. Strecker, G. Wortmann, P.L. Paulose, and Y. Ueda, J. Magn. Magn. Mater. **185**, L135 (1998); S. Majumdar, M. Mahesh Kumar, and E.V. Sampathkumaran, J. Alloys Compd. **288**, 61 (1999); S. Majumdar, E.V. Sampathkumaran, D. Eckert, A. Handstein, K.-H. Mueller, S.R. Saha, H. Sugawara, and H. Sato, J. Phys.: Condens. Matter **28**, L337 (1999); S. Majumdar, R. Mallik, E.V. Sampathkumaran, P.L. Paulose, and K.V. Gopalakrishnan, Phys. Rev. B **59**, 4244 (1999); S. Majumdar, M. Mahesh Kumar, R. Mallik, and E.V. Sampathkumaran, Solid State Commun. **110**, 509 (1999); S. Majumdar, R. Mallik, E.V. Sampathkumaran, K. Rupprecht, and G. Wortmann, Phys. Rev. B **60**, 6770 (1999); S. Majumdar and E.V. Sampathkumaran, *ibid.* **61**, 43 (2000), and references therein.

[2] R. Mallik, E.V. Sampathkumaran, and P.L. Paulose, Solid State Commun. **106**, 169 (1998).

[3] A. Szytula, M. Hofmann, B. Penc, M. Slaski, S. Majumdar, E.V. Sampathkumaran, and A. Zygmunt, J. Magn. Magn. Mater. **202**, 365 (1999).

[4] S.R. Saha, H. Sugawara, T.D. Matsuda, H. Sato, R. Mallik, and E.V. Sampathkumaran, Phys. Rev. B **60**, 12162 (1999).

[5] S.R. Saha, H. Sugawara, T.D. Matsuda, Y. Aoki, H. Sato, and E.V. Sampathkumaran, Phys. Rev. B **62**, 425 (2000).

[6] P.A. Kotsanidis, J.K. Yakinthos, and E. Gamari-Seale, J. Magn. Magn. Mater. **87**, 199 (1990); R.A. Gordon, C.J. Warren, M.G. Alexander, F.J. Di Salvo, and R. Pöttgen, J. Alloys Compd. **248**, 24 (1997).

[7] G. Graw, H. Bitterlich, W. Löser, G. Behr, J. Fink, and L. Schultz, J. Alloys Compd. **308**, 193 (2000).

[8] R. Mallik and E.V. Sampathkumaran, Phys. Rev. B **58**, 9178 (1998).

[9] See, for instance, I. Tsukada *et al.*, Phys. Rev. B **60**, 6601 (1999); I. Tsukada J. Takeya, T. Masuda, and K. Uchinokura, *ibid.* **62**, 6061 (2000).

[10] R.A. Gordon, C.J. Warren, M.G. Alexander, F.J. DiSalvo, and R. Pöttgen, J. Alloys Compd. **248**, 24 (1997); also our work on Eu_2PdSi_3 by Mallik *et al.*, J. Magn. Magn. Mater. in Ref. 1.

[11] E.V. Sampathkumaran, I. Das, R. Rawat, and S. Majumdar, Appl. Phys. Lett. **77**, 418 (2000), and references therein; see, for a review, V.K. Pecharsky and K.A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).

[12] A. Gupta and J.Z. Sun, J. Magn. Magn. Mater. **200**, 24 (1999), and references therein.