Pressure-induced phase transitions in PrB_6: Electrical resistivity measurements

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We have studied the electrical resistivity of PrB_6 under pressure up to $P=0.8$ GPa, with magnetic fields applied along the [001] and [111] directions. The commensurate (C) magnetic ordered phase is significantly stabilized by pressure, and another extra phase (denoted phase A) is observed under a low pressure of ~0.3 GPa. This phase appears above the transition temperature $T_{IC1}=7$ K at which the incommensurate magnetic order sets in at the ambient pressure. The magnetic phase diagram for $H\parallel[111]$ changes drastically under pressure. Short-range interactions, which are strongly dependent on the Pr-Pr distances, are likely to play a dominant role in the relative stability of the different phases.

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Multipole order is one of the recent topics in the f electron systems. RB_6 (R=rare-earth element) is a good system to study the multipole interactions because of the cubic simple crystal structure. The crystalline electric-field (CEF) level schemes of CeB_6, PrB_6, and NdB_6 are known and the CEF ground state of these compounds contains the multipole degrees of freedom.[1] It is well known that CeB_6 exhibits the unusual antiferroquadrupole (AFQ) order dominated by the O_{xy}-type AFQ and T_{xyz}-antiferro-octupole interactions.[2–4] Here, $O_{xy}=\sqrt{3}/2\,\overline{J_xJ_y}$ and $T_{xyz}=\sqrt{15}/6\,\overline{J_xJ_yJ_z}$ where the bars denote the sums of all possible permutations of indices. In CeB_6, there exist three phases called as I, II, and III. Phase I is paramagnetic. Phase II below $T_Q=3.2$ K is the O_{xy}-type AFQ ordered phase with the wave vector $\mathbf{Q}=[1/2,1/2,1/2]$. Phase III below $T_N=2.3$ K is the noncollinear magnetic ordered phase with the wave vectors $\mathbf{k}^{(1,2)}=[1/4,\pm1/4,1/2]$ and $\mathbf{k}'^{(1,2)}=[1/4,\pm1/4,0]$, which is dominated by the O_{xy}-type AFQ order.[2] In PrB_6 and NdB_6, while the dipole interaction is dominant, the magnetic structures are affected by the higher order multipole interactions.

In PrB_6, there exist four magnetic ordered phases of C, IC1, IC2, and C_H as are shown in Fig. 1(a).[5–9] We define the transition temperature from the paramagnetic to IC1 phase as T_{IC1} and that from the IC1 to C phase as T_N. The C phase is the commensurate (C), double-**k** magnetic ordered phase with the wave vectors $\mathbf{k}_C^{(1,2)}=[1/4,\pm1/4,1/2]$, where the nonclolinear alignment of the magnetic moment with the easy axis along the twofold one is realized.[5] The magnetic structure in the C phase is similar to that in phase III of CeB_6. This similarity strongly suggests the importance of the O_{xy}-type AFQ interaction also in PrB_6. The IC1 phase is the incommensurate (IC), double-**k** magnetic ordered phase with the wave vectors $\mathbf{k}_{IC1}^{(1,2)}=[1/4-\delta,\pm1/4,1/2]$, where $\delta=0.05$.[5] At $H=0$, there exist the planar-type three domains of K_{xy}, K_{yz}, and K_{zx}. The K_{xy} domain is dominated by the O_{xy}-AFQ order, etc. In the IC1 phase, there exist K_{xy}^{IC1}, K_{yz}^{IC1}, and K_{zx}^{IC1}. The magnetic phase diagram for $H\parallel[001]$ is normal as is observed in a usual antiferromagnetic (AF) magnet where T_N decreases with decreasing magnetic field. The magnetic phase diagram for $H\parallel[110]$ is similar to that for $H\parallel[001]$. However, that for $H\parallel[111]$ is unusual. T_N shows the unusual increase from $H\sim2$ to ~10 T and the IC phase is divided into two phases of IC1 and IC2 below and above $H\sim8$ T. The IC2 phase appears above 8 T in a narrow magnetic-field direction around $H\parallel[111]$. Very recently, the IC2 phase was proved to be the incommensurate, single-**k** magnetic ordered phase with the wave vector $\mathbf{k}_{IC2}=[1/4-\delta',1/4-\delta',1/2]$.[10] The C_H phase appears for $H\parallel[110]$ and [111] above $H\sim1$ T but not for $H\parallel[001]$. For $H\parallel[001]$, the K_{xy} single domain state is realized at low magnetic fields and continues to exist up to high fields where the $\chi_\perp$ configuration with a larger Zeeman energy gain is realized. Here, the $\chi_\perp$ configuration means the domain state where the $\chi_\parallel$ component disappears and $\chi_\perp$ component remains by applying magnetic field. In the C phase for $H\parallel[110]$ and [111], the domains containing the $\chi_\parallel$ component with a smaller Zeeman energy gain inevitably exist. To get the larger Zeeman energy gain, the C phase is changed to the C_H phase at $H\sim2$ T. In the C_H phase for $H\parallel[110]$, the neutron-diffraction experiment showed that the single-**k** magnetic structure with the $\chi_\perp$ configuration is realized.[5] In the C_H phase, the large lattice distortion along the magnetic-field direction was observed.[9] These results strongly suggest that the single domain state of the O_{xy}-ferroquadrupole (FQ) order is realized in the C_H phase. Figure 1(b) shows the magnetic phase diagram of $Pr_{0.8}La_{0.2}B_6$.[11] The C phase does not exist at $H=0$ and the ground state is the IC1 phase. This indicates that T_N is rapidly suppressed by La doping. For $H\parallel[001]$ and [110], there exists only the IC1 phase. For $H\parallel[111]$, the C phase

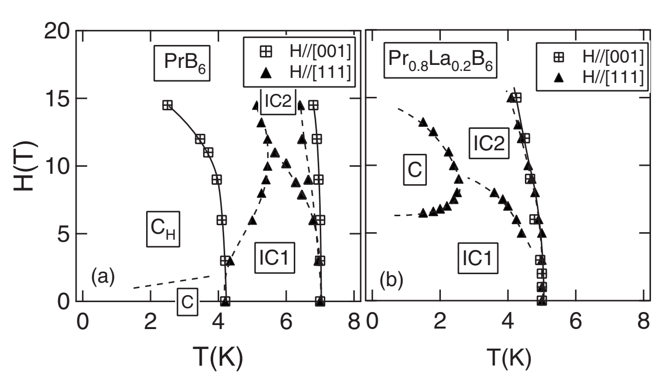

FIG. 1. Magnetic phase diagram of (a) PrB_6 (Ref. 7) and (b) $Pr_{0.8}La_{0.2}B_6$ (Ref. 11) at the ambient pressure. As for four phases of C, IC1, IC2, and C_H and the C-C_H phase boundary for $H\parallel[111]$ indicated by a dashed line below 4 K, see the text in details.

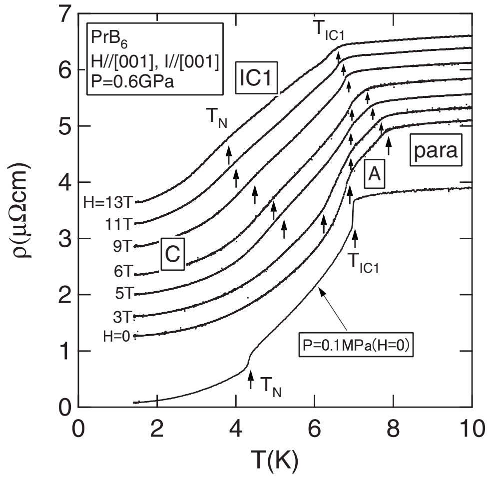

FIG. 2. Temperature dependence of the electrical resistivity of PrB_6 for $H \| [100]$ under the pressure of $P=0.6$ GPa. The result at the ambient pressure at $H=0$ is also shown. The origin of the vertical axis is shifted in each curve. The transition temperatures are shown by arrows.

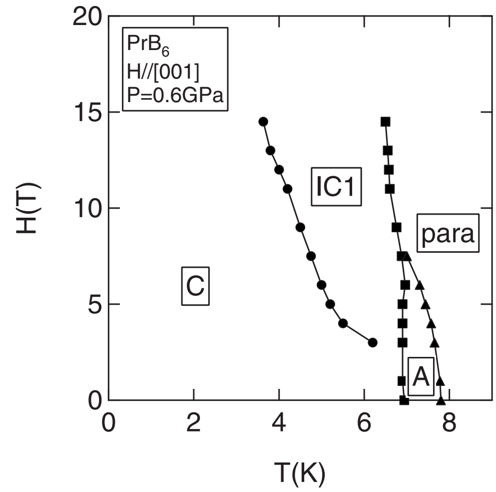

FIG. 3. Magnetic phase diagram of PrB_6 for $H \| [001]$ under the pressure of $P=0.6$ GPa.

exists in finite magnetic fields at low temperatures and the critical field from the IC1 to IC2 phase is shifted down to lower magnetic fields.

Although the O_{xy}-AFQ interaction plays an important role both in CeB_6 and PrB_6, there exists the difference in the ordering vector. The **Q**-vectors of the AFQ interaction are [1/2,1/2,0] in the C phase of PrB_6 and [1/2,1/2,0] in phases II and III in CeB_6.[6–8] The ordering of $\mathbf{Q}=[1/2,1/2,1/2]$ is easily realized when the nearest-neighbor (nn) AFQ interaction is dominant but in the case of $\mathbf{Q}=[1/2,1/2,0]$, at least, the contribution from the second nn AFQ interaction is necessary. In such a situation, it is interesting to study the pressure effect of PrB_6 and compare the results with those of CeB_6.[12–14]

The single crystals of PrB_6 used in the present study were prepared by a floating zone melting method by using an image furnace with four xenon lamps.[15] The electrical resistivity under pressure was measured by a standard four-probe ac method in magnetic fields up to 14.5 T along the [001] and [111] directions using a usual piston cylinder. The magnitude of the applied pressure was determined by measuring the superconducting transition temperature of Sn.

Figures 2 and 3 show the temperature (T) dependence of the electrical resistivity ρ and the magnetic phase diagram of PrB_6 for $H \| [001]$ under pressure of $P=0.6$ GPa, respectively. In Fig. 2, the result at the ambient pressure at $H=0$ is also shown. Before discussing the present results, we summarize the results at the ambient pressure briefly. With a decrease in temperature at $H=0$, ρ shows a discontinuous decrease both at T_{IC} and T_N.[7] T_N is suppressed by magnetic field and seems to disappear at $H=17\sim18$ T, while T_{IC} is almost constant up to $H=15$ T. The T dependence of ρ in the ordered phase changes largely by applying pressure. At $H=0$, a concave T dependence is observed in ρ up to ~7 K without showing any anomaly. However, above 7 K, we found the appearance of the phase. Hereafter, we call it the A phase and the transition temperature T_N^A. While $T_{IC1}\sim7$ K is little affected by magnetic field, T_N^A shows a suppression with increasing magnetic field and coincides with T_{IC} at ~8 T. It is also clearly seen that the C phase is expanded largely at low magnetic fields under pressure.

Figures 4 and 5 show the magnetoresistance and magnetic phase diagram of PrB_6 for $H \| [111]$ under the pressure of $P=0.35$ GPa, respectively. Both results are unusual. The magnetoresistance is very different from that at the ambient pressure. At the ambient pressure, ρ shows a monotonic increase with increasing magnetic field in the C phase, which is seen in Fig. 5(b) of Ref. 7. However, in the present case, the unexpected anomalous broad maximum appears between $H\sim6$ and ~9 T at $T=1.5$ K and the magnetic-field region of this broad maximum expands with increasing temperature. Thus, three phases appear as a function of magnetic field at low temperatures. We call the phase at high fields above the broad maximum the C′ phase. The low-field region is considered to be the C phase from the T dependence of ρ at low magnetic fields and the magnetic phase diagram for $H \| [001]$. If the broad maximum of ρ around $H\sim7$ T does

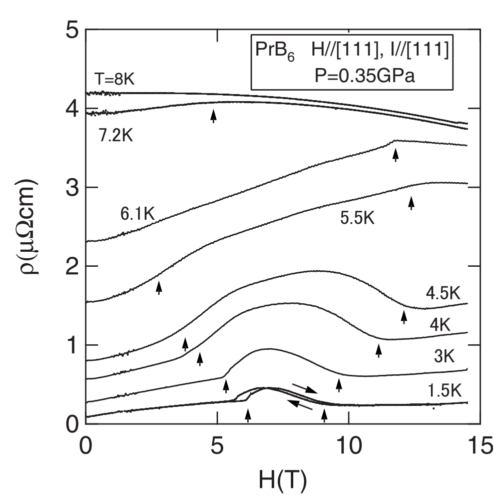

FIG. 4. Temperature dependence of the electrical resistivity of PrB_6 for $H \| [111]$ under the pressure of $P=0.35$ GPa.

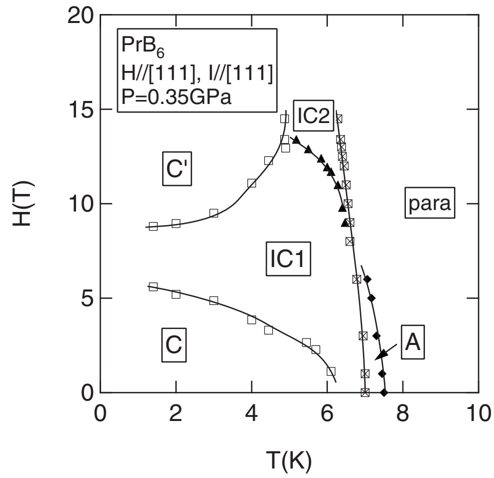

FIG. 5. Magnetic phase diagram of PrB_6 for $H\|[111]$ under the pressure of $P=0.35$ GPa.

not exist, the H dependence of ρ at low fields is connected continuously to that at high fields. Namely, ρ shows the monotonic increase with magnetic field as is observed in PrB_6.[7] Thus, we conjecture that the C′ phase has the same nature as that in the C_H phase at the ambient pressure. Namely, the C and C_H phases at the ambient pressure are separated into C and C′ phases by the intrusion of the intermediate phase characterized by the broad maximum of ρ. From the large electrical resistivity, which is expected from the IC magnetic ordered phase and the magnetic phase diagram of Fig. 5, the intermediate phase is assigned to the IC1 magnetic ordered one. The magnetic-field region of this IC1 phase expands with increasing temperature. Another phase A is recognized above T_{IC} from the similar temperature dependence of ρ for $H\|[001]$ shown in Fig. 2. The critical field from IC1 to IC2 is pushed up to higher fields by applying pressure.

Figures 6(a) and 6(b) show the x dependence of the transition temperatures of $Pr_xLa_{1-x}B_6$ (Ref. 11) and the pressure dependence of those of PrB_6, respectively. In $Pr_xLa_{1-x}B_6$, while T_{IC1} seems to exist down to $x\sim0.4$, T_N is very rapidly suppressed and does not exist already at $x=0.8$. While all the Pr-Pr interactions should be suppressed by La doping, the suppression rates are different. The larger suppression of T_Q

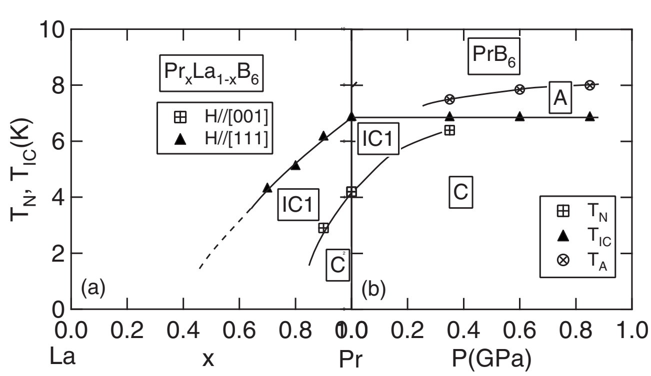

FIG. 6. (a) x dependence of the transition temperatures of $Pr_xLa_{1-x}B_6$ (Ref. 11) and (b) the pressure dependence of those of PrB_6.

than T_N by La doping was observed also in $Ce_xLa_{1-x}B_6$.[16] These indicate that the magnetic order coexisting with the quadrupole order in the C phase is weak for the local lattice disturbance because the quadrupole moment is accompanied with the anisotropic charge cloud.[11] When the pressure is applied, T_N is rapidly enhanced and seems to coincide with T_{IC} at $P\sim0.4$ GPa. On the other hand, T_{IC} is surprisingly insensitive to the pressure. T_N^A appears above the IC1 phase at very small pressure of ~0.2 GPa and increases with increasing pressure.

Now, we discuss the following points of the pressure effect on PrB_6: (1) the stabilization of the C phase, (2) the unusual magnetic phase diagram for $H\|[111]$ shown in Fig. 5, and (3) the order parameter in the discovered A phase which appears above T_{IC}.

(1) The pressure makes the Pr-Pr distance shorter and generally we expect that this shrinkage modifies the magnitudes of the exchange and quadrupole interactions. From the results of Figs. 6(a) and 6(b), it is clearly found that the stability of the C phase is much more sensitive to the Pr-Pr distance than that in the IC1 phase. The C phase becomes unstable by expanding the Pr-Pr distance and stable by shrinking it. Here, we propose the following explanation for the stability of the C phase. The pressure sensitive phase transition between C and IC1 indicates that the nn interaction is important to determine the magnetic order of the C phase. We note that this is not the case for the IC1 phase where the interaction has the nature of the long-range one. In the C phase, the O_{xy}-type AFQ interaction plays an important role. As mentioned before, the **Q** vector of the O_{xy}-type AFQ interaction in the C phase is [1/2,1/2,0] and that in phases II and III of CeB_6 is [1/2,1/2,0]. In both cases, there exist three planar types of K_{xy}, K_{yz}, and K_{zx} domains and the nn intraplane magnetic moments in each domain are orthogonal to each other. On the other hand, the interplane magnetic-moment alignment is different between the C phase of PrB_6 and phase III of CeB_6. In the latter, the nn interplane magnetic moments are also orthogonal to each other. In the former, those are not orthogonal but antiparallel to each other. Then, it is expected that when the interplane nn Pr-Pr distance in the C phase is reduced by applying pressure, the interplane nn AF exchange energy gain is enhanced. Here, we conjecture that the tetragonality of each domain is enhanced and the easy-plane magnetic anisotropy is enhanced under pressure. On the other hand, in phase III of CeB_6, as the interplane nearest-neighbor magnetic moments are orthogonal to each other, the AF exchange energy gain is not expected. This is consistent with the suppression of phase III by pressure.[12] Here, we comment on the difference of the stability between the C and IC1 phases at $H=0$. In both phases, the nn interplane magnetic moments are antiparallel to each other. However, the in-plane quadrupole moment alignment is different. It is orthogonal to each other in the C phase but is the IC alignment in the IC1 phase. Then, we expect that the energy gain due to the AFQ interaction is larger in the C phase than in the IC1 phase. This may be the reason why the C phase is more stable than the IC1 phase under pressure.

(2) The magnetic phase diagram for $H\|[111]$ in Fig. 5 looks quite unusual. However, if we see it from the following

standpoint, it is found to be not so strange. The C-IC1-C′ successive phase transitions with the increase in magnetic field occur at low temperatures under pressure, while at the ambient pressure the direct C-C_H transition occurs. When we compare these results, the C-C_H phase boundary at the ambient pressure seems to be replaced by the IC1 phase under pressure because the C′ phase is considered as the same phase as C_H. Now, we discuss the origin of the unusual phase boundaries of the magnetic phase diagram in Fig. 5. At low magnetic fields for $H \parallel [111]$, three domains of K_{xy}, K_{yz}, K_{zx} and K_{xy}^{IC1}, K_{yz}^{IC1}, K_{zx}^{IC1} exist in the C and IC1 phase, respectively. In the C and IC1 phases, both $\chi_\parallel$ and $\chi_\perp$ components exist. However, in the C′ phase the single domain dominated by the O_{xy}-FQ order is realized, where there exists only the $\chi_\perp$ component. Therefore, at high magnetic fields, the C′ phase is the most stable because of the largest Zeeman energy gain. The IC1-C′ phase transition occurs at $H \sim 9$ T with a positive slope of dT_N'/dH. This is related to $M_{IC1} < M_{C'}$. The present results show that under pressure, the C phase becomes more stable at $H=0$, where there exist three domains and the easy-plane magnetic anisotropy is larger than that at the ambient pressure. However, with increasing magnetic field, the C phase becomes unstable because the small Zeeman energy gain due to the enhanced $\chi_\parallel$ component increases and the energy difference between C and C′ increases. Thus, the enhanced energy difference between these two phases makes it possible for the IC1 phase to invade between the C and C′ phases, as a buffer, in place of the direct C-C_H phase boundary at the ambient pressure. As for the IC1 and IC2 phases, the experiment shows that the IC1 phase is more stable than the IC2 phase under pressure. This is consistent with the reduction in the IC1-IC2 critical field of $Pr_xLa_{1-x}B_6$ with decreasing x, which increases the Pr-Pr distance.

(3) When we consider the candidate for the order parameter in the A phase, the following two points should be taken into account. One is that ρ in the A phase is smaller than that in the paramagnetic phase and larger than those in the C and IC1 phases. The other is that the appearance of the A phase is very sensitive to the pressure. The smaller ρ than that in the paramagnetic phase indicates the reduction in the magnetic scattering indicates the reduction in the magnetic scattering in the A phase which may be caused by the lifting of the threefold degeneracies in the CEF ground state. Also by considering the larger ρ than those in the C and IC1 phases, the IC magnetic order or the quadrupole one is considered as the candidate. The pressure sensitive appearance of the A phase suggests that the interaction forming the A phase is that of the short range. Then, the IC magnetic order dominated by the quadrupole interaction or the quadrupole order is considered as the candidate. However, at present, it is difficult to determine the order parameter in the A phase. Further studies are necessary to clarify the nature of the A phase.

In summary, the electrical resistivity of PrB_6 under pressure was investigated. We found that the C phase was significantly stabilized by pressure and phase A appears above T_{IC1} by only a small pressure. The magnetic phase diagram for $H \parallel [111]$ changes drastically under pressure. These indicate the importance of the short-range interactions in the C and A phases in PrB_6.

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