Effects of Ga doping on the magnetic ordering of Pr in PrBa$_2$Cu$_3$O$_7$

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Neutron-diffraction and ac-susceptibility measurements have been performed to study the effects of Ga doping on the magnetic ordering of Pr in PrBa$_2$(Cu$_{1-x}$Ga$_x$)$_3$O$_7$. The Ga atoms preferentially replace the Cu atoms in the CuO-chain layers, and this substitution is found to decrease the antiferromagnetic ordering temperature as the Ga concentration is increased. In addition, the spin arrangement along the c axis is found to change from nearest neighbors being antiparallel for $x=0$ to nearest neighbors being parallel for $x=0.08$ (24% Cu chain substitution); for an intermediate $x$ of 0.04 a mixture of the two spin structures is observed. The susceptibility results exhibit Curie-Weiss behavior above $T_N$, and departures from this behavior in the ordered state.

Among high-$T_c$ oxides, PrBa$_2$Cu$_3$O$_7$ has attracted considerable attention because of its unexpected electric and magnetic properties. The introduction of Pr in YBa$_2$Cu$_3$O$_7$ suppresses superconductivity, and the Pr ions have a Neel temperature as high as 17 K, and an ordered moment as small as 0.74$\mu_B$. It is thus clear that interactions other than dipolar are responsible for the Pr magnetism. If superexchange is the dominant key, then those atoms located between the Pr atoms may also play important roles in Pr magnetism. An understanding of the coupling between the Pr atoms and the intermediate atoms located between them is then essential to a full understanding of the interactions involved.

There are three different types of layers of atoms that are located between the Pr atoms in PrBa$_2$Cu$_3$O$_7$: the CuO-chain layer, the CuO$_2$-plane layer, and the BaO layer. Metallic doping with Zn atoms, which substitutes for the Cu atoms located in the CuO$_2$-plane layers, causes the spin arrangement of Pr along the c axis to realign from antiparallel to parallel, without affecting its ordering temperature significantly. On the other hand, a full replacement of the CuO-chain layers by TiO layers, i.e., PrBa$_2$(Ti$_x$Cu$_{3-x}$)O$_7$, does not alter the spin structure of Pr but reduces its ordering temperature by a factor of 2.

In this paper we report neutron-diffraction and ac-susceptibility measurements made on the PrBa$_2$(Cu$_{1-x}$Ga$_x$)$_3$O$_{7-y}$ compounds to examine the effect of Ga doping on the ordering of the Pr spins. The Ga atoms replace the Cu atoms located in the CuO-chain layers. Two systems with $x=0.04$ and 0.08 (12% and 24% replacement, respectively) were studied, and we found that the spin structure and the ordering temperature of Pr ions are sensitive to the presence of Ga atoms. The ordering temperature decreases with increasing Ga doping, and the nearest-neighbor spins along the c axis have the tendency to realign from antiparallel to parallel.

Powder samples of PrBa$_2$(Cu$_{1-x}$Ga$_x$)$_3$O$_{7-y}$ were prepared by the standard solid-state reaction technique; the details of the sample preparation techniques can be found elsewhere. Both x-ray and high-resolution neutron diffractions were used to characterize the samples. The nominal oxygen concentration, determined from neutron profile refinement analysis, is 6.98(4) and 6.96(4) for the $x=0.04$ and 0.08 compounds, respectively. Neutron-diffraction measurements were performed using the H1-9 triple-axis spectrometer at the Research Reactor at the U. S. National Institute of Standards and Technology. A pyrolytic graphite PG(002) monochromator was employed, with a PG filter placed after the monochromator position to suppress the higher-order wavelength contaminations. The energy of the incident neutrons was 14.8 meV (2.352 $\AA$), and the angular collimations before and after the monochromator and after the sample were 40', 48', and 48' full width at half maximum (FWHM), respectively. No analyzer crystal was used in these measurements. For the low-temperature experiments, the sample was mounted in a cylindrical aluminum can filled with helium exchange gas to facilitate thermal conduction. A pumped He cryostat was used to cool the samples, and the lowest temperature obtained was 1.36 K.

A standard subtraction technique was used to isolate the magnetic signal from the nuclear one, where the diffraction pattern taken at a temperature well above the ordering temperature was subtracted from the one taken at low temperature. Figures 1(a) and 1(b) show the magnetic Bragg peaks observed at low temperatures for the $x=0.04$ and 0.08 compounds, respectively. The indices shown are based on the chemical unit cell. Both the $\{110\}$ type and the $\{\bar{1}1\bar{1}\}$ type of reflections are needed in explaining the data shown in Fig. 1(a). If only one reflection is assumed for the peak that occurs at around 2$\theta$=25°, it turns out that not only the width of this peak is much too broad in comparison with the instrumental resolution but the peak position also would fit neither to the $\{1\bar{1}\bar{0}\}$ reflection nor to the $\{1\bar{1}1\}$ reflection. In addition, the presence of the $\{1\bar{1}1\}$ and $\{1\bar{1}\bar{1}\}$ reflections suggests the existence of the $\{1\bar{1}0\}$ and $\{\bar{1}1\bar{1}\}$ reflections, respectively. The expected separation of the peak positions between the $\{1\bar{1}0\}$ and the $\{1\bar{1}\bar{1}\}$ reflections is 0.7°, which is beyond our resolution limit. A calculation assuming the presence of both the $\{1\bar{1}0\}$ type and the $\{1\bar{1}\bar{1}\}$ type of reflections gives excellent agreement for the peak positions and widths consistent with the instrumental resolution. The results of this calculation are...
Scattering Angle 2θ (deg)

PIG. 1. Magnetic intensities in PrBa$_2$(Cu$_{1-x}$Ga$_x$)$_3$O$_{7-δ}$ with (a) $x=0.04$ at $T=4.5$ K and (b) $x=0.08$ at $T=1.36$ K. Both the $\{\frac{1}{2}0\}$ type and the $\{\frac{1}{2}\frac{1}{2}\}$ type of reflections were observed in the $x=0.04$ compound, while only the $\{\frac{1}{2}0\}$ type appeared in the $x=0.08$ compound.

shown as the solid lines in Fig. 1(a). No $\{\frac{1}{2}\frac{1}{2}\}$ type of reflections were observed in the data shown in Fig. 1(b), and the solid lines are fits based on the presence of only the $\{\frac{1}{2}0\}$ type of reflections.

The corresponding magnetic structure for the $\{\frac{1}{2}\frac{1}{2}\}$ wave vector is that the spins are aligned antiparallel along all three crystallographic directions, and that for the $\{\frac{1}{2}0\}$ wave vector is that nearest-neighbor spins along the $c$ axis aligned parallel rather than antiparallel. Only the $\{\frac{1}{2}0\}$ type of reflections was observed in the undoped system. The observations shown in Fig. 1 then indicate that introducing Ga atoms into PrBa$_2$Cu$_3$O$_7$ causes the Pr spins along the $c$ axis to change from antiparallel to parallel. A 12 at. % replacement of the Cu atoms located in the CuO-chain layers by Ga atoms partially reverses the Pr spins arrangement along the $c$ axis, and a 24 at. % replacement completes this reverse.

The temperature dependence of the $\{\frac{1}{2}\frac{1}{2}\}$ peak intensity of the $x=0.04$ compound is shown in Fig. 2(a), while that of the $\{\frac{1}{2}0\}$ reflection of the $x=0.08$ compound is shown in Fig. 2(b). Both plots reveal a typical order parameter, that measures the square of the magnetization, for powder samples. The ordering temperatures determined from the data shown in Fig. 2 give $T_N=14$ and 10 K for the $x=0.04$ and 0.08 compounds, respectively. We note that the $T_N$ for the undoped system is 17 K. It is then clear that the ordering temperature of Pr is quite sensitive to the presence of Ga atoms.

The effective moment $\mu_{eff}$ that we obtained using the fitted values for the Curie–Weiss constants $C$ are 3.39 and

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FIG. 3. Portions of the measured ac susceptibility as a function of temperature. The solid lines shown are fitted Curie-Weiss curves using data collected in the temperature range of 30 K<T<320 K. Departures from the fitted curves at low temperatures are clearly seen. The temperatures at which the departures begin match very well to the Néel temperature determined using neutron diffraction.

3.01\mu_B for the x=0.04 and 0.08 compounds, respectively. These values are smaller than the value of 3.58\mu_B expected for free ions. We believe that the reduction of the effective moment is likely due to the crystalline electric field effects.

As the Ga doping is increased the effect becomes more pronounced and hence the effective moment is much reduced.

In conclusion, the ordering temperature of the Pr spins is effectively reduced by Ga doping, while it is not affected by Zn doping. The Ga atoms substitute into the CuO-chain layers, and the Zn atoms into the CuO_2-plane layers. It is then clear that the CuO-chain layers are more responsible than the CuO_2-plane layers for the high ordering temperature of Pr observed in PrBa_2Cu_3O_7.

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