$Ce_3Pd_{20}Ge(Si)_6$: A new Kondo system?

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Some compounds which were recently synthesized for the first time, $Ce_3Pd_{20}Ge_6$ and $Ce_3Pd_{20}Si_6$, have a previously unknown type of crystalline superstructure. The temperature dependence of the resistivity and also the temperature dependence and the field dependence of the magnetic moment have been measured over the temperature range 4–300 K in magnetic fields up to 5 kOe. The resistivity increases logarithmically at low temperatures, indicating a possible Kondo effect in this system. © *1995 American Institute of Physics.*

Cerium-based intermetallic compounds exhibit a rich diversity of properties, including superconductivity, heavy-fermion properties, and magnetic order.[1] The compound $Ce_3Pd_{20}Ge(Si)_6$ was synthesized in 1994 by Gribanov *et al.*[2] Analysis of its structure by x-ray diffraction revealed that this intermetallic compound has a previously unknown superstructure[3] with respect to a crystal lattice of the $Cr_{23}C_6$ type (space group $Fm3m$). The presence in the $Ce_3Pd_{20}Ge(Si)_6$ lattice of two nonequivalent sites[2] of Ce atoms (Ce1 and Ce2), with different neighborhoods (corresponding to the replacement of Ge by Si), and the existence in the crystal structure of a cube formed by eight Ce2 atoms, inside which there are no Ce1 sites, raise the hope that this compound may exhibit some nontrivial physical properties.

In this letter we are reporting measurements of the temperature dependence of the resistivity and the temperature and field dependence of the magnetic moment of polycrystalline samples over the temperature range 4–300 K in magnetic fields up to 5 kOe. As the temperature is lowered from 300 K, the resistivity $\rho(T)$ falls off monotonically down to $T_{\min}$ (which is 50 and 10 K, respectively, for $Ce_3Pd_{20}Si_6$ and $Ce_3Pd_{20}Ge_6$; Fig. 1). Below $T_{\min}$, each compound exhibits a region of logarithmic growth, which can be described, within the experimental error (3%), by

$$\rho(T) = 130 - 18 \ln T, \quad Ce_3Pd_2Si_6, \quad T < 40 \text{ K};$$

$$\rho(T) = 38 - 0.5 \ln T, \quad Ce_3Pd_{20}Ge_6, \quad T < 8 \text{ K}$$

(ρ is in $\mu\Omega$, and T is the temperature).

Figure 2 shows the temperature dependence of the reciprocal susceptibility, $\chi^{-1}(T)$. We see that $Ce_3Pd_{20}Ge_6$ can be thought of as a Curie–Weiss paramagnet. The nonlinear $\chi^{-1}(T)$ dependence of $Ce_3Pd_{20}Si_6$ requires further study. It will be discussed below.

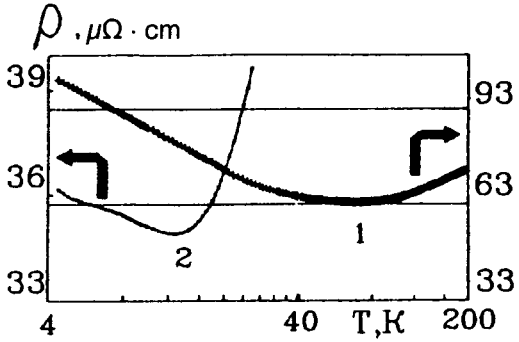

FIG. 1. Temperature dependence of the resistivity of polycrystalline samples. 1—$Ce_3Pd_{20}Si_6$; 2—$Ce_3Pd_{20}Ge_6$.

Figure 3 shows the magnetic moment versus the applied magnetic field. The compounds $Ce_3Pd_{20}Ge_6$ and $Ce_3Pd_{20}Si_6$ differ substantially in behavior here. While the magnetic moment of the first of these compounds increases linearly with increasing field, that of the other increases in a nonlinear way in weak fields (below 1500 Oe).

To analyze the experimental temperature dependence $\chi^{-1}(T)$ we use the effective magnetic moment found from the Curie–Weiss law:

$$\chi^{-1}(T)=\frac{H}{M(T)}=\frac{3k_B(T-\theta)}{N\mu_{\text{eff}}^2}, \tag{1}$$

where μ_{eff} is generally a function of the temperature, N is the number of paramagnetic centers, and θ is the paramagnetic Curie temperature. It follows from the experimental behavior in Fig. 2 that μ_{eff} for $Ce_3Pd_{20}Ge_6$ is close to $2.5\mu_B$ at temperatures of 10–100 K. For the compound $Ce_3Pd_{20}Si_6$, $\mu_{\text{eff}}(T)$ increases with decreasing temperature, from $1.7\mu_B$ (100 K) to $5\mu_B$ (10 K). This increase cannot be attributed to either an "admixture" of the first excited multiplet ($J=7/2$) or a splitting in the crystal field, since $\mu_{\text{eff}}(T)$ typically decreases with decreasing temperature for each of these mechanisms.[4]

The nonlinear low-field feature on the $M(H)$ curve for $Ce_3Pd_{20}Si_6$ can be attributed to a "cluster magnetism" due to Ce2 ions forming a cube (more on this below). The inset in Fig. 3 shows the result found by subtracting the linear part from the $M(H)$ curve for

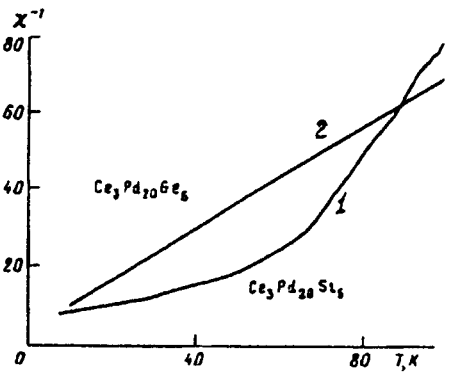

FIG. 2. Temperature dependence of the static magnetic susceptibility of polycrystalline samples. 1—$Ce_3Pd_{20}Si_6$; 2—$Cd_3Pd_{20}Ge_6$. These measurements were carried out in a field of 200 Oe.

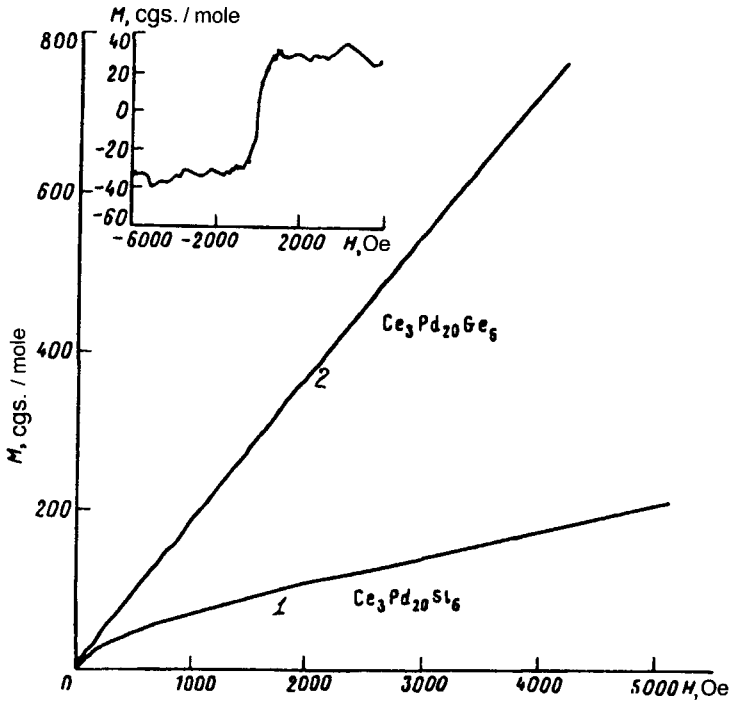

FIG. 3. Magnetization curves of polycrystalline samples. 1—$Ce_3Pd_{20}Si_6$; 2—$Ce_3Pd_{20}Ge_6$. The inset shows the nonlinear part of the magnetization curve of $Ce_3Pd_{20}Si_6$.

$Ce_3Pd_{20}Si_6$. At $T=5$ K, there is saturation in fields $H_{sat}\sim 1500$–2000 Oe. An estimate of the magnetic moment of the cluster from the relation $2\mu_{eff}H_{sat}\sim k_BT$ yields ~ 24–18 μ_B.

According to the model which has been proposed, the change in the slope of the $\chi^{-1}(T)$ curve for $Ce_3Pd_{20}Si_6$ (Fig. 2) is due to an increase in the effective magnetic moment of a cluster with decreasing temperature. According to calculations in the crystal-field model (more on this below), the effective magnetic moments of Ce1 and Ce2 are comparable at high temperatures (Fig. 4), and the contributions of the two subsystems to the magnetic susceptibility are comparable. At low temperatures (below 50 K), the ratio μ_{Ce2}/μ_{Ce1} increases (Fig. 4). As a result, the Ce2 atoms apparently form magnetic clusters. At low temperatures, clusters of Ce2 should thus make the predominant contribution to the susceptibility: $\chi(T)\approx\chi_{clust}(T)$. Since there are three cerium atoms (one Ce1 atom and two Ce2 atoms) per unit cell,[1] and since the clusters consist of eight Ce2 atoms, we find the following estimate of μ_{clust} at low temperatures, assuming that the Ce1 component of the susceptibility is negligible in comparison with the Ce2-cluster component at low temperatures:

$$\chi(T)\approx \frac{2N_A}{8}\frac{\mu_{clust}^2}{3k_B(T-\theta)}. \qquad (2)$$

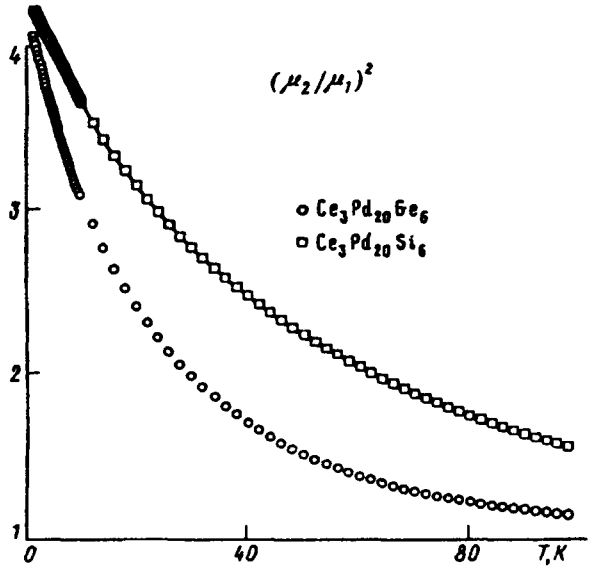

FIG. 4. Temperature dependence of the square of the ratio of the effective magnetic moments for the two nonequivalent Ce sites in the compounds $Ce_3Pd_{20}Si_6$ (□) and $Ce_3Pd_{20}Ge_6$ (○). The calculation was carried out on the basis of crystal-field theory.

Here N_A is Avogadro's number, 8 is the number of ions in a cluster, and μ_{clust} is the effective magnetic moment of a cluster of Ce2 ions.

A comparison with experiment yields $\mu_{\text{clust}} \approx 17\mu_B$ (at 10 K).

We can propose another estimate, of a maximum value of μ_{clust}, assuming that the energy of the exchange interaction in a cluster is greater than the splitting in the crystal field. The maximum effective moment (in units of μ_B) of a cluster of eight cerium ions with $J=5/2$ is $\sqrt{J_{\max}(J_{\max}+1)} \approx 20.5$, where $J_{\max} = 8 \cdot 5/2 = 20$.

According to our assumption, the cerium ions in Ce2 sites in the compound $Ce_3Pd_{20}Si_6$ thus form clusters. The cerium ions also determine the low-field feature on the $M(H)$ curve, while cerium ions in Ce1 sites are responsible for the $M(H)$ behavior in high fields.

To put our proposed cluster model on a firmer foundation, we calculated the splitting of the levels of the ground multiplet of Ce^{3+} ions for the Ce1 and Ce2 sites on the basis of crystal-field theory.[5] The results of this calculation indicate that Ce atoms in Ce1 and Ce2 sites in the compound $Ce_3Pd_{20}Si_6$ have quite different magnetic properties. Although the crystal structures of $Ce_3Pd_{20}Si_6$ and $Ce_3Pd_{20}Ge_6$ are of the same type, the neighborhood of a Ce1 site changes when Ge is replaced by Si (Ref. 2). The nearest neighbor of Ce1 in the case of $Ce_3Pd_{20}Si_6$ is Si, while that in the case of $Ce_3Pd_{20}Ge_6$ is Pd. The neighborhoods of the Ce2 sites are identical in the two compounds.

Our calculations show that the magnetic moment of Ce in Ce2 sites is considerably larger than that in Ce1 sites and that the ratio of these moments (μ_2/μ_1) increases with decreasing temperature (Fig. 4). It follows that, at low temperatures, magnetic interactions of the Ce2–Ce2 type within a cluster of eight Ce2 atoms may be stronger than interactions of the Ce2–Ce1 and Ce1–Ce1 types. If the Ce2–Ce2 interactions are ferro-

magnetic, and the ground state of the cluster has the maximum magnetic moment, the model of cluster magnetism is capable of explaining the observed increase in the effective magnetic moment per cerium atom at low temperatures [Eq. (2)]. In the model proposed here (Fig. 4), this effect should be manifested in $Ce_3Pd_{20}Si_6$ at a temperature higher than in $Ce_3Pd_{20}Ge_6$; this prediction does not contradict observations. The absence of a hysteresis from the magnetization curves is further evidence in favor of the cluster model.

We note in conclusion that the compound $Ce_3Pd_{20}Ge(Si)_6$ has a property characteristic of Kondo systems: a logarithmic increase in the resistivity with decreasing temperature. The existence of two nonequivalent Ce sites suggests that we can discuss two cerium subsystems in this compound; one of them (Ce1) determines Kondo properties (the logarithmic increase in resistivity), while the other (Ce2) is responsible for the unusual magnetism at low temperatures.

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[1] J. G. Sereni, "Low-Temperature Behavior of Cerium Compounds," in *Handbook on the Physics and Chemistry of Rare Earths*, ed. by K. A. Gschneider and L. Eyring (Elsevier Science, 1991), Chap. 98, p. 1.
[2] A. V. Gribanov, Yu. D. Seropegin, and O. I. Bodak, J. Alloys and Compounds **204**, L9–L11 (1994).
[3] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM International, Material Park, Ohio, 1985), p. 1509.
[4] S. V. Vonsovskiĭ, *Magnetism* [in Russian] (Nauka, Moscow, 1971).
[5] M. T. Hutchings, in *Solid State Physics, Advances in Research and Applications*, ed. by F. Seitz and Turnbull (1964), Vol. 16, p. 227.

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