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Molecular magnetism and crystal field effects in the Kondo system $Ce_3Pd_{20}(Si,Ge)_6$ with two Ce sublattices

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ABSTRACT

The unusual electronic and magnetic properties of the systems $Ce_3Pd_{20}T_6$ (T=Ge, Si) with two non-equivalent Ce positions are discussed. The logarithmic growth of resistance for both systems confirms the presence of the Kondo effect in the two respective temperature ranges. The two-scale behavior is explained by consecutive splitting of Ce ion levels in the crystal field. The effects of the frustration caused by the coexistence of the different Ce positions are treated, which may also significantly enhance the observed values of specific heat. A model of "molecular magnetism" with Ce2 cubes is developed.

1. Introduction

The Kondo systems $Ce_3Pd_{20}T_6$ (with T=Ge, Si) have unique electronic properties [1–4]. The interesting feature of this cubic system is two nested cubes composed of cerium ions, Ce1 and Ce2, in two non-equivalent positions [3,4]. These systems have a high electron heat capacity: estimations above $T=6$ K give the value of $\gamma=0.21$ and 0.3 J/mol K^2 for T=Si and Ge. $Ce_3Pd_{20}Si_6$ yield at ultralow temperatures anomalous heat capacity which is almost constant at very low temperatures $0.3-2$ K, and formally calculated γ grows up to about 10^4 mJ/mol K^2. The structural features (high symmetry with cluster motifs) lead to additional peculiarities of electronic and magnetic properties.

First magnetic and transport properties of the 3-20-6 system (in particular, manifestations of the Kondo effect) were reported in 1994 [1,2]. After discussion of this report, the paper [3] was published. In detail, magnetic and electrical properties have been investigated in [3,4], where a large role of magnetic frustrations caused by features of the lattice (cluster "superstructure") was revealed.

Studies of the magnetic structure were performed in [5]. A model of quadrupolar ordering below 1 K proposed for $Ce_3Pd_{20}(Si,Ge)_6$ [6]. However, this model apparently does not describe the whole variety of anomalies in the systems discussed. At the same time, the "molecular magnetism" approach in the framework of the crystal field (CEF) theory [3–4] allows us to describe a broader set of properties in the range from 2 K to room temperatures. This analysis is the focus of the present work.

2. Experimental and structure

For the first time, $Ce_3Pd_{20}Si_6$ and $Ce_3Pd_{20}Ge_6$ single phase samples were synthesized at the Chemistry Department of Moscow State University. These samples have a high quality, and the properties were found to be consistent with the literature data. X-ray analysis carried out by group (Yu.D. Seropegin, Moscow) revealed that both the compounds have a cubic symmetry (space group *Fm*-3*m*) and correspond to the $Mg_3Ni_{20}B_6$ structural type which is an ordered derivative from the binary $Cr_{23}C_6$ type [7]. The most intriguing fact is the existence of two non-equivalent positions of cerium (Fig. 1).

Nowadays, there are a number of compounds belonging to this superstructure, e.g., silicides $R_3Pd_{20}Si_6$ (R= La, Ce, Sm, and Yb) and germanide $Ce_3Pd_{20}Ge_6$. Measurements were made for many 4f-compounds (except for $La_3Pd_{20}Si_6$), which allowed to explore the replacement of the rare-earth and the third element.

Investigations of the temperature dependence of the resistivity, magnetic susceptibility, specific heat, thermal conductivity,

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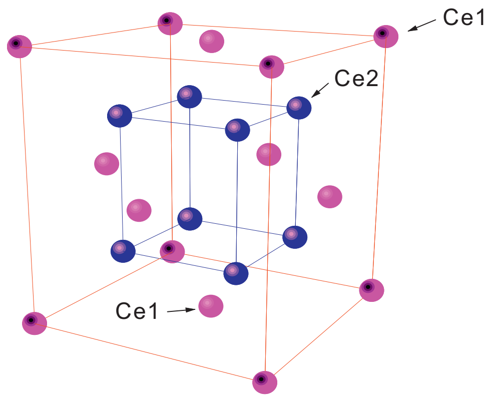

Fig. 1. Crystal structure of $Ce_3Pd_{20}T_6$ containing small and big cubes.

Seebeck coefficient for a large group of the synthesized samples were performed. The heat capacity and transport properties were measured by standard dc four probe techniques on an Quantum Design Physical Property Measurement System. The static magnetic moment was measured by using a vibrating sample magnetometer PARC-M155 and a SQUID magnetometer Quantum Design.

3. Results on electronic and magnetic properties

The specific heat measurements performed on $Ce_3Pd_{20}Ge_6$ down to 0.3 K yield a giant value of the Sommerfeld coefficient $\gamma = 3$ J/mol K^2. However, calorimetric experiments at 4–25 K show moderate γ about 300 mJ/mol K^2. One can see from inset in Fig. 2 that γ starts to decrease at low T. The dependence $T^{-0.35}$ seems to indicate a spin-glass-like behavior.

Ultralow-temperature anomalies in $C(T)$ can be due to antiferromagnetic ordering and quadrupole transition [6]. Besides that, a local symmetry lowering of the Γ_8 ground state and CEF level splitting may play a role.

Temperature dependences of magnetization in a small field and of resistivity are presented in Figs. 3 and 4.

A fundamental difference between the behavior of $M(T)$ in a field of 500 Oe for $Ce_3Pd_{20}Si_6$ and $Ce_3Pd_{20}Ge_6$ is the existence of

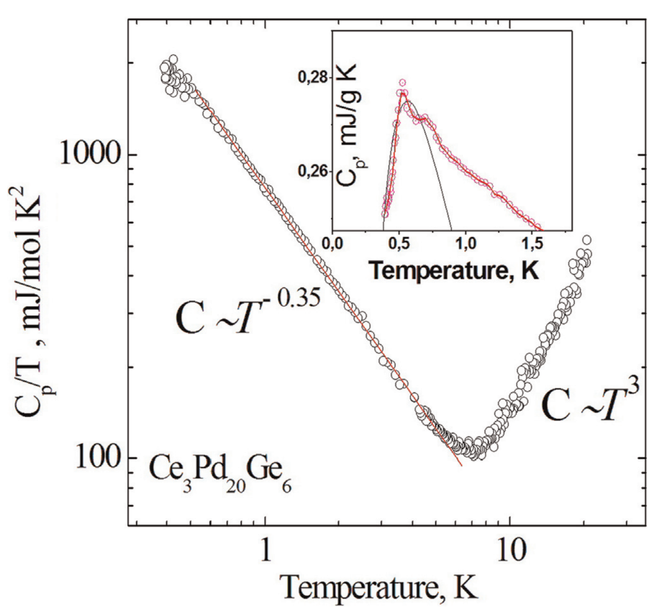

Fig. 2. Temperature dependences of specific heat al low temperatures (the line is the $T^{-0.35}$ fit). The inset shows the ultralow temperature region, the line being a Schottky-like fit.

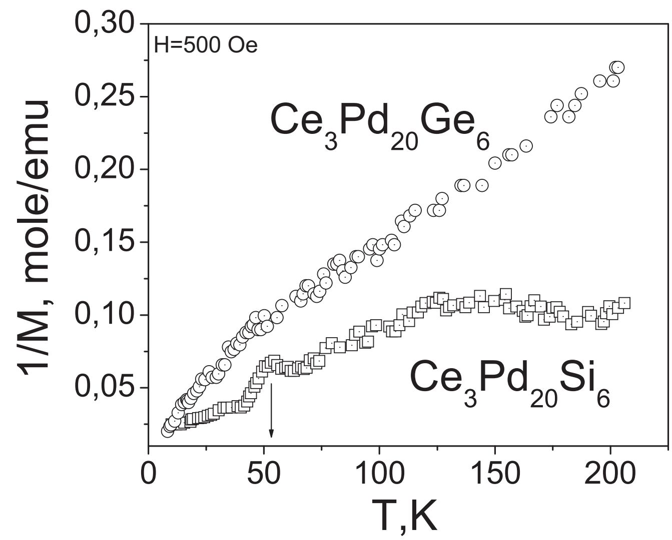

Fig. 3. Temperature dependencies of inverse magnetization in a weak field $H = 500$ Oe for $Ce_3Pd_{20}Ge_6$ (circles) and $Ce_3Pd_{20}Si_6$ (squares).

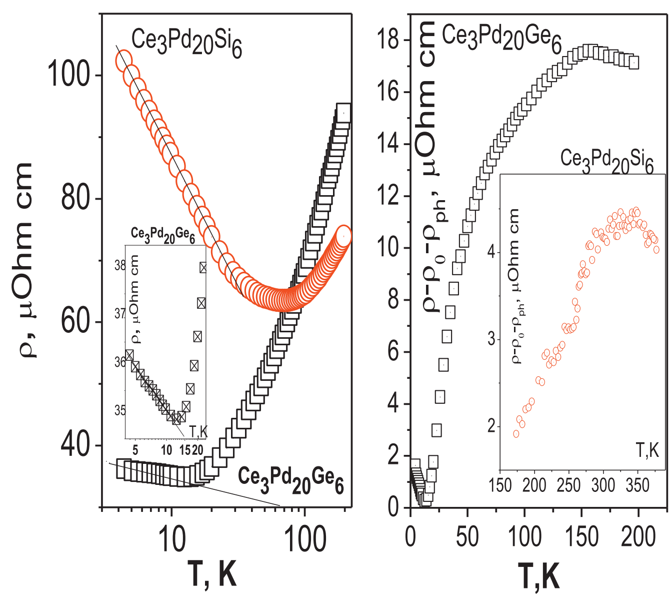

Fig. 4. Temperature dependencies of resistivity al low temperature (left) and at more high temperatures (right, the phonon contribution is subtracted according to the Blokh–Gruneisen formula, the Debye temperature being obtained from T^3 specific heat contribution). The lines show the logarithmic dependence.

anomalies of rather complicated form for $Ce_3Pd_{20}Si_6$ in the range 40–50 K, indicating a change in the magnetic structure of this compound. This anomaly is not typical for both ferro- and antiferromagnetic transition in all the spin structure of the compound, but seems to be due to the existence of a two-sublattice spin structure It is clearly seen that this anomaly is imposed on the normal behavior of $M(T)$ in the case of the Curie–Weiss paramagnetism. It should be noted that in this temperature range the transition from the linear to nonlinear dependence M(H) in low fields.

For all the samples, picking out the magnetic part $\rho_M(T)$ of resistivity was carried out by subtracting the phonon contribution. The logarithmic growth of resistivity for both the systems confirms the presence of the Kondo effect in the two respective temperature ranges. Namely, the temperature corresponding to the resistance minimum is $T_{min} = 71$ K and 12.5 K, and $T_{max} = 332$ K and 151 K for silicon and germanium systems respectively.