# Possible quadrupolar ordering in a Kondo-lattice compound $Ce_3Pd_{20}Ge_6$

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Magnetic and transport properties of the cubic ternary compound $Ce_3Pd_{20}Ge_6$ are herein reported. The electrical resistivity exhibits the Kondo lattice behavior and a large $T^2$ coefficient at low temperatures, indicating that this compound is a heavy-electron system with a Kondo temperature of a few degrees Kelvin. The low-temperature specific heat revealed two successive anomalies at $T_1=1.2$ K and $T_2=0.7$ K. The $\Gamma_8$ quartet crystalline-field ground state of Ce ions is conjectured from the thermal variation of magnetic entropy deduced from the specific-heat data. The anomaly at $T_1$ is probably a result of quadrupolar interaction between $\Gamma_8$ ground states, while the other one at $T_2$ is due to antiferromagnetic ordering.

We recently reported the low-temperature physical properties of $Ce_3Pd_{20}Si_6$, which possesses a very much enhanced $C/T$, the specific heat divided by temperature, at low temperatures, reaching as high as 8 J/Ce mol K$^2$ at 0.2 K.[1] The compound is at present classified as one of the heaviest Kondo compounds. $Ce_3Pd_{20}Ge_6$ is an isostructural compound of the silicate and the crystal structure belongs to a cubic space group of $Fm\overline{3}m$ (No. 225).[2] The Ce ions in the structure occupy two different crystallographic sites but both sites have a cubic symmetry. In this work, we present the results of the magnetic susceptibility, the electrical resistivity, and the low-temperature specific heat of $Ce_3Pd_{20}Ge_6$.

Polycrystalline samples were prepared by arc melting the stoichiometric constituents on a water-cooled copper hearth under an argon atmosphere. The arc-melted samples were annealed in an evacuated quartz tube at 800 °C for 1 week. The x-ray powder diffraction study did not show any appreciable amount of second phases, but the metallography indicated the presence of a small amount of unknown impurity phases. The lattice parameter was found to be 12.457 Å, which is comparable with the reported value of Ref. 2. We also synthesized $La_3Pd_{20}Ge_6$ which was confirmed to be isostructural to $Ce_3Pd_{20}Ge_6$ and the lattice parameter was 12.482 Å.

The magnetic susceptibility, $\chi$, was measured between 2 and 300 K with a commercial SQUID magnetometer at a magnetic field of 3 kOe and the low-temperature ac susceptibility, $\chi_{ac}$, was measured by a conventional mutual-inductance method down to 0.4 K. The results of $\chi$ are shown in Fig. 1 with those of $\chi_{ac}$ in the inset. $\chi$ follows a Curie-Weiss law at higher temperatures than about 50 K. The effective moment and the Weiss temperature are 2.45 $\mu_B$/Ce and $-6.1$ K, respectively. The effective moment is nearly equal to that of free trivalent $Ce^{3+}$. The ac susceptibility shows a sharp cusp at 0.7 K suggesting an antiferromagnetic transition.

The electrical resistivity, $\rho(T)$, was measured by a four-probe dc method down to 20 mK and the result is plotted as a function of temperature in Fig. 2. As the temperature is lowered, $\rho(T)$ monotonically decreases down to about 10 K and then changes to an upturn to make a broad peak around 2 K. Below 1.3 K, a slightly more rapid decrease is noticeable and a clear inflection point is seen at 0.7 K, where the antiferromagnetic (AF) order occurs (see the inset). In order to check whether the increase below 10 K is ascribable to the Kondo effect or not, we also measured the resistivity of a diluted sample of $La_{2.7}Ce_{0.3}Pd_{20}Ge_6$. The result exhibits a similar but much less pronounced rise than for $Ce_3Pd_{20}Ge_6$, as shown in Fig. 2. Thus the broad peak around 2 K may be considered as one of the characteristic features of a Kondo-lattice compound. From this thermal variation of $\rho(T)$, we may estimate the Kondo temperature a few degrees K for $Ce_3Pd_{20}Ge_6$. It should be further noted that $\rho(T)$ below 0.7 K is expressed as $\rho_0+AT^2$, where $\rho_0$ and $A$ are 2 $\mu\Omega$ cm and 13.9 $\mu\Omega$ cm/K$^2$, respectively. The latter value for $A$ is very large, which is comparable to that of $CeCu_2Si_2$.[3]

The specific heat was measured by an adiabatic heat pulse method between 0.1 and 20 K. The data below 0.6 K were taken with another calorimeter in a dilution refrigerator. The results are shown together with those of $La_3Pd_{20}Ge_6$ in Fig. 3 and the low-temperature part of $Ce_3Pd_{20}Ge_6$ in the inset. The electronic specific-heat coefficient and the Debye temperature of $La_3Pd_{20}Ge_6$ were determined to be 33.2 mJ/mol K$^2$

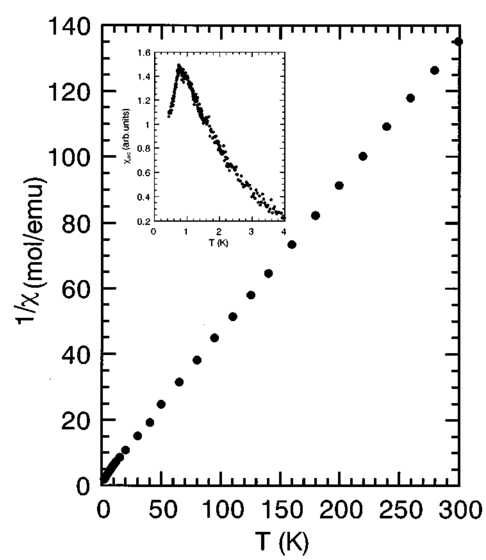


FIG. 1. The temperature dependence of $1/\chi$ and $\chi_{ac}$ (inset) of $Ce_3Pd_{20}Ge_6$.

 

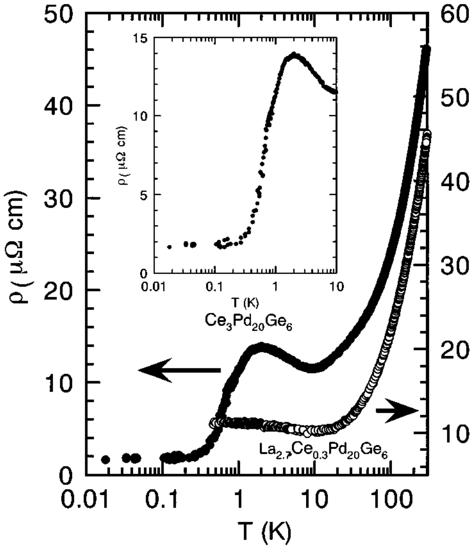


FIG. 2. The temperature dependence of $\rho$ of $Ce_3Pd_{20}Ge_6$ (●) and $La_{2.7}Ce_{0.3}Pd_{20}Ge_6$ (○). The inset shows the low-temperature $\rho$ of $Ce_3Pd_{20}Ge_6$.

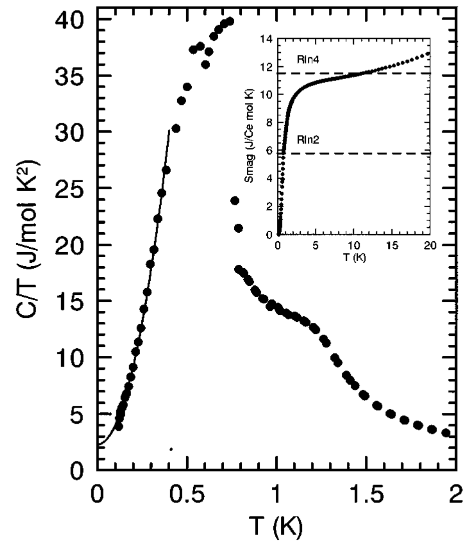


FIG. 4. The $C/T$ vs $T$ for $Ce_3Pd_{20}Ge_6$ and the temperature dependence of magnetic entropy, $S_{\mathrm{mag}}=S_{\mathrm{mag}}(T)-S_{\mathrm{mag}}(0.1\ \mathrm{K})$ of $Ce_3Pd_{20}Ge_6$ (inset).

and 242 K. The specific heat $C(T)$ of $Ce_3Pd_{20}Ge_6$ demonstrates a sharp peak of AF ordering at 0.7 K, as suggested above in $\chi_{\mathrm{ac}}(T)$ and $\rho(T)$. In addition to this anomaly, there is another small anomaly around 1.2 K, implying an incomplete phase transition, as can be more clearly seen in the inset. It is remarked that the anomaly around 1.2 K could not be reproduced by a Schottky specific heat. A small anomaly was also confirmed around 1.3 K in $\rho(T)$, as noted above, although no appreciable anomaly was detected in $\chi_{\mathrm{ac}}(T)$. The nature of this anomaly will be discussed below in relation to the possibility of quadrupolar ordering. It is further noted here that the specific heat below 0.4 K is well represented by $2.28T+173.93T^3$, which is indicated with the solid curve in the $C/T$ vs $T$ plot of Fig. 4. The large value of

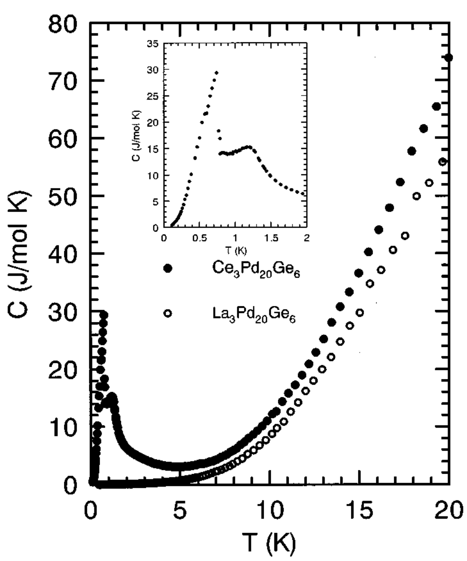


FIG. 3. The temperature dependence of the specific heat of $Ce_3Pd_{20}Ge_6$ (●) and $La_3Pd_{20}Ge_6$ (○) and the inset shows the low-temperature specific heat of $Ce_3Pd_{20}Ge_6$.

the first term indicates that the compound is really a heavy-electron system and the second term signifies the presence of three-dimensional AF spin waves.

Under a crystalline field of cubic symmetry, the energy level of $Ce^{3+}$ in $4f^1$ configuration splits into the $\Gamma_7$ doublet and the $\Gamma_8$ quartet. In order to find which ground state is realized in our compound, we evaluated the magnetic entropy, $S_{\mathrm{mag}}$ by subtracting the specific heat of $La_3Pd_{20}Ge_6$ as a nonmagnetic part. We show the thermal variation of $S_{\mathrm{mag}}$ per Ce ion in the inset of Fig. 4. As seen in the figure, $R$ ln2 is already recovered at the AF transition (0.7 K) in spite of our negligence of the low-temperature contribution below 0.1 K and the entropy monotonously increases up to 10 J/Ce mol K around 2 K. This smooth variation below 2 K is inconsistent with a possibility of the $\Gamma_7$ doublet ground state. Furthermore, the magnetic entropy gradually increases above about 3 K until it crosses $R$ ln4 around 10 K. These facts strongly suggest that the $\Gamma_8$ quartet is the ground state for the Ce ions at both crystallographic sites. The $\Gamma_8$ quartet ground state is not, however, very common in Ce compounds. $CeB_6$ and CeAg are known as rare examples with a $\Gamma_8$ quartet ground state.[4,5] Because the $\Gamma_8$ quartet possesses an electric quadrupole moment as well as a magnetic dipole moment, there exists a quadrupolar interaction besides the RKKY interaction between Ce ions. In the manner the RKKY interaction leads to a magnetic phase transition, the quadrupole-quadrupole interaction mediated by conduction electrons or phonons often leads to a quadrupolar ordering or a lattice instability.[6] In fact, such quadrupolar effects manifest themselves at low temperatures in $CeB_6$ and CeAg. $CeB_6$ shows two successive transitions at 3.3 and 2.3 K, where quadrupolar and antiferromagnetic ordering are believed to occur, respectively.[4,7] In CeAg, a quadrupolar ordering accompanied by a structural transition and a ferromagnetic order occur at 15.85 and 5.2 K, respectively.[5] Although the precise nature of quadrupolar effects in these compounds has not, however, been clarified yet, the anomalies around 1.2 K found in $Ce_3Pd_{20}Ge_6$ resemble very much the cases of $CeB_6$ and CeAg just described above. The anomaly of the specific heat above the sharp peak of AF ordering looks very much like the one for the quadrupolar ordering in $CeB_6$,[7] and no corresponding anomaly in $\chi(T)$ was found, as in CeAg.[5] We further noticed that the Néel temperature and the temperature where the quadrupolar anomaly takes place are closely correlated, as observed in $CeB_6$ and CeAg.[5,7] Both are diminished by a dilution of Ce by La atoms and by additional heat treatments, strongly suggesting an appreciable magnetoelastic effect through the quadrupolar interaction in the present compound. We are therefore tempted to assume that the anomaly of the specific heat at $T_1 = 1.2$ K is real and probably due to a small strain caused by quadrupolar ordering. If this is proved to be the case, $Ce_3Pd_{20}Ge_6$ would be the first ternary compound with a complex crystal structure revealing a quadrupolar ordering. Quadrupolar ordering has been mostly found in cubic binary compounds of CsCl or $Cu_3Au$ type.[8]

In conclusion, we have presented the experimental results of the magnetic susceptibility, the electrical resistivity, and the low-temperature specific heat of $Ce_3Pd_{20}Ge_6$ and found that the compound forms a Kondo lattice with a relatively low Kondo temperature and exhibits two successive anomalies at 1.2 and 0.7 K. From the analysis of the magnetic entropy we postulate that the crystalline-field ground state is the $\Gamma_8$ quartet and the anomaly at 1.2 K may be induced by the quadrupolar interaction originated from the $\Gamma_8$ quartet ground state. It would be, then, very important to further investigate the interplay between the quadrupolar and Kondo couplings in this compound, as postulated for $CeB_6$.[7] Some more experiments are at present under way to clarify the nature of this anomaly and the results will be published elsewhere.

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