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Unexpected modification of magnetic properties by Y substitution in Eu_2PdSi_3

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The results of dc and ac magnetization, magnetic relaxation, electrical resistivity (ρ) and heat-capacity (C) measurements on Eu_2PdSi_3 and its Y-substituted alloys, $Eu_{2-x}Y_xPdSi_3$ ($x=0.5$ and 1.5), crystallizing in a AlB_2-derived hexagonal structure, are reported. The parent Eu compound has been found by us to show two magnetic transitions, at 40 and 10 K, arising from Eu sites (called $2b$ and $6h$ sites, respectively) with two different chemical surroundings. While the available data for the parent compound suggest the existence of long-range magnetic ordering below these temperatures, partial Y substitution brings out interesting changes in the magnetic properties. For instance, for an initial replacement of Eu by Y ($x=0.5$ alloy), (i) the low-temperature divergence of zero-field-cooled (ZFC) and field-cooled magnetic susceptibility (χ) sets in at a much higher temperature, compared to that in $x=0.0$. (ii) The temperature-dependent χ and C are considerably broadened at low temperatures, compared to those in the parent compound; apparently, the features due to onset of magnetic ordering from the $2b$ site become more prominent in these bulk measurements by Y substitution. (iii) The hysteresis curves reveal a nonzero remanent magnetization in the magnetically ordered state for the Y-substituted alloys, unlike in the parent compound. (iv) Isothermal remanent magnetization (M_{IRM}) undergoes a slow relaxation with time at low temperatures, while, for $x=0.0$, it falls to zero immediately after the field is switched off. (v) Interestingly, there is a sudden drop in the ZFC M_{IRM} at 5 K about 10 min after the field is switched off while undergoing slow relaxation with time. Thus, Y substitution for Eu brings out peculiar changes in the magnetic properties of Eu_2PdSi_3 and appears to favor metastability in the magnetic response, presumably due to magnetic disorder in such substituted alloys. [S0163-1829(99)02006-8]

I. INTRODUCTION

Recently, ternary compounds of the type R_2PdSi_3, crystallizing in an AlB_2-type hexagonal structure have evoked considerable interest.[1–6] It is to be noted that we have reported the formation of Ce and Eu compounds in Refs. 2,5. This crystal structure is characterized by two sites[5,6] for R ions, 25% occupying the $2b$ site (hereafter called $R1$ ions) and 75% occupying the $6h$ site ($R2$ ions) following crystallographic order at the Pd and Si sites. The majority Eu2 ions order magnetically at a lower temperature (10 K), while the minority ones (Eu1) order at a higher temperature (40 K). Our previous investigations[5] on Eu_2PdSi_3 suggested that, while there is enough evidence for the existence of both antiferromagnetic and ferromagnetic exchange interactions in this compound, there is no spin-glass (SG) behavior. This gains importance considering that the U compounds, U_2PdSi_3 (Ref. 7) and U_2PtSi_3 (Ref. 8), have been shown to exhibit SG characteristics due to exchange of atoms between Pd(Pt) and Si sites. This might imply therefore that there is a high degree of crystallographic order between Pd and Si sites in this Eu compound. It is therefore interesting to probe whether chemical substitution at the Eu site by nonmagnetic Y leads to magnetic frustration. Keeping this in mind, we have investigated the electrical resistivity (ρ), heat capacity (C), and magnetization behavior in the alloys, $Eu_{2-x}Y_xPdSi_3$ ($x=0.0$, 0.5, and 1.5), the results of which are reported in this article. We find drastic changes in the magnetic behavior and significant magnetic disorder effects as a result of Y substitution.

II. EXPERIMENT

The samples were prepared by induction melting stoichiometric amounts of constituent elements, followed by vacuum annealing at 700 °C for one week; the loss due to evaporation of Eu while melting was compensated by taking suitable excess amount of Eu. The samples were found to be single phase by x-ray diffraction and the sharpness of the diffraction lines is not found to diminish in the Y-substituted samples; the lattice constants are also found to decrease with Y substitution as expected. The ρ measurements were performed by a conventional four-probe method employing a conducting silver paint for making electrical contact of the leads with the samples, and C data were collected by a semiadiabatic heat-pulse method. The ac susceptibility (χ) measurements (2–300 K) were performed employing a ac field of 0.8 Oe at different frequencies and dc χ measurements were performed in the presence of a magnetic field (H) of 2 kOe [zero-field cooled (ZFC)] (2–300 K) employing a Quantum Design superconducting quantum interference device. In addition, ZFC and field-cooled (FC) behavior of χ have been studied below 100 K for $H=100$ Oe; the magnetic relaxation and hysteresis behavior were also measured at selected temperatures.

III. RESULTS AND DISCUSSION

The results of magnetic susceptibility studies obtained in different ways for all the three compositions are shown in Fig. 1. The findings are (i) the effective magnetic moment (μ_β) obtained from the high temperature (100–300 K) linear region of the plots of inverse dc χ versus temperature (Fig.

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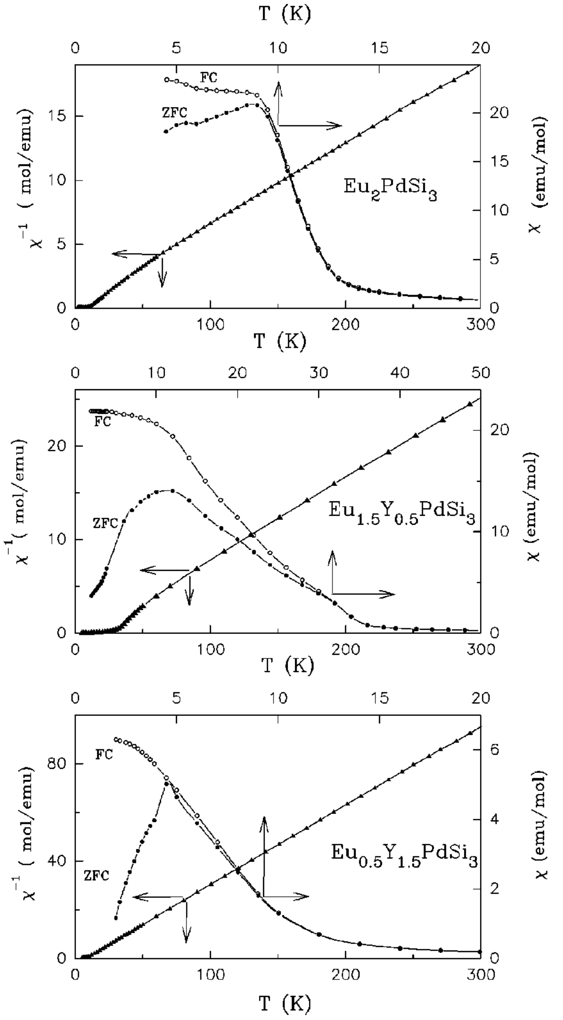

FIG. 1. Inverse susceptibility versus temperature measured in the presence of a magnetic field of 2 kOe and zero-field-cooled (ZFC) and field-cooled (FC) susceptibility ($H=100$ Oe) for Eu$_{2-x}$Y$_x$PdSi$_3$ ($x=0.0,0.5,1.5$) alloys.

1), measured in the presence of a magnetic field of 2 kOe, is nearly $8\mu_B$, thereby suggesting that Eu remains divalent though Y substitution exerts positive chemical pressure, (ii) The paramagnetic Curie temperature (θ_p in the range 100–300 K) for $x=0.0$, 0.5, and 1.5 are -3, 8, and 6 K, respectively, thus indicating that Y substitution in fact diminishes the strength of antiferromagnetic correlations; it is to be remarked that the field required to saturate the magnetization at 5 K is rather small (about 5 kOe) for the $x=0.5$ alloy, indicative of stronger ferromagnetic correlations consistent with this inference, compared to the absence of complete saturation even for higher fields for the parent compound,[5] (iii) The inverse χ (Fig. 1) tends to saturate at a higher temperature (about 30 K) for the $x=0.5$, compared to the $x=0.0$ composition, intercepting the x axis on the positive side, which is more evidence for the prominence of ferromagnetic correlations with initial Y substitution. This can be correlated to the appearance of a distinct peak in the ac χ data at about 34 K for $x=0.5$. The corresponding feature for $x=0.0$, expected to appear at 40 K, is rather smeared out by a continous change in the slope of the plot due to short-range correlation effects with decreasing temperature below 60 K as mentioned in Ref. 5. For the Y-rich composition, however, the plot of inverse χ versus temperature tends to saturate only below 10 K. An important point to be noted is that there are qualitative changes in the temperature dependence of ZFC and FC susceptibility ($H=100$ Oe) as Y is substituted for Eu: while, for $x=0.0$, the difference sets in only near the peak in ZFC data (10 K), for $x=0.5$ and 1.5, interestingly, FC and ZFC data tend to diverge from far above the peak (30 and 8 K, respectively); the peak temperatures represent the magnetic transitions from Eu2 ions.[5]

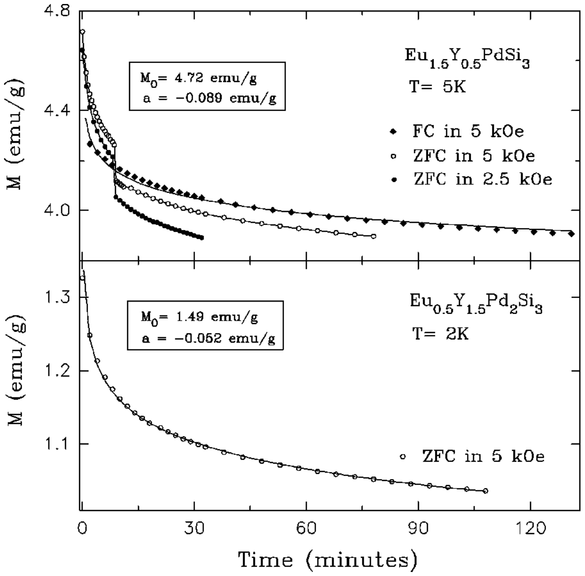

FIG. 2. Time dependence of the isothermal remanent magnetization $M_{\mathrm{IRM}}(T,t)$ of Eu$_{2-x}$Y$_x$PdSi$_3$ ($x=0.5$ and 1.5) at different temperatures in the magnetically ordered state. The lines through the points represent least squares fit to the expression $M_{\mathrm{IRM}}(T,t)=M_0(T)+a(T)\ln t$, except for the 5 K (ZFC) data for $x=0.5$, in which case it serves as a guide to the eyes.

We also measured the isothermal remanent magnetization (M_{IRM}) as a function of time t for all the samples at selected temperatures (2 and 70 K for $x=1.5$ and 5, 15, and 70 K for $x=0.0$ and 0.5). The samples were first zero-field cooled from 100 K to the desired temperature, then a magnetic field of 5 kOe was applied for 5 mins and switched off (at $t=0$ min). For all the samples, the values at 70 K drop to zero as soon as the field is switched off. While for the parent compound the magnetization dropped to zero within seconds at all temperatures, a nonzero M_{IRM} could be detected even after 2 h for the Y-substituted samples, at 2 K for $x=1.5$ and 5 and 15 K for $x=0.5$. Thus a metastable and irreversible state in the Y substituted samples at these temperatures is created by the application of H; it may be noted that even if these samples are cooled in the presence of the field, similar relaxation behavior is seen.

We would like to emphasize on an unusual finding in the ZFC M_{IRM} data for $x=0.5$ at 5 K: there is a logarithmic relaxation of M_{IRM} for about 10 min, after which there is a sudden drop, the origin of which is unclear, and this feature is reproduceable even if the field values are different. We find that this drop is absent if the sample is field cooled from 100 K (see Fig. 2, upper panel). This drop is also absent at 15 K (data not shown). It is not clear whether this drop is related to a decoupling of the Eu moments between the two different sites after the system is allowed to relax for some period of time. Very recently,[9] a coexistence of long-range (canted antiferromagnetic) interaction and SG behavior has been proposed for copper hydroxy salts which have a layered structure, and in which the magnetic Cu ion has two distinct crystallographic sites; considering a similar situation of two sites for (magnetic) Eu in our system, such a scenario is not ruled out for the Y-substituted alloys. It will be interesting to explore this aspect further. The magnitude and the net variation of the remanent magnetization is, however, small at 15 K, compared to that at 5 K; at $t=0$, the value is about 1.005 emu/g, which drops logarithmically to 0.995 emu/g only in 10 min, remaining constant thereafter (over the measured period of time of 1 h). This is presumably related to modification of magnetic structure as the temperature is lowered from about 15 to 5 K, following magnetic ordering of the Eu ions at the $6h$ site below about 10 K. All these results are shown in Fig. 2 (except for the 15 K data for $x=0.5$ as the variation is small). For the FC 5 K data for $x=0.5$ and ZFC 2 K data for $x=1.5$, the observed time dependence follows closely the relationship $M_{\text{IRM}}(T,t)=M_0(T)+a(T)\ln t$.

We have also compared the hysteresis loops of the magnetization for all these samples at the same temperatures at which M_{IRM} data were recorded. The results are shown in Fig. 3. It is clear that the parent compound does not exhibit any hysteresis, while the Y-substituted alloys show hysteresis with a nonzero remanent magnetization at 5 K; the loop, though small, is present even at 15 K for $x=0.5$. It may be remarked that these features are characteristic of SG phenomena also. Due to complexities of the magnetic behavior, we are not able to precisely define the characteristic freezing temperature T_f if the features in Y-substituted samples are to be attributed to SG phenomenon; the temperature at which χ peaks is conventionally taken as T_f, which turns out to be 10 and 5 K for $x=0.5$ and 1.5, respectively. It is to be noted that there is a difference between FC and ZFC χ data for Eu_2PdSi_3 as well without any other signatures of SG phenomena and this result establishes that this criterion is not sufficient to call any such compound a SG; a similar conclusion has been arrived at in the past from the investigations on systems known to exhibit long-range magnetic order.[10]

With respect to the ac χ data (Fig. 4), for $x=0.0$, while the feature at 40 K due to the magnetic transition from Eu1 site is not visible, there is a prominent peak at about 10 K arising from a magnetic transition from Eu2 ions. For $x=0.5$, there is a significant and monotonous increase of ac χ down to 10 K; thus the magnetic transition below 30 K is very broad, which is indicative of the disordered nature of the exchange interaction. A distinct peak is seen for $x=1.5$ at about 6 K attributable to Eu2 ions. Here, we would like to emphasize on the observation that in $Eu_{1.5}Y_{0.5}PdSi_3$, the magnetic transition due to the $2b$ site (above 30 K) is very prominent in the ac χ data, a feature which is not transparent in the data for the parent Eu compound (at 40 K). It may be recalled[5] that taking crystallographic features into account, the magnetism from the $2b$ site was proposed to be quasi-one-dimensional in character for $x=0.0$. It is interesting to see that the breaking of the Eu chains by the substitution by nonmagnetic ions appear to make the feature in the ac susceptibility very prominent. We believe that this observation is of relevance to the physics of one-dimensional magnetism.

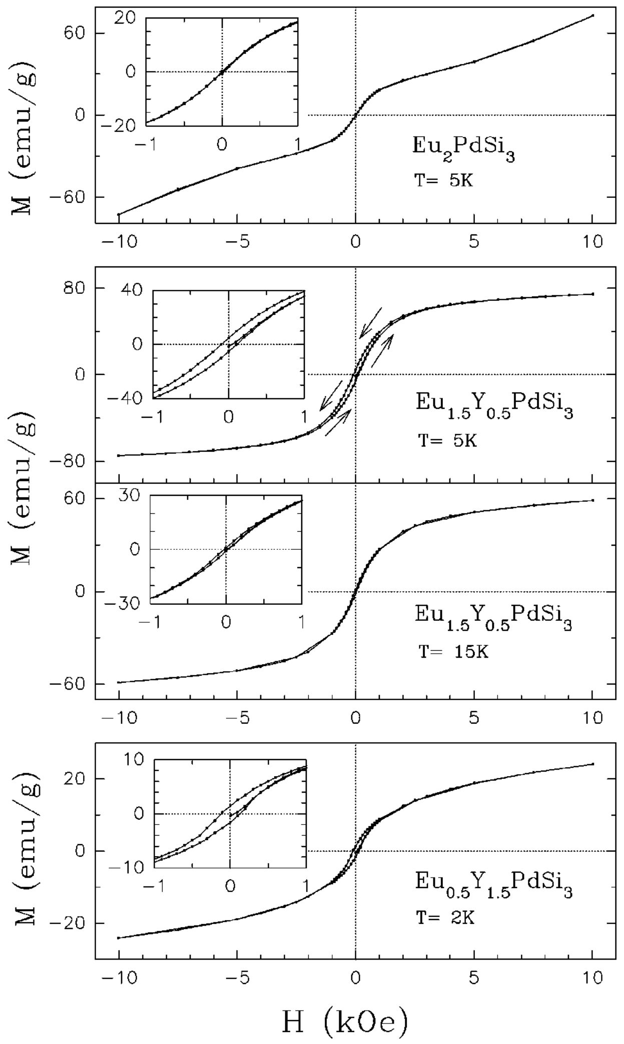

FIG. 3. Hysteresis loop of the magnetization of $Eu_{2-x}Y_xPdSi_3$ alloys at selected temperatures. The data close to zero field are shown in the expanded form in the insets. The lines through the data points serve as guides to the eyes.

The heat-capacity data are shown in Fig. 5, along with the resistivity behavior. As reported earlier, for $x=0.0$, there is a sharp peak in C below 10 K and a weak one below 40 K, arising from the magnetic transitions from Eu ions at the $6h$ and $2b$ sites, respectively. These results were analyzed in detail in Ref. 5. If Eu prefers to occupy the $2b$ site, then, for $x=1.5$, one should not see the features around 10 K at all (and a feature should appear only around 30–40 K). On the contrary, we find that this alloy in fact shows the features due to magnetic ordering, though broad, below 10 K. The magnetic entropy could be obtained only approximately due to the absence of proper reference for lattice contribution as described in Ref. 5, and such an estimate is found to attain nearly full value around 15 K for this composition; these findings establish that Eu, substituted for Y in Y_2PdSi_3, prefers to occupy the $6h$ site and not the $2b$ site in $Eu_{0.5}Y_{1.5}PdSi_3$. It appears that as the Eu concentration increases, some fraction tends to occupy $2b$ site as well. This is established in the following way: In the alloy, $x=0.5$, if Eu prefers $6h$ site alone, one would naively expect a sharp feature below 10 K only, without any additional magnetic ordering well above 10 K due to the $2b$ site. However, there

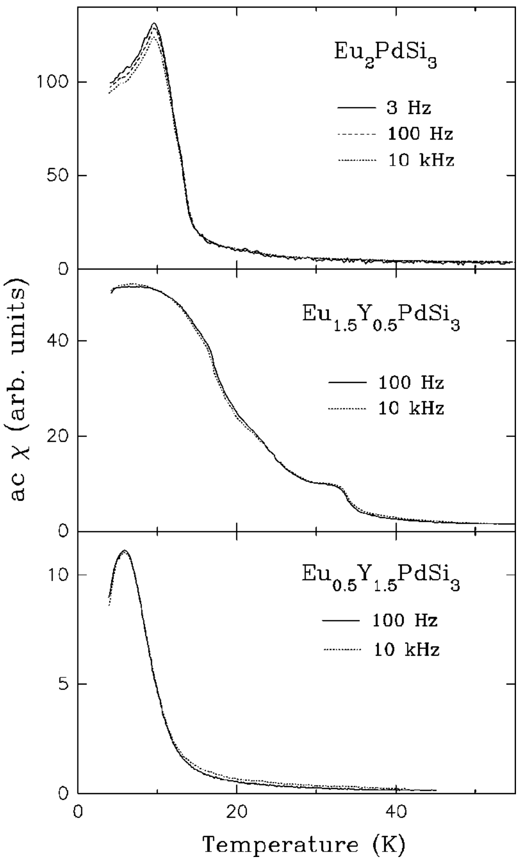

FIG. 4. ac susceptibility data at different frequencies below 60 K with an ac field of 0.8 Oe for the alloys $Eu_{2-x}Y_xPdSi_3$.

is an additional prominent feature near 34 K (as established by ac χ and ρ data more clearly) attributable to the magnetic transition from the $2b$ site. From the depression of magnetic ordering temperature from 40 to 34 K and assuming the validity of the indirect exchange interaction, it is estimated that about 85% of the $R2$ site is occupied by Eu for this composition. The facts that there are two magnetic transitions, one near 34 K and the other at 8 K, for $x=0.5$ and that there is a prominent one near 8 K for $x=1.5$ are established by anomalies in electrical resistivity as well, though the absolute values of ρ may not be reliable, considering microcracks in the sample. The observation that the heat-capacity features are rather smeared out, resulting in broader anomalies, with Y substitution may be in favor of SG behavior.

IV. CONCLUSIONS

To conclude, Y substitution modifies magnetic ordering in favor of a disorder-dominated magnetism, particularly considering broadening of heat capacity and ac susceptibility features. We also observe time dependence of isothermal magnetization and magnetic hysteresis loops in Y substituted alloys, which are absent in the parent Eu compound. It is to be noted that these features are also characteristic of spin glasses.[11] We, however, could not resolve any frequency dependence in ac χ data of the Y-substituted samples (characterizing spin glasses) which, if present, may be masked by the width of these features. Though the magnetic behavior is influenced by disorder effects, we are at present hesitant to firmly claim that these Y-substituted alloys are spin glasses, considering that the low-temperature divergence of FC and ZFC χ, relaxation behavior of M_{IRM}, and hysteretic behavior of magnetization have also been seen in compounds with long-range magnetic order.[10,12–15] It should, however, be noted that the coercive field of our alloys is rather small compared to those magnetic systems[12] and the field employed to magnetize for magnetic relaxation studies in our case is larger than the coercive field. Therefore, one is tempted to believe that these Y alloys are spin glasses. Further work is required to confirm or rule out this possibility. Finally, we would like to mention that the $x=0.5$ alloy is an interesting system, considering a sudden jump in ZFC isothermal remanent magnetization after about 10 min, which warrants further investigation for deeper understanding. In short, Y substitution for Eu in Eu_2PdSi_3, a compound with two (long-range) magnetic orderings from two different Eu chemical environments, brings out interesting changes in the magnetic behavior, some of which are apparently related to an element of metastability in the magnetic response of these alloys.

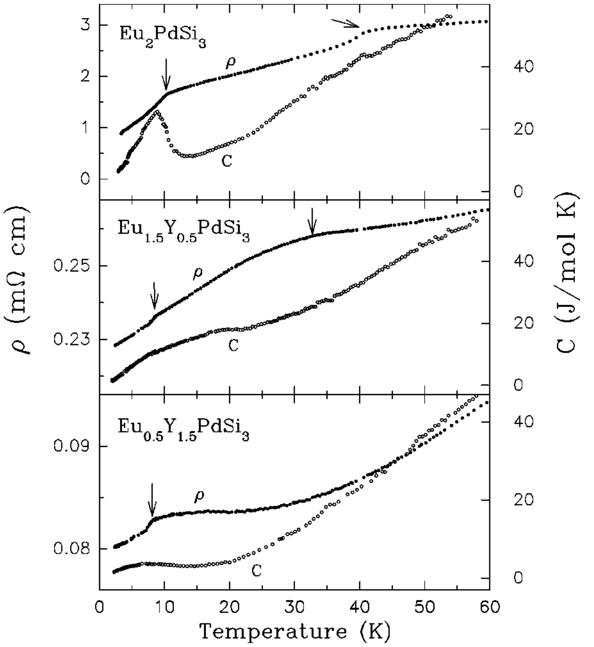

FIG. 5. Heat capacity and electrical resistivity for $Eu_{2-x}Y_xPdSi_3$ ($x=0.0,0.5,1.5$) below 60 K, with the arrows marking features due to magnetic transitions in the ρ data.

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