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Observation of a minimum in the temperature-dependent electrical resistance above the magnetic-ordering temperature in Gd_2PdSi_3

R. Mallik[1], E. V. Sampathkumaran[1](*), M. Strecker[2] and G. Wortmann[2]

[1] *Tata Institute of Fundamental Research*
Homi Bhabha Road, Colaba, Mumbai-400 005, India
[2] *Fachbereich 6-Physik, Universität Paderborn - D-33095, Germany*

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Abstract. – Results on electrical resistivity, magnetoresistance, magnetic susceptibility, heat capacity and ^{155}Gd Mössbauer measurements on a Gd-based intermetallic compound, Gd_2PdSi_3, are reported. A finding of interest is that the resistivity unexpectedly shows a well-defined minimum at about 45 K, well above the long-range magnetic-ordering temperature (21 K), a feature which gets suppressed by the application of a magnetic field. This observation in a Gd alloy presents an interesting scenario. On the basis of our results, we propose electron localization induced by *s-f* (or *d-f*) exchange interaction prior to long-range magnetic order as a mechanism for the electrical resistance minimum.

Ever since a minimum in the electrical resistance (R) at a characteristic temperature in noble metals containing 3d magnetic impurities was reported several decades ago, the consequences of this phenomenon, known as the Kondo effect, in metallic solids remains an active area of research. In concentrated Kondo alloys of Ce, Sm, Yb or U [1], if the strength of the intersite indirect exchange interaction (given by T_{RKKY}) is comparable to that of the Kondo effect (given by the Kondo temperature, T_K), one also observes magnetic ordering well below the temperature at which resistivity shows a minimum. However, such a feature in R is not expected for Gd alloys, since the Gd $4f$ orbital is so well localized that it cannot exhibit the Kondo effect. In this article, we report the observation of a pronounced minimum in the plot of R *vs.* temperature (T) well above the magnetic-ordering temperature in a Gd-based intermetallic compound, Gd_2PdSi_3 (which is presumably antiferromagnetic [2], $T_N = 21$ K), resembling the behavior in magnetic Kondo lattices. This finding implies that a minimum in

(*) E-mail: SAMPATH@tifrvax.tifr.res.in

$R(T)$ can also occur from a completely different mechanism as a magnetic precursor effect, which, we believe, is an exchange-interaction–induced electron localization.

The polycrystalline sample, Gd_2PdSi_3, was prepared by arc melting followed by homogenization at 750 °C in an evacuated sealed quartz tube. We have also investigated alloys with Gd substituted by Y, *i.e.* $(Gd_{1-x}Y_x)_2PdSi_3$ ($x = 0.2$, 0.5 and 0.8). The X-ray powder diffraction patterns (Cu K_α) confirm that these alloys are single phase forming the hexagonal AlB_2-type structure [2]. The homogeneity of the samples was checked by scanning electron microscopy. The electrical-resistance measurements (4.2–300 K) were performed by a conventional four-probe method. Additional experiments carried out to support the line of our arguments and conclusions are: i) The magnetoresistance measurements in the longitudinal geometry in a magnetic field (H) of 50 kOe as a function of T and as a function of H at selected temperatures for the $x = 0.0$ alloy; ii) ^{155}Gd($5/2 \rightarrow 3/2$, 86.5 keV transition) Mössbauer measurements in the transmission geometry with a 2 mCi ^{155}Eu($SmPd_3$) source for $x = 0.0$ alloy below 25 K at selected temperatures; iii) Heat-capacity (C) measurements as a function of temperature (2-70 K); iv) Magnetic-susceptibility (χ) measurements (2–300 K) in a field of 100 Oe and in 2 kOe.

The temperature dependence of the normalized electrical resistivity below 200 K is plotted in fig. 1 for all compositions investigated. The values of ρ at 300 K and 4.2 K for Gd_2PdSi_3 are of the order of 400 and 280 $\mu\Omega$ cm, respectively. Due to the presence of microcracks in the sample, the error of these values might be smaller by about 40%. For this reason, the data shown in fig. 1 are normalized to the values at 300 K. It is obvious from fig. 1 that the $\rho(T)$ of the Gd_2PdSi_3 compound gradually decreases as the temperature is lowered down to 60 K, followed by an upturn below about 45 K, thus giving rise to a resistivity minimum at about ($T_{\min} =$)45 K; the value before the onset of magnetic ordering (say, at 22 K) is about 5% higher compared to the minimum resistivity. There is a kink in $\rho(T)$ *vs.* T at about 20 K, close to the temperature where the Gd sublattice exhibits long-range magnetic ordering presumably of antiferromagnetic-type, as one may conclude from the well-defined peak in the magnetic susceptibility and from the shoulder in the heat-capacity data (*vide infra*). Further lowering of temperature does not result in a drop in $\rho(T)$ as expected due to the loss of the spin-disorder contribution below the Néel temperature (T_N). We presently attribute this to the opening of a pseudogap at some portions of the Fermi surface due to the onset of antiferromagnetism in this compound [3]. The magnetic-ordering temperatures for the compositions $x = 0.2$, 0.5 and 0.8 are lowered (see the heat-capacity data described below) as expected on the basis of indirect exchange mechanism; however, the resistivity minimum persists well above T_N for all compositions. Even in the diluted limit of our investigation, $x = 0.8$, the resistance increases by about 2% as the temperature is lowered from $T_{\min}$ towards 4.2 K. The fact that the minimum is also observable in the sample with the highest Y content ($x = 0.8$) may exclude the explanation based on the opening of an energy gap (above 21 K).

Now turning to the influence of the application of a magnetic field, the negative $d\rho/dT$ behavior in zero field vanishes in the presence of a field of 50 kOe (shown in fig. 2 (a) for $x = 0.0$ only for the sake of clarity). The exact dependence of T_N on H could not be inferred from the present data and it is not relevant to the main conclusion of this article. The magnetoresistance, defined as $\Delta\rho/\rho = \{\rho(H) - \rho(0)\}/\rho(0)$, is obtained from this data as a function of T (shown in fig. 2 (b) for all the compositions). For $x = 0.0$, it is found that $\Delta\rho/\rho$ is as large as about -10% at 40 K in the presence of $H = 70$ kOe (fig. 2 (c)). For comparison, the magnitude of the magnetoresistance values for the isostructural Ce-based Kondo lattice Ce_2PdSi_3 (ref. [4]) as well as for the alloys, $(Ce_{1-x}Y_x)_2PdSi_3$, is less than 1% down to 4.2 K. This establishes that the observed large magnetoresistance effect is Gd-related, as noted by us for some other Gd alloys [5].

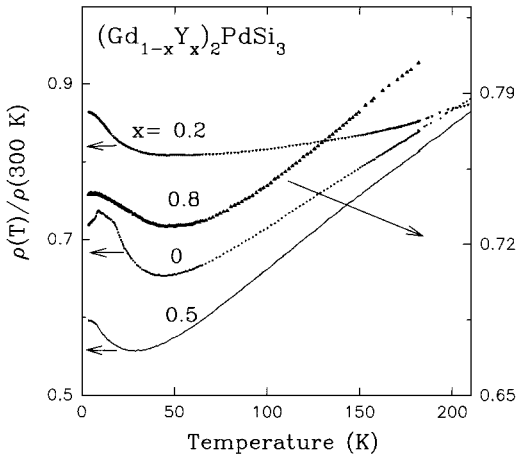

Fig. 1

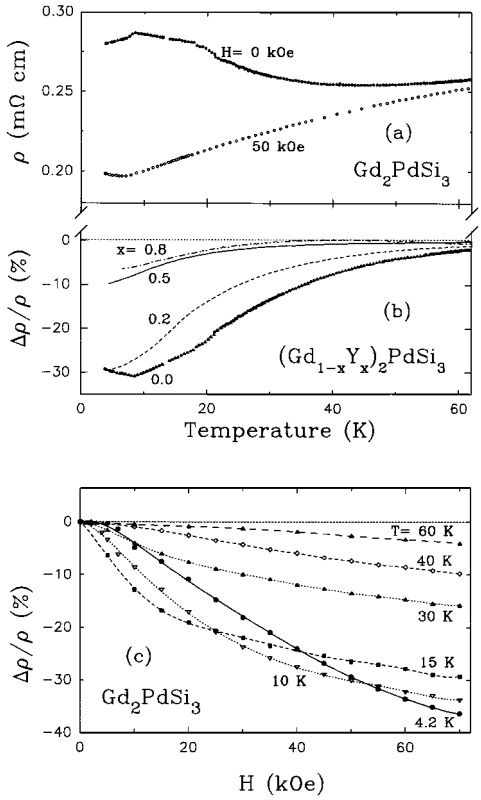

Fig. 2

Fig. 1. – The electrical resistance (R) of the alloys, $(Gd_{1-x}Y_x)_2PdSi_3$ (x = 0.0, 0.2, 0.5 and 0.8), normalized to 300 K values.

Fig. 2. – (a) The electrical resistivity (ρ) as a function of temperature for Gd_2PdSi_3 in the presence and in the absence of a magnetic field of 50 kOe. (b) The magnetoresistance ($\Delta\rho/\rho$) obtained from the data shown in (a) for $x = 0.0$ is plotted; in addition, the data obtained in a similar way for other compositions are also shown. (c) For $x = 0.0$, the $\Delta\rho/\rho$ as a function of magnetic field at selected temperatures; the lines through the data points serve as guides to the eye. The error in $\Delta\rho/\rho$ is estimated to be less than 0.5%.

It is not out of place to add that, as the temperature is lowered below T_N, the $\rho(T)$ curve at 50 kOe does not show an upturn. If the upturn in ρ below T_N is attributed to magnetic Brillouin-zone boundary gaps, this finding implies that these gaps are essentially getting washed out by the application of a magnetic field; there is a feeble rise below 7 K in the data in the presence of a field, due to possible non-vanishing gap at low temperatures. The magnitude of $\Delta\rho/\rho$ thus increases below 20 K for the $x = 0.0$ alloy (fig. 2 (b)), attaining a peak value of about -32% at 7 K. In order to highlight this feature further, the $\Delta\rho/\rho$ is plotted as a function of H in fig. 2 (c) for various temperatures. The overall shape of the plot of $\Delta\rho/\rho$ *vs.* H gets significantly modified as the temperature is lowered across T_N due to suppression of the proposed magnetic Brillouin-zone boundary gap. The observation of a large negative value of $\Delta\rho/\rho$ is of importance considering the current interest in the phenomenon of giant magnetoresistance.

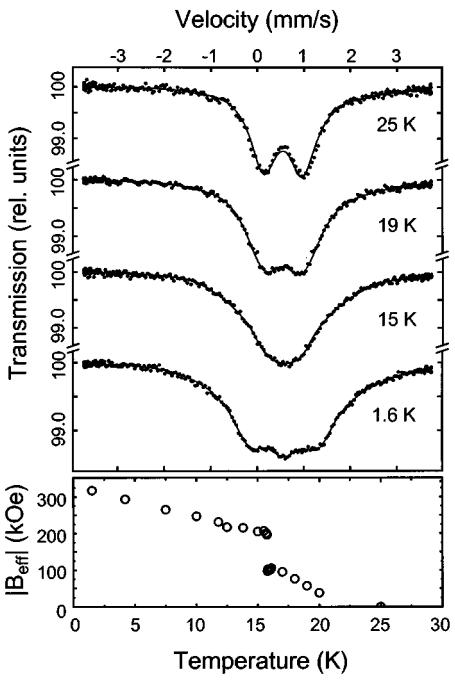

Fig. 3

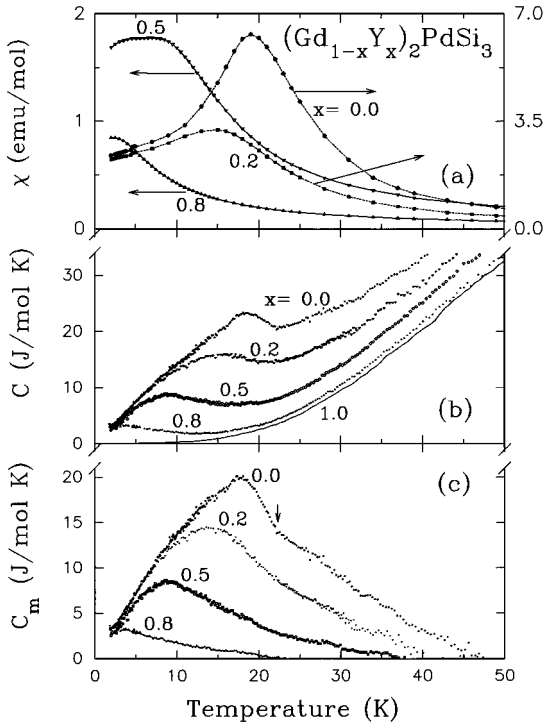

Fig. 4

Fig. 3. – ^{155}Gd Mössbauer spectra of Gd_2PdSi_3 at selected temperatures. The continuous lines represent standard least-square fit of the data. At the bottom, the effective magnetic-hyperfine-field values obtained from the data are shown as a function of temperature.

Fig. 4. – (a) The magnetic susceptibility ($H = 2$ kOe) as a function of temperature, (b) the heat capacity and (c) the $4f$ contribution ($C_{\rm m}$) to C as a function of temperature for the alloys, $(Gd_{1-x}Y_x)_2PdSi_3$. The lines through the data points in (a) serve as guides to the eyes.

In order to be sure that the upturn in R below $T_{\rm min}$ is not due to the opening-up of magnetic Brillouin-zone boundary gaps, it is desirable to confirm the $T_{\rm N}$ value by a microscopic technique as well. We therefore show the results of ^{155}Gd Mössbauer (only for $x = 0.0$), χ and C measurements in fig. 3, 4 (a) and 4 (b), respectively. The Mössbauer spectra below 20 K are found to undergo Zeeman splitting, which is well-resolved below 15 K. The magnetic hyperfine field at the Gd nucleus obtained by a standard least-square fitting procedure of the Mössbauer spectra are also shown in fig. 3 for $x = 0.0$. The temperature at which the magnetic hyperfine field extrapolates to zero (near 20 K) marks the magnetic-ordering temperature and this serves as a conclusive microscopic proof for paramagnetism above 20 K (which is also confirmed by our Mössbauer thermal scan experiment) in this compound. The spectral analysis of the data for 25 K gave evidence for a quadrupolar splitting only (the magnitude of which is 0.88 mm/s).

We have also probed the magnetic behavior by other bulk measurements. With respect to χ ($H = 2$ kOe), the low-temperature data show a distinct cusp in χ at about 20 K in this alloy, indicative of antiferromagnetic-like ordering. The feature due to magnetic ordering shifts to lower temperatures with dilution of the Gd sublattice (fig. 4 (a)). The plot of the χ^{-1} *vs.* temperature (not shown in a figure) is found to be linear down to the critical temperature,

thus suggesting that the peak in $\chi(T)$ marks the onset of long-range magnetic order. Consistent with this, in the heat capacity there is a peak attributable to the onset of magnetic ordering at different temperatures (fig. 4 (b)) for each of the three compositions, $x = 0.0$, 0.2 and 0.5 with magnetic-ordering temperatures of 20, 15 and 8 K, respectively. For $x = 0.8$, there is no clear-cut anomaly due to the onset of long-range magnetic ordering above 2 K. We obtained the $4f$ contribution ($C_{\rm m}$) to C, shown in fig. 4 (c), using the procedure suggested in ref. [6] employing the C values of Y_2PdSi_3 as a reference for the lattice contribution. A point to be noted [7] is that there is a broad shoulder (marked by a vertical arrow in fig. 4 (c)) at about 22 K (which is a measure of $T_{\rm N}$ from heat capacity [6]) for $x = 0.0$, beyond which $C_{\rm m}$ falls gradually with temperature, extending to about 20 K above $T_{\rm N}$, similar to that in other Gd alloys [8]. The magnetic entropy ($S_{\rm m}$) at $T_{\rm N}$ obtained from our data is only about 75% of the saturation value of $R \ln 8$ (R = gas constant) for all the magnetically ordered alloys; the full value is reached far above $T_{\rm N}$ only, for instance, only around 45 K in Gd_2PdSi_3. Clearly, the heat-capacity tail persists for about 20 K due to magnetic precursor effects [8] even in the case of the dilute alloy, $x = 0.8$, mimicking heavy-fermion behavior, though this alloy does not undergo long-range magnetic order above 4 K.

Thus, all the results, including those from the Mössbauer spectroscopy, conclusively establish the onset of long-range magnetic ordering in the vicinity of 21 K for $x = 0.0$. Hence the upturn in R below 45 K is not a consequence of a long-range antiferromagnetic-ordering (gap) effect. It is important to note that the temperature till which the heat-capacity tail above $T_{\rm N}$ persists and the one below which a negative $\Delta\rho/\rho$ is noticeable beyond experimental error shift down with increasing x (compare the data for $x = 0.0$ and 0.8 in fig. 2 (b)) [9]. These observations suggest that these anomalies arise from a common physical origin and thus the minimum in R is a manifestation of a Gd $4f$ magnetic precursor effect. We would like to add that there is no difference between the field-cooled and zero-field-cooled susceptibility ($H = 100$ Oe) above $T_{\rm N}$ in these alloys and hence spin-glass effects need not be considered in the temperature region of interest.

It should be mentioned that the temperature-dependent X-ray diffraction studies do not show any structural change down to 12 K; no anomaly is apparent in the lattice constants across $T_{\rm N}$ as well [10]. This rules out structural anomalies in the vicinity of $T_{\rm N}$ as a cause of this R minimum. It is not clear whether anomalous critical scattering effects or spin fluctuations involving Pd $4d$ [11] and/or Gd $5d$ conduction electrons are responsible for the minimum in $R(T)$. The spin fluctuations cannot be of the conventional Kondo type, as the $4f$ level of Gd in general is believed to be situated well below the Fermi level. It may be added that reports confirming Pd $4d$ ion Kondo effect exist only in the single-ion limit [12]; if the effect is caused by Pd $4d$, it is clearly an effect induced by Gd, since no R minimum has been observed in Y_2PdSi_3 [4]. Above all, the sign of the Curie-Weiss temperature obtained from the high-temperature χ data is not negative [2] as it should be negative for conventional Kondo systems. Therefore, these spin fluctuations, if they exist, are triggered by Gd $4f$ short-range correlations *prior to long-range magnetic ordering*. We propose that the origin of the $R(T)$ minimum lies in a *localization* or trapping of the electron cloud polarized by the s-f (or d-f) exchange interaction as one lowers the temperature towards long-range magnetic-transition temperature; this could be triggered by Gd $4f$ short-range magnetic order [8], just as crystallographic disorder results in electron localization [13], thereby reducing the mobility of charge carriers. The application of a magnetic field suppresses the spin fluctuations or alters the localization length (as proposed for La manganites [14] above the Curie temperature) resulting in an enhancement of the mobility of the electron cloud; this explains the suppression of the R minimum in the paramagnetic state in a magnetic field. The concepts of exchange-interaction–mediated localization, *i.e.* some kind of magnetic-polaronic effects, have been proposed for

semiconducting rare-earth compounds before [15]. Through this article we point out that the essential concept discussed in refs. [14] and [15] may to some extent be applicable even in some metallic alloys, particularly to those behaving as poor metals, *i.e.* in which the residual resistivity ratio is low, as appears to be the case in Gd_2PdSi_3.

Summarising, the intermetallic compound, Gd_2PdSi_3, is shown to exhibit an electrical resistivity minimum as a function of temperature above T_N. We propose that a novel magnetic precursor effect, possibly electron localization *the rootcause of which lies in magnetism even in metallic systems*, may result in an upturn of the electrical resistance before long-range order sets in. Finally, we have also made several other interesting observations in this compound. These are: i) Positive Curie-Weiss temperature indicative of canted antiferromagnetism; ii) The absence of downturn in electrical resistance below T_N; iii) A sudden jump in the $|B_{\text{eff}}|$ at the Gd nucleus at 15 K, related to lower ordering temperature for one of the two Gd sites [2], [4] and iv) Negative magnetoresistance with the magnitude increasing with decreasing temperature (large near T_N), an observation of significance to the field of giant magnetoresistance.

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