Competition between ferromagnetic and antiferromagnetic interactions in Pr$_{1-x}$Gd$_x$B$_4$

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Abstract. We have prepared single crystals of Pr$_{1-x}$R$_x$B$_4$ (R = La, Ce and Gd) and measured the magnetic susceptibility and specific heat in order to elucidate the origin of the ferromagnetic interaction in PrB$_4$ and the competition of the ferro- and antiferromagnetic interactions in this system. The ferromagnetic transition temperature decreases with x at nearly the same rate in Pr$_{1-x}$La$_x$B$_4$ and Pr$_{1-x}$Gd$_x$B$_4$, suggesting that the magnetic moments of Gd do not affect the ferromagnetic order. In Pr$_{0.6}$Gd$_{0.4}$B$_4$ and Pr$_{0.8}$Gd$_{0.2}$B$_4$, ferromagnetic to antiferromagnetic transitions appear with decreasing temperature. The development of antiferromagnetic correlation between Pr and Gd breaks the ferromagnetic order and induces antiferromagnetic correlation among Pr atoms. These results indicate that two types of magnetic interactions with different origin are present in PrB$_4$.

1. Introduction
Investigation of basic physical properties of rare earth metal tetraboride RB$_4$ family started more than 30 years ago and continued extensively within the next decade [1-4]. After that, the discovery of the geometrical frustration of quadrupole moments of 4f electrons in DyB$_4$ [5] triggered the re-examination of physical properties of rare earth metal tetraborides RB$_4$ in the viewpoint of multipolar ordering [6-8]. Among RB$_4$ containing magnetic R elements, only PrB$_4$ shows a ferromagnetic transition with the transition temperature $T_c = 23$ K [2]. The origin of the strong ferromagnetic interactions appearing in PrB$_4$ and its relatively high $T_c$ in comparison with that considered from the de Gennes factor have been studied but are still under discussion [9]. In order to investigate these problems, we have prepared single crystals of Pr$_{1-x}$R$_x$B$_4$ (R = La, Ce and Gd), where LaB$_4$ and CeB$_4$ are Pauli paramagnets and GdB$_4$ is an antiferromagnet ($T_N = 42$ K) [2], by a self-flux method and have studied physical properties by means of magnetic susceptibility and specific heat measurements.

2. Experimental
Single crystals of Pr$_{1-x}$R$_x$B$_4$ (R = La, Ce and Gd) were prepared by arc melting with excess amounts of rare earth metals to boron. Crystals were grown in a melt after one cycle of heating-cooling process where the excess rare earth metals acted as flux. The crystals were picked up from the melt by dissolving the excess rare earth metals in diluted hydrochloric acid. The size of the single crystals obtained in this method is up to $2 \times 2 \times 0.5$ mm$^3$. The stoichiometry of the single crystals was examined using the (004)-X-ray diffraction peak by applying the Vegard’s law; and it was very close to the starting ratio of Pr : R. The X-ray diffraction peaks are as narrow as those of PrB$_4$ so that there is no distinct distribution of the chemical composition x in a crystal. The magnetic susceptibility and magnetization curves of Pr$_{1-x}$R$_x$B$_4$ were measured using a SQUID magnetometer in the temperature
range from 1.8 to 300 K, and the magnetization curves were recorded at 1.8 K in fields up to 5 T. The specific heat measurement was carried out by the heat-relaxation method down to 2.0 K. The magnetic transition temperatures of Pr\(_{1-x}\)Gd\(_x\)B\(_4\) are defined by the heat capacity (\(x = 0, 0.15, 0.2, 0.25\) and 0.3) or the magnetization (\(x = 0.18\) and 0.22).

3. Results and discussion

Figures 1 and 2 show the temperature dependence of the magnetization divided by magnetic field \(M/B\) for zero-field cooling (ZFC) and field-cooling (FC) processes, as well as the magnetization curves at 1.8 K for Pr\(_{1-x}\)Gd\(_x\)B\(_4\) (\(x = 0, 0.15, 0.18, 0.2, 0.22, 0.25\) and 0.3).

The magnetization of PrB\(_4\) (\(x = 0\)) steeply increases with decreasing temperature and saturates below the ferromagnetic transition temperature of \(T_c = 23.0\) K. The easy axis of the magnetization is the \(c\)-axis as a result of the crystalline electric field splitting of the 4f states of Pr. It should be noted that the magnetizations below \(T_c\) after the FC or ZFC processes show nearly the same behaviours and there is no hysteresis in the magnetization curves. Such behaviours characteristic for “soft” magnets are unusual for the ferromagnets with strong single-ion magnetic anisotropy, because significant energy is required to rotate magnetic domains toward the direction of the applied magnetic fields.

The ferromagnetic behaviour is found for Pr\(_{0.85}\)Gd\(_{0.15}\)B\(_4\) (\(T_c = 19.5\) K), Pr\(_{0.82}\)Gd\(_{0.18}\)B\(_4\) (\(T_c = 19.0\) K) and Pr\(_{0.8}\)Gd\(_{0.2}\)B\(_4\) (\(T_c = 18.2\) K). In Pr\(_{0.85}\)Gd\(_{0.15}\)B\(_4\) (\(x = 0.15\)), difference of magnetization in the FC and ZFC process appears below 13 K, provably originating from the pinning of magnetic domains by the introduction of Gd. The magnetization curves of Pr\(_{0.85}\)Gd\(_{0.15}\)B\(_4\) exhibit a small hysteresis with the coercive force of 0.05 T. In Pr\(_{0.82}\)Gd\(_{0.18}\)B\(_4\) (\(x = 0.18\)) and Pr\(_{0.8}\)Gd\(_{0.2}\)B\(_4\) (\(x = 0.2\)), the magnetization shows a ferromagnetic plateau below \(T_c\) and then it abruptly decreases to get into an antiferromagnetic state at \(T_N = 7.5\) and 10.7 K, respectively. The antiferromagnetic states below \(T_N\) are confirmed by the presence of the metamagnetic transition seen in the magnetization curves at the critical magnetic field of \(B_c = 0.4\) T for \(x = 0.18\) and \(B_c = 0.5\) T for \(x = 0.2\). These ferromagnetic to antiferromagnetic transitions suggest that the evolution of the antiferromagnetic correlation between the magnetic moments of Pr and Gd breaks the ferromagnetic order of Pr and even induces the antiferromagnetic correlation among the magnetic moments of Pr.

The magnetization of Pr\(_{0.78}\)Gd\(_{0.22}\)B\(_4\) (\(x = 0.22\)), Pr\(_{0.75}\)Gd\(_{0.25}\)B\(_4\) (\(x = 0.25\)) and Pr\(_{0.7}\)Gd\(_{0.3}\)B\(_4\) (\(x = 0.3\))

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** Temperature dependence of the magnetization divided by magnetic field \(M/B\) for Pr\(_{1-x}\)Gd\(_x\)B\(_4\).

**Figure 2.** Magnetization curves of Pr\(_{1-x}\)Gd\(_x\)B\(_4\).
shows a sharp cusp at $T_N = 17.0$, 18.8 and 21.5 K, respectively. The low-temperature phase is antiferromagnetic, which is also assured by the presence of metamagnetic transition at $B_c = 1.0$, 1.8 and 2.5 T, respectively. The sharp cusp of the magnetization indicates that, with decreasing temperature, the ferromagnetic correlation among the magnetic moments of Pr is developed but, before occurrence of ferromagnetic order, the Pr-Gd antiferromagnetic interactions overcome the Pr-Pr ferromagnetic interactions to go into the antiferromagnetic phase without undergoing the ferromagnetic state.

Above the critical magnetic field of the metamagnetic transition $B_c$ for Pr$_{1-x}$Gd$_x$B$_4$ with $x > 0.18$, the magnetization gradually increases with magnetic field, in contrast to the behaviour of PrB$_4$. In the antiferromagnetic phase, the magnetic moments of Pr and Gd are both antiferromagnetically arranged. Above $B_c$, the magnetic moments of Pr are directly flipped to the direction of the external magnetic field because of the Ising-like single-ion anisotropy of Pr 4f moments due to the crystalline electric field. On the other hand, the single-ion anisotropy of Gd is very small since the Gd$^{3+}$ ion does not have orbital angular momentum $L$. In this case, the magnetic moments of Gd are considered to have a spin-flop state above $B_c$, namely, the magnetic moments of Gd are nearly perpendicular to the direction of the external magnetic field. The increase of the magnetization above $B_c$ can be explained in terms of the contribution of the spin-flopped magnetic moments of Gd.

Figure 3 is the temperature dependence of the magnetic specific heat of Pr$_{1-x}$Gd$_x$B$_4$ ($x = 0$, 0.15, 0.2, 0.25 and 0.3). For all the compounds, the main peaks, corresponding to the transition from paramagnetic to ordered phase, are $\lambda$-type, indicating that the transitions are of second order. In comparison with PrB$_4$, the specific heat of Pr$_{0.85}$Gd$_{0.15}$B$_4$ has large values below $T_c$ and shows a broad peak at around 5 K. The low-temperature contribution of the specific heat can be attributed to the remaining magnetic entropy of Gd below $T_c$, namely, the magnetic moments of Gd are not ordered but paramagnetic even though they feel strong internal magnetic field from surrounding ferromagnetic moments of Pr.

The specific heat of Pr$_{0.8}$Gd$_{0.2}$B$_4$ shows additional two peaks at 12.5 and 10.7 K, the latter corresponding to the antiferromagnetic transition temperature $T_N$. The peak shape of the specific heat at 12.5 K suggests that the transition is of first order. From our limited experimental data, further discussion of the intermediate phase is limited. Complicated magnetic phases are expected to exist between the ferromagnetic and antiferromagnetic phases in this system.

Figure 4 shows the summarized phase diagram of Pr$_{1-x}$Gd$_x$B$_4$. The variations of the ferromagnetic transition temperature of Pr$_{1-x}$La$_x$B$_4$ and Pr$_{1-x}$Ce$_x$B$_4$ are also illustrated.
Considering all the experimental results, we may conclude that there exist two, almost independent types of magnetic interactions in PrB$_4$. One is the antiferromagnetic interaction, which commonly exists in magnetic RB$_4$ and is mediated by conduction electron (the RKKY interaction). Another is additional ferromagnetic interaction explicitly appearing only in PrB$_4$. The transition temperature is determined by the competition of these two types of interactions.

In Pr$_{1-x}$R$_x$B$_4$, the elements La, Pr and Gd are present as R$^{3+}$ ions, while Ce as nonmagnetic R$^{4+}$ ions. Therefore, the Pr ions are replaced by nonmagnetic ions both in Pr$_{1-x}$La$_x$B$_4$ and Pr$_{1-x}$Ce$_x$B$_4$ and the conduction carrier density is changed in Pr$_{1-x}$Ce$_x$B$_4$ but not in Pr$_{1-x}$La$_x$B$_4$. As seen in figure 4, the ferromagnetic transition temperature drops more rapidly in Pr$_{1-x}$Ce$_x$B$_4$ than in Pr$_{1-x}$La$_x$B$_4$. Therefore, the increase of the carrier density enhances the antiferromagnetic interaction among the Pr ions and increases the competition between ferro- and antiferromagnetic interactions, resulting in the rapid drop of $T_c$ in Pr$_{1-x}$Ce$_x$B$_4$.

In Pr$_{1-x}$Gd$_x$B$_4$, the ferromagnetic transition temperature $T_c$ shows nearly the same variation with $x$ as in Pr$_{1-x}$La$_x$B$_4$. The result means that the Gd$^{3+}$ ions behave like nonmagnetic La$^{3+}$ ions and the magnetic moments of Gd do not affect the ferromagnetic ordering, namely, the magnetic moments of Gd stay in the paramagnetic state even the magnetic moments of Pr are in the ferromagnetic state.

If ferro- and antiferromagnetic interactions in Pr$_{1-x}$Gd$_x$B$_4$ directly compete with each other, it is expected that $T_c$ drops much more rapidly and disappears, and then, antiferromagnetic order appears with increasing $x$. Alternatively, the ferromagnetic transition disappears and instead the spin-glassy state appears in a specific range of $x$, as a result of frustration due to the competing interactions. As shown in the phase diagram, even within the ferromagnetic state, the antiferromagnetic correlation between Pr and Gd seems to develop independently of the ferromagnetic correlation. Therefore, the ferromagnetic interaction in PrB$_4$ is not from the RKKY-type interaction. The direct exchange interaction between the Pr 4f-electrons might be an origin, because it can be enhanced in the case the Pr 4f energy level is closer to the Fermi energy than in other rare earth compounds. This conclusion originates from the fact that the Ce 4f electron is completely delocalized to result in Ce$^{3+}$. Similar situation of the Pr 4f state is known in skutterudite compound PrOs$_4$Sb$_{12}$, where the Pr 4f level is close to the Fermi level. In that case, the interactions between the Pr 4f electron and conduction electron cause the heavy Fermion superconductivity [10].

4. Summary

We have found the transitions from ferromagnetic to antiferromagnetic state in Pr$_{0.82}$Gd$_{0.18}$B$_4$ and Pr$_{0.8}$Gd$_{0.2}$B$_4$, where the ferromagnetic and antiferromagnetic correlations develop independently. The origin of the ferromagnetic interaction is still unclear but it is completely different from the RKKY-type origin of antiferromagnetic interactions.

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