Anisotropic magnetic phase diagram of the Kondo-lattice compound $Ce_3Pd_{20}Ge_6$: Observation of antiferromagnetic and quadrupolar ordering

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From the measurement of the specific heat of single crystalline samples of $Ce_3Pd_{20}Ge_6$, we have constructed magnetic phase diagrams for a magnetic field up to 4 T, which disclose a pronounced anisotropy along the three principal directions of [100], [110], and [111]. We have found that both the quadrupolar and antiferromagnetic ordering temperatures exhibit distinct directional dependences on the external magnetic field and that new phase transitions evolve in the antiferromagnetic phase as well as in the ordered quadrupolar phase. These facts strongly suggest the existence of a complicated form of anisotropic interaction between the electric quadrupolar moment and the magnetic dipolar moment. The present result is briefly discussed in comparison with the reported one for CeB_6. [S0163-1829(98)04913-3]

Quadrupolar ordering has been observed in several Ce-, Pr-, Tm-, and U-based compounds.[1] For Ce-based compounds, quadrupolar ordering has been so far observed only in compounds with a Γ_8 quartet ground state which results from the splitting of $J=5/2$ multiplet of the Ce^{3+} ion under a cubic crystalline electric field. CeAg and CeB_6 are well-known compounds with the Γ_8 ground state: CeAg shows a ferroquadrupolar (FQ) ordering accompanied by a structural transition and a ferromagnetic ordering at 15.85 and 5.2 K, respectively,[2] and CeB_6 is believed to exhibit an antiferroquadrupolar (AFQ) ordering at 3.3 K and an antiferromagnetic (AFM) ordering at 2.3 K under the influence of the Kondo effect.[3,4] The latter compound has been extensively investigated in the last decade, but still remains controversial on several points, for example, concerning the type of order parameter realized in the AFQ phase, the origin of the strong magnetic field dependence of the AFQ ordering temperature T_Q, and the detailed interplay of the Kondo effect and quadrupolar effect. Several theories based on different models have been put forward to attempt to clarify these important questions about CeB_6.[5–9]

Similar AFQ and AFM orderings as in CeB_6 have been recently proposed for another Kondo-lattice compound $Ce_3Pd_{20}Ge_6$.[10] This compound crystallizes into a cubic structure of C_6Cr_{23} type with two inequivalent crystallographic sites for Ce atoms, both having a cubic symmetry (O_h and T_d),[11] and it is an AFM Kondo-lattice compound ($T_N=0.75$ K) with the Γ_8 ground state. In addition this compound shows a phase transition around 1.2 K detected by the specific-heat measurement, whereas the magnetic susceptibility does not exhibit any anomaly there. By slightly adjusting the composition we found that this anomaly in the specific heat is strongly correlated with the one at T_N. Furthermore, the temperature dependence of the specific heat resembles very much that of CeB_6. From these facts was it suggested that a quadrupolar ordering takes place around 1.2 K, as in CeB_6.[10] $Ce_3Pd_{20}Ge_6$ would then provide us with a good opportunity for further investigating the interplay between the AFQ ordering and the Kondo effect, and unresolved problems concerning CeB_6. We have already reported some preliminary experimental results,[12] but herein present more detailed experimental results exhibiting some evidence for a direct interaction between the magnetic dipolar and electric quadrupolar moments, obtained by a specific-heat measurement carried out on single-crystalline samples in external magnetic fields up to 4 T along the three principal directions of [100], [110], and [111]. We also give a brief discussion by comparing the present magnetic phase diagram with that of CeB_6.

Single crystals were grown by a Czochralski pulling method either in a tetra-arc furnace for sample No. 1 or in an induction furnace for sample No. 2. The specific heat was measured by a semiadiabatic heat-pulse method in a dilution refrigerator in the temperature range between 0.1 and 6 K. Most of the measurements were carried out with sample No. 2 except for the high-field data ($\geqslant 1$ T) of the [100] direction. Other characterizations about sample Nos. 1 and 2 are given in our previous report.[12]

Figure 1 exposes the temperature dependence of the specific heat, $C(T)$, for several magnetic fields applied along the [100] direction. The AFM ordering temperature T_N shifts to lower temperatures with increasing magnetic field as expected for ordinary antiferromagnets, but a small peak (denoted as T_3) sprouts below T_N around 0.5 T and outgrows the Néel peak above 0.9 T, fading out around 2 T (see the inset for $B=0.8$, 0.85, and 0.9 T). It should be noted here that the nature of the transition appears to change from the mean-field type at T_N to the λ-type at T_3. On the other hand, the conjectured quadrupolar ordering temperature T_1 slowly shifts to higher temperatures with a considerable breadth in magnetic fields. This broadening of the anomaly of $C(T)$ contrasts with the peculiar enhancement by the magnetic field observed for CeB_6.[13] Although several explanations have been proposed for the enhanced anomaly of $C(T)$ for CeB_6,[7] it is not well understood yet. At present, we do not know the reason for the contrasted behavior of these com-

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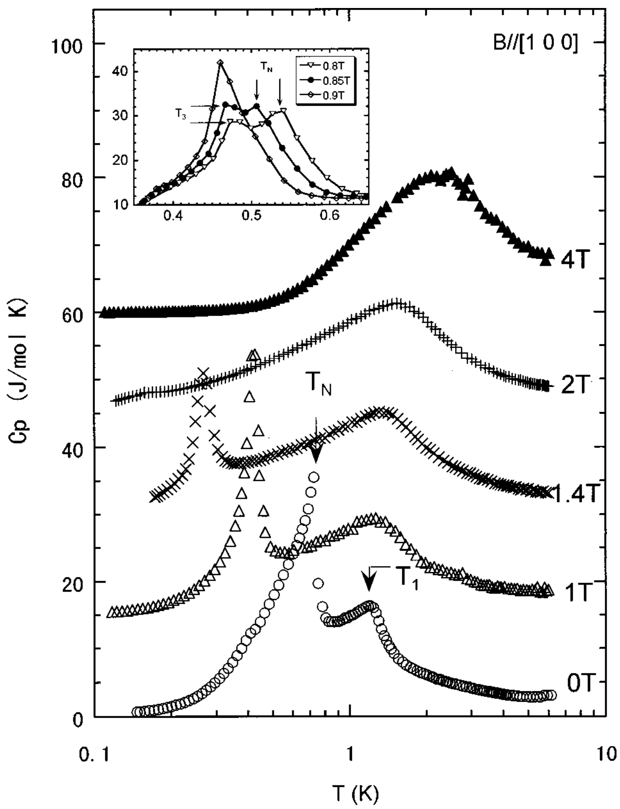

FIG. 1. Temperature dependence of the specific heat of $Ce_3Pd_{20}Ge_6$ in several external magnetic fields applied along the [100] direction. The origin for the ordinate is shifted by every 15 J/mol K for clarity. The inset shows the temperature dependence of the specific heat at 0.8, 0.85, and 0.9 T.

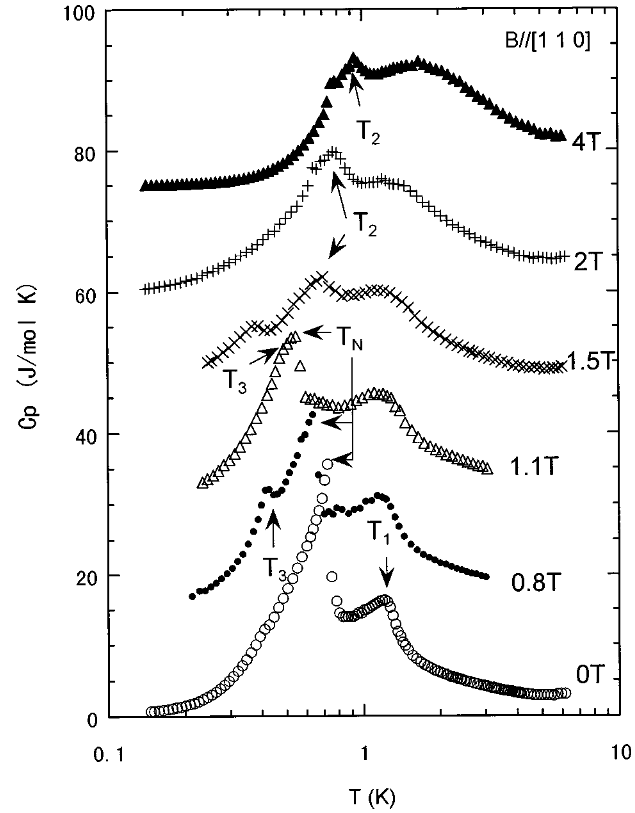

FIG. 2. Temperature dependence of the specific heat of $Ce_3Pd_{20}Ge_6$ in several external magnetic fields applied along the [110] direction. The origin for the ordinate is shifted by every 15 J/mol K for clarity.

pounds, but it may be attributed to the difference in the quality of the single crystals. Other possible causes will be discussed in the following.

Similar plots of $C(T)$ are shown in Figs. 2 and 3 for the [110] and [111] directions, respectively. T_N in both directions is gradually depressed by the magnetic field and lowered below 0.2 K above about 1.8 T. Below T_N a weaker anomaly is clearly recognized at T_3 also for these directions. It should be noticed further that another phase transition denoted by T_2 in the figures evolves above about 1.2 T. The anomaly at T_1 broadens considerably above 1 T for both directions as for [100], and in particular the assignment of T_1 along [111] becomes ambiguous around 3 T probably by the closeness to T_2. The anomaly at T_2 for both directions becomes distinct above around 1.5 T and has a slight tendency to shift to higher temperatures with the magnetic field, as can be seen in Figs. 2 and 3. We finally notice that there exists a faint inflection just below T_2 on the $C(T)$ curves around 4 T, which may not, however, be considered as a distinct phase transition. At present, we do not know what all these anomalies are, although T_3 has also been observed in magnetization experiments.[14] Neutron diffraction experiments in magnetic fields are awaited for a definitive clarification.

From the experimental results described above, the magnetic phase diagram for the three directions can be constructed as shown in Fig. 4, where we call the paramagnetic phase above T_1 as phase I, the quadrupolar phases between T_1 and T_N as phases II and II′, and the AFM one above and below T_3 as phases III and III′, respectively, after the magnetic phase diagram of CeB_6.[3] The very large anisotropic variation of T_N, T_1, T_2, and T_3 along the three principal directions is evident, rendering the phase diagram more complex than that of CeB_6. It is pointed out here that the variation of T_1 especially along [100] is not so linear as for CeB_6 up to 4 T and the anisotropic difference in T_1 attains about 0.8 K at 4 T, which is much bigger than that for CeB_6.[4] Although the phase diagrams along [110] and [111] are qualitatively identical, the different variation of T_N with the magnetic field and the absence of T_2 along [100] are particularly noteworthy, suggesting that there exists a very anisotropic interaction between the ordered magnetic dipolar moment and the electric quadrupolar moment. It is also pointed out that the appearance of the new phases II′ and III′ may be direct evidence for the interaction of the magnetic dipolar moment with the quadrupolar moment and it makes a sharp contrast with the phase diagram of CeB_6. The AFM phase of CeB_6 looks simpler than the present case.[15]

NMR and neutron diffraction experiments have confirmed that magnetic dipolar moments are induced in the phase II of CeB_6 by external magnetic fields,[16,17] although both results are contradictory on details. According to theories,[5,8] the existence of these induced magnetic dipolar moments is essential to account for some peculiar features of the magnetic phase diagram of CeB_6. It is therefore important to verify whether or not magnetic dipolar moments are also induced by the external magnetic field in the phase II and/or II′ of $Ce_3Pd_{20}Ge_6$. Furthermore, we notice therein that $T_{N[100]} < T_{N[110]} \lesssim T_{N[111]}$ and $T_{1[111]} \lesssim T_{1[110]} < T_{1[100]}$ generally

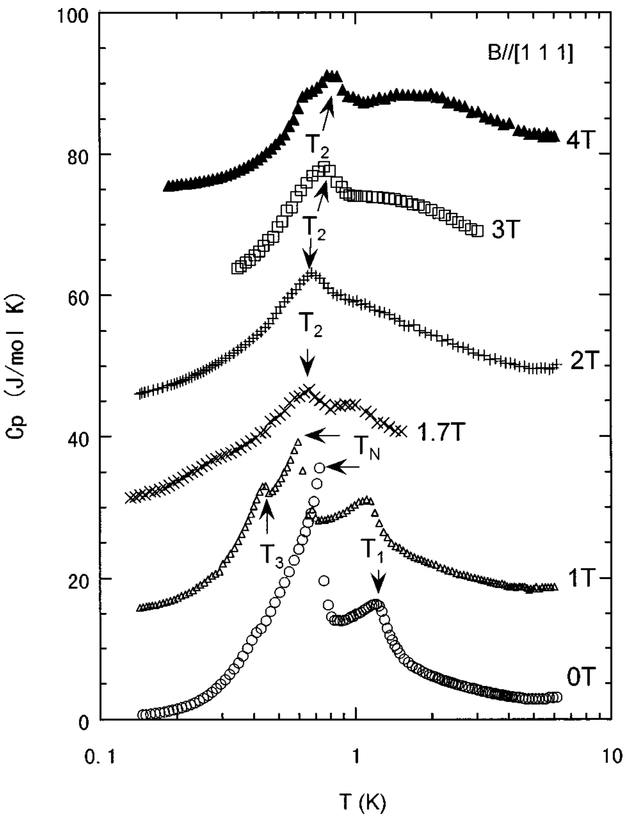

FIG. 3. Temperature dependence of the specific heat of $Ce_3Pd_{20}Ge_6$ in several external magnetic fields applied along the [111] direction. The origin for the ordinate is shifted by every 15 J/mol K for clarity.

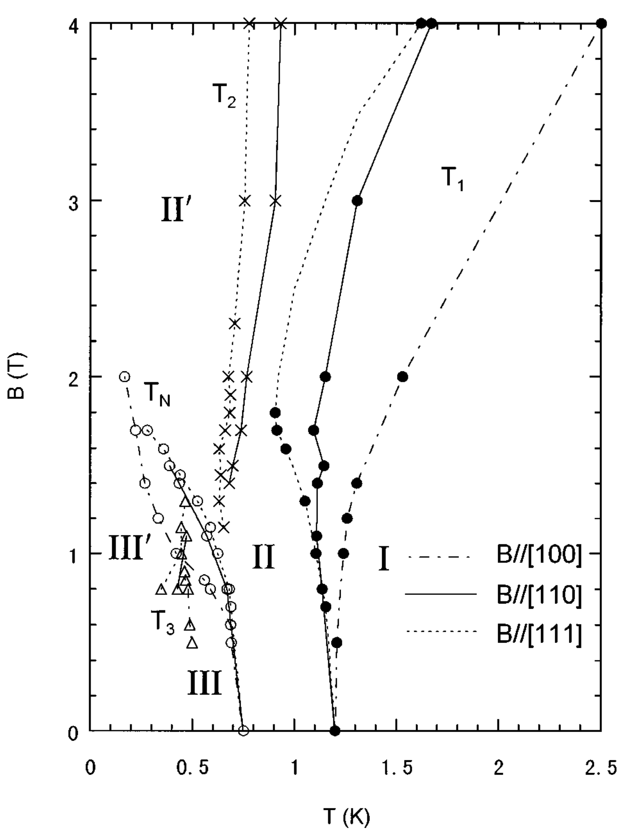

FIG. 4. Magnetic phase diagrams along the three principal directions of $Ce_3Pd_{20}Ge_6$. T_N, T_1, T_2, and T_3 are denoted by ○, ●, ×, and △, respectively.

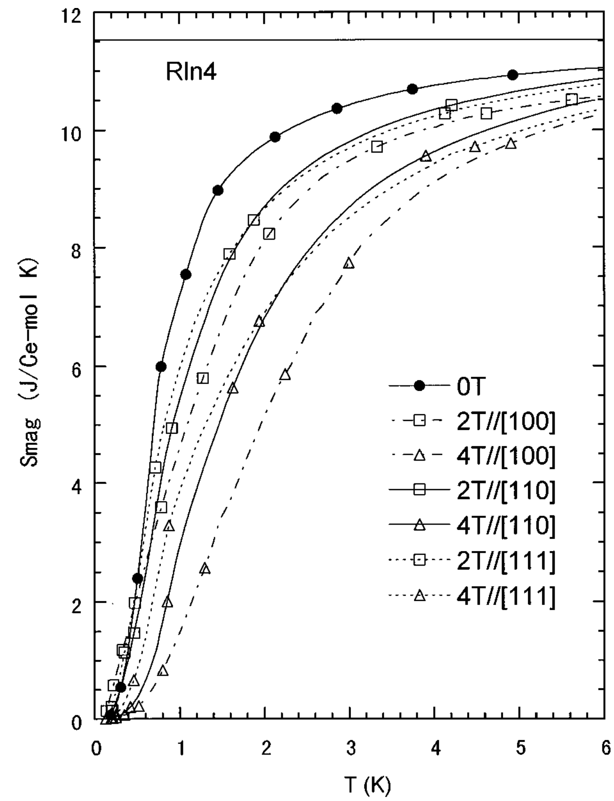

FIG. 5. Temperature dependence of S_{mag} per Ce ion of $Ce_3Pd_{20}Ge_6$ at 2 and 4 T applied along three principal directions. S_{mag} at 0 T is also shown for sample No. 2.

hold, i.e., ''an anticorrelation'' between T_N and T_1 at least in low magnetic fields (<1.5 T). This fact may indicate that the exchange interaction between magnetic dipolar moments and that between electric quadrupolar moments also compete with each other in the present compound, as pointed out for CeB_6.[4] It is interesting to note further that T_1 shifts to either lower or higher temperatures below about 2 T depending on the field direction, whereas it tends to increase above 2 T where AFM ordering is suppressed in all three directions. It may be considered to be consistent with the anticorrelation between T_N and T_1 just remarked above for low magnetic fields.

The temperature dependence of the magnetic entropy, $S_{mag}(T)$, at 0, 2, and 4 T up to 6 K is compared for the three directions in Fig. 5. Here $S_{mag}(T)$ is deduced by subtracting $C(T)$ of $La_3Pd_{20}Ge_6$ as the nonmagnetic part and by assuming it independent of the magnetic field. $S_{mag}(T)$ below about 0.1 K is neglected in the calculation because of its probable irrelevance to the discussion of the ground state. All curves tend to smoothly approach toward R ln 4 up to 6 K, and so one can conclude that $C(T)$ in a magnetic field up to 4 T shown in Figs. 1–3 really originates from the Γ_8 quartet ground state, as concluded earlier from the zero-field data.[10]

Although we have just seen above that $Ce_3Pd_{20}Ge_6$ and CeB_6 reveal a somewhat different magnetic phase diagram, it is interesting to note that they are akin to Kondo-lattice compounds with a close Kondo temperature (≈ a few degrees kelvin) (Refs. 3, 4, and 10) and T_Q (or T_1) $/T_N \sim 1.5$. The fact may signify that their low-temperature properties represented by the magnetic phase diagrams are governed by some similar mechanism. The induced magnetic dipolar moment which is observed for CeB_6 by neutron diffraction and NMR (Refs. 16 and 17) is the most characteristic and important fact of the AFQ phase under a magnetic field. So it is very important to verify whether such dipolar moments are also induced in $Ce_3Pd_{20}Ge_6$ and this may in turn provide useful information about the broadened anomaly at T_1 in a magnetic field. In this regard, one could not neglect possible contributions from the Zeeman splitting of the Γ_8 ground state or the Kondo effect. The measurement of $C(T)$ or other physical properties in a magnetic field higher than 4 T will be helpful to clarify the nature of this transition.

It is recently reported that CeB_6 also has an anisotropic magnetic-field dependence of T_Q,[4] although it is much smaller than that of T_1 in $Ce_3Pd_{20}Ge_6$. Moreover, the anisotropy seems to be reversed, i.e., $T_{Q[100]}<T_{Q[111]}<T_{Q[110]}$ and $T_{N[110]}<T_{N[111]}<T_{N[100]}$ for CeB_6,[4] while $T_{1[111]}<T_{1[110]}<T_{1[100]}$ and $T_{N[100]}<T_{N[110]}<T_{N[111]}$ for $Ce_3Pd_{20}Ge_6$, as described above. The anisotropy in both compounds seems, however, to be consistent with a picture of the competing AFM exchange interaction with the quadrupolar interaction. The difference of the anisotropy in these compounds may merely come from the difference in the crystal structure and/or the magnetic structure. It should be recalled that $Ce_3Pd_{20}Ge_6$ possesses a face-centered-cubic Ce sublattice in addition to the simple cubic one in CeB_6. The magnetic structure of $Ce_3Pd_{20}Ge_6$ should be resolved in any case for further discussions.

In summary, we have measured the $C(T)$ of $Ce_3Pd_{20}Ge_6$, which is a Kondo-lattice compound with AFM and quadrupolar ordering, in a magnetic field applied along [100], [110], and [111], and constructed a magnetic phase diagram which is much more complex than that of CeB_6. We found a large anisotropic magnetic-field dependence of T_N and T_1, and a new phase at lower temperatures in the AFM phase III for the three directions. For the [110] and [111] directions, we confirmed an extra new phase transition to evolve in the low-temperature region of the quadrupolar phase II. These results may be interpreted as a consequence of an interaction between the magnetic dipolar moments and the electric quadrupolar moments. It certainly needs more experiments to clarify the nature of these new phase transitions as well as the quadrupolar ordering and their relevance to the Kondo effect. A more complete version of the present work including results of magnetoresistance is planned to be published soon.

[1] P. Morin and D. Schmitt, in *Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (North-Holland, Amsterdam, 1990), Vol. 5, p. 1.

[2] P. Morin, J. Magn. Magn. Mater. **71**, 151 (1988).

[3] N. Sato, S. Kunii, I. Oguro, T. Komatsubara, and T. Kasuya, J. Phys. Soc. Jpn. **53**, 3967 (1984).

[4] For a more recent work, see, for example, M. Hiroi, M. Sera, N. Kobayashi, and S. Kunii, Phys. Rev. B **55**, 8339 (1997).

[5] F. J. Ohkawa, J. Phys. Soc. Jpn. **52**, 3897 (1983); **54**, 3909 (1985).

[6] K. Hanzawa and T. Kasuya, J. Phys. Soc. Jpn. **53**, 1809 (1984).

[7] G. Uimin, Y. Kuramoto, and N. Fukushima, Solid State Commun. **97**, 595 (1996); G. Uimin, Phys. Rev. B **55**, 8267 (1997).

[8] R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. **66**, 1741 (1997).

[9] O. Sakai, R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. **66**, 3005 (1997); R. Shiina, O. Sakai, H. Shiba, and P. Thalmeier (unpublished).

[10] J. Kitagawa, N. Takeda, and M. Ishikawa, Phys. Rev. B **53**, 5101 (1996).

[11] A. V. Gribanov, Yu. D. Seropegin, and O. I. Bodak, J. Alloys Compd. **204**, L9 (1994).

[12] J. Kitagawa, N. Takeda, M. Ishikawa, T. Yoshida, A. Ishiguro, and T. Komatsubara, Physica B **230-232**, 139 (1997); A. Ishiguro, M. Yasumoto, N. Sato, T. Yoshida, A. Sawada, M. Suzuki, O. Sugie, M. Ishikawa, and T. Komatsubara, *ibid.* **230-232**, 142 (1997).

[13] Y. Peysson, C. Ayache, B. Salce, J. Rossat-Mignod, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **47&48**, 63 (1985).

[14] T. Sakon, H. Nojiri, A. Ishiguro, N. Tateiwa, A. Sawada, T. Komatsubara, and M. Motokawa (unpublished).

[15] T. Tayama, T. Sakakibara, K. Tenya, H. Amitsuka, and S. Kunii, J. Phys. Soc. Jpn. **66**, 2268 (1997); T. Sakakibara (private communication).

[16] J. M. Effantin, J. Rossat-Mignod, P. Burlet, H. Bartholin, S. Kunii, and T. Kasuya, J. Magn. Magn. Mater. **47&48**, 145 (1985).

[17] M. Takigawa, H. Yasuoka, T. Tanaka, and Y. Ishizawa, J. Phys. Soc. Jpn. **52**, 728 (1983).