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Effects of Zn and Ga substitution on the magnetic properties of $PrBa_2Cu_3O_{7-y}$

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Powder x-ray diffraction and magnetization measurements were used to study the magnetic properties of $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ $(0 \le x \le 0.1)$ and $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ $(0 \le x \le 0.15)$. The magnetic-susceptibility data show a Curie-Weiss behavior and the effective magnetic moments are close to $3.0\mu_B$ per mole Pr ion. The variation of magnetic-ordering temperature T_N depends dramatically on the doping element. In the $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ system, T_N remains essentially constant with Zn substitution. However, for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$, T_N is reduced rapidly with increasing Ga substitution. The marked difference in ordering temperatures for the mentioned systems is discussed on the basis of the Pr $4f$-electron hybridization mediated by conduction electrons in the Cu-O chains and/or Cu-O planes.

The superconducting and magnetic properties of $PrBa_2Cu_3O_{7-y}$ have been a puzzle ever since the material was synthesized. $PrBa_2Cu_3O_{7-y}$ forms in the same orthorhombic structure as $YBa_2Cu_3O_{7-y}$ and other rare-earth high-T_c compounds, but it is strangely not superconducting.[1] The nature of the quenching of superconductivity in $PrBa_2Cu_3O_{7-y}$ is not yet clear. Several mechanisms have been proposed to explain this phenomenon.[1-8] In addition, an antiferromagnetic order of Pr in $PrBa_2Cu_3O_{7-y}$ was observed below $T_N = 17$ K by magnetic susceptibility,[7,9,10] heat capacity,[7,9] and neutron-diffraction[11] measurements. $PrBa_2Cu_3O_{7-y}$ exhibits at least the following unusual magnetic properties compared to its isomorphic magnetic rare-earth compounds. (1) The value of μ_{eff} derived from magnetic susceptibility is considerably lower than the $3.54\mu_B$ expected for a Pr^{3+} free ion. (2) The magnetic ordering temperature 17 K of $PrBa_2Cu_3O_{7-y}$ is about 2 orders-of-magnitude higher than expected if one scales the T_N for $GdBa_2Cu_3O_{7-y}$ ($T_N = 2.2$ K) assuming either purely dipolar interactions or Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange. (3) A similar antiferromagnetic ordering structure between $PrBa_2Cu_3O_{7-y}$ and $GdBa_2Cu_3O_{7-y}$ was observed via neutron-diffraction experiments, while the ordered moment of Pr is only as low as $0.74\mu_B$.[11] (4) In contrast to the suppression of T_N by magnetic field in $GdBa_2Cu_3O_{7-y}$,[12] the T_N of $PrBa_2Cu_3O_{7-y}$ is basically field independent up to 50 kOe.[7] (5) The magnetic susceptibility of $PrBa_2Cu_3O_{7-y}$ increases below the apparent ordering temperature, unlike $\chi(T)$ for conventional antiferromagnetic ordering, where the magnetic susceptibility decreases below T_N.[7] (6) The magnetic ordering temperature T_N in $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$ decreases in both Gd and Pr sublattice sites with dilution, suggesting different mechanisms for Gd and Pr magnetic ordering.[10,13] Therefore it is of particular interest to understand the correlation between the quenching of superconductivity and the unusual magnetic properties in $PrBa_2Cu_3O_{7-y}$. Furthermore, the magnetic coupling mechanism in $PrBa_2Cu_3O_{7-y}$, whether it is idenitical to that in $GdBa_2Cu_3O_{7-y}$ or not, is also intriguing. In this work, we present the magnetic data for $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ and $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ to examine the effects of Zn and Ga substitution on the magnetic properties of $PrBa_2Cu_3O_{7-y}$.

All polycrystalline samples were prepared by the standard solid-state-reaction method under identical conditions. High-purity Pr_6O_{11}, $BaCO_3$, CuO, and ZnO or Ga_2O_3 powders were mixed and fired in air at 920 °C for 24 h. The resultant powders were pressed into pellets and heated in air at 920 °C for 24 h. This process was repeated at least four times with intermediate grinding. These pellets were then heated in flowing oxygen at 920 °C for 48 h followed by an additional anneal at 450 °C for 12 h. Finally the samples were slowly cooled in oxygen over several hours to room temperature. The structural analysis was carried out by the power x-ray diffraction. Most samples showed single-phase oxygen-deficient perovskite structure. The lattice parameters were calculated from the diffraction peak positions by the method of least squares. The dc magnetization for each sample was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) over the temperature range 5–40 K at a field of 1 kOe. The antiferromagnetic ordering temperature T_N was determined by the change of slope in the $M-T$ or the relative minimum in the $dM/dT-T$ curves. A field of 5 kOe was used to measure the magnetic susceptibility in the range 10–300 K from which the Curie-Weiss temperature Θ and effective magnetic moment μ_{eff} were deduced.

The lattice parameters a, b, and c for $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ and $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ are listed in Table I. The parent compound $PrBa_2Cu_3O_{7-y}$ is orthorhombic but with less orthorhombicity than $YBa_2Cu_3O_{7-y}$. Both systems studied tend to become tetragonal with the substitution of Zn or Ga for Cu, but Ga is more effective than Zn in reducing the orthorhombic distortion. This is shown clearly in Fig. 1 and Table I. The characteristic x-ray-diffraction peaks of orthorhombic symmetry at (020) (200) and (123) (213) are distinguishable in $PrBa_2Cu_3O_{7-y}$ and $PrBa_2(Cu_{0.95}Zn_{0.05})_3O_{7-y}$, but not resolvable in $PrBa_2(Cu_{0.95}Ga_{0.05})_3O_{7-y}$. The rapid increase of parameter c in $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ at $x = 0.075$ indicates the orthorhombic-tetragonal transition. These results are similar to those observed in the

TABLE I. Structural and magnetic parameters of $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ and $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$.

x	a (Å)	b (Å)	c (Å)	T_N (K)	μ_{eff} (μ_B)	Θ (K)
0	3.866(5)	3.900(6)	11.715(6)	17.5	3.02	−6.0
			Zn			
0.025	3.877(5)	3.902(2)	11.717(6)	17.5	3.01	−8.6
0.05	3.895(1)	3.897(1)	11.691(2)	18.0	2.98	−11.0
0.075	3.906(2)	3.902(1)	11.706(2)	17.5	2.93	−6.8
0.10	3.905(2)	3.902(1)	11.705(3)	17.5	2.82	−7.3
			Ga			
0.025	3.906(6)	3.909(2)	11.728(5)	14.0	3.02	−5.2
0.05	3.908(3)	3.912(2)	11.737(4)	10.5	3.18	−5.3
0.075	3.917(2)	3.923(1)	11.768(2)	7.5	3.28	−5.7
0.10	3.920(3)	3.928(1)	11.785(4)	< 5	3.17	−6.3
0.15	3.917(2)	3.926(1)	11.777(2)		2.99	−8.8

$RBa_2(Cu_{1-x}M_x)_3O_{7-y}$ (R = Y and Gd, M = Zn and Ga) systems.[14,15] It is commonly agreed that the Zn and Ni substitute preferentially in the Cu-O_2 planes [Cu(2)], and Fe, Co, Ga, and Al in the Cu-O chains [Cu(1)]. Such preferential substitution is accommodated by the different valence states of Zn and Ga. The Cu(2) site has a valence of +2, well suited for the Zn^{2+} ions. The Cu(1) site may be in the +3 state or in the mixed-valence state of +3 and +2, making it more favorable for the Ga^{3+} ions. López-Morales *et al.*[16] showed that the T_N of $PrBa_2Cu_3O_{6.46}$ is about 14 K. We use the relation obtained by Cava *et al.*[17] to estimate the variation of oxygen content from the change of parameter c in our systems to be ±0.21. Therefore, it is reasonable to believe that the differences in magnetic properties of $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ and $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ arise mainly from the intrinsic electronic structure of Zn and Ga.

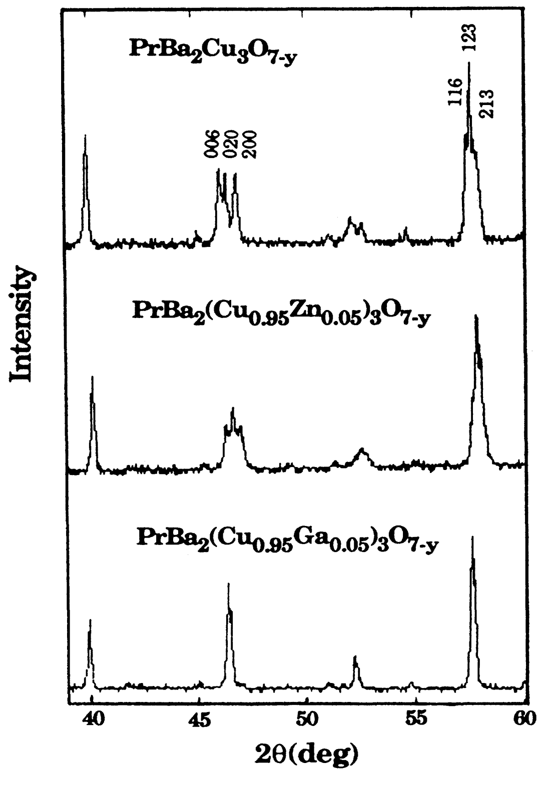

FIG. 1. The main doublet peaks of x-ray diffraction with Cu $K\alpha$ radiation in $PrBa_2Cu_3O_{7-y}$, $PrBa_2(Cu_{0.95}Zn_{0.05})_3O_{7-y}$, and $PrBa_2(Cu_{0.95}Ga_{0.05})_3O_{7-y}$.

The magnetic susceptibility can be approximated by

$$\chi = \chi_0 + C/(T-\Theta)\,, \tag{1}$$

where C is the Curie-Weiss coefficient, which is related to the effective magnetic moment μ_{eff}, Θ is the paramagnetic Curie-Weiss temperature, and χ_0 is a sum of temperature-independent terms. Presumably the χ_0 is constant for all samples and chosen to have the same value (3.6×10^{-4} emu/mol) as that found for $PrBa_2Cu_3O_{7-y}$ in our previous report.[6] The calculated values of the μ_{eff} and Θ for all samples from the best fits to Eq. (1) are also collected in Table I. The Θ is only weakly dependent on the doping concentration in both systems. On the other hand, the values of μ_{eff} are scattered from 2.99 to $3.28\mu_B$ in $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ and decreased slightly with x in $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$, indicating a perceivable effect on magnetic properties by the Zn or Ga substitution in these compounds. As mentioned by some workers,[17,18] the relatively small effective magnetic moments of Pr obtained from simple Curie-Weiss fits most likely result from strong crystalline electric fields, which can partially quench a nominal Pr^{3+} moment. Thus the substitution of Zn or Ga may influence the crystalline electric fields and the effective magnetic moment of Pr as well.

The magnetization M and the temperature derivative of magnetization dM/dT as a function of temperature for $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ ($0 \le x \le 0.1$) and $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ ($0 \le x \le 0.15$) are shown in Figs. 2 and 3, respectively. The similar features of the parent compound $PrBa_2Cu_3O_{7-y}$ to those reported[7] are observed, namely, the $M(T)$ continues to increase as the temperature is lowered and a change of slope occurs at about 17.5 K, which is taken as an antiferromagnetic ordering temperature T_N. The dM/dT vs T curve also shows an anomaly at the same temperature. The striking observations which deserve pointing out are that the T_N remains essentially unchanged in $PrBa_2(Cu_{1-x}Zn_x)_3$-

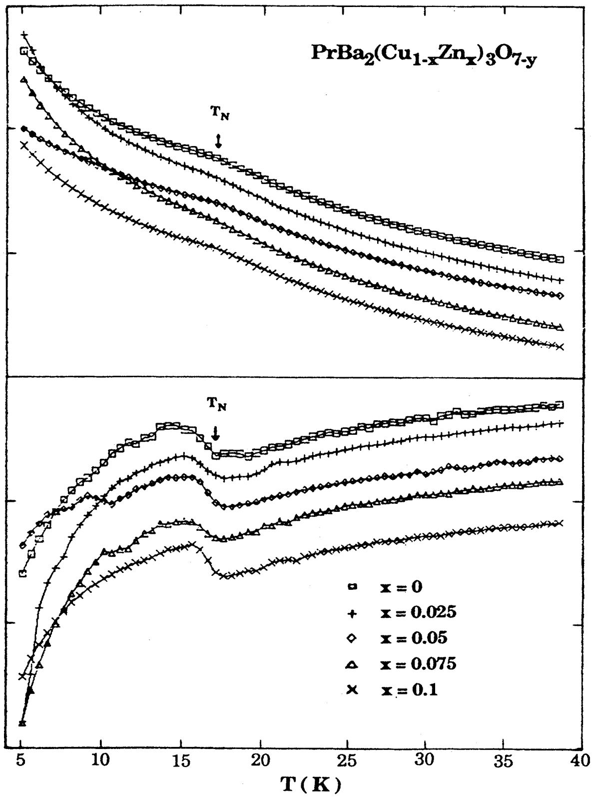

FIG. 2. Low-temperature magnetization $M(T)$ (taken at $H=1$ kOe) and the temperature derivative of magnetization dM/dT vs temperature for $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ with $x=0$, 0.025, 0.05, 0.075, and 0.1. For clarity, the M and dM/dT have been shifted by an appropriate value. T_N determined from the change of slope in the $M(T)$ or the relative minimum in the dM/dT curves is indicated by an arrow.

O_{7-y}, however, it is suppressed dramatically in $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ with $dT_N/dx=-1.2$ K/at.%. The doping-concentration dependence of T_N for these two systems is clearly shown in Fig. 4. These results are totally in contrast to those observed in $GdBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ (Ref. 19) and $GdBa_2(Cu_{1-x}Co_x)_3O_{7-y}$ (Ref. 20), where the T_N is reduced in the former and remains almost constant in the latter. Thus it indicates that the Cu-O_2 plane is an important factor in $GdBa_2Cu_3O_{7-y}$ magnetic ordering,[19,20] while the Cu-O chain may play a crucial role in $PrBa_2Cu_3O_{7-y}$ magnetic ordering. This observation gives an alternative evidence that the magnetic interactions in $GdBa_2Cu_3O_{7-y}$ and $PrBa_2Cu_3O_{7-y}$ are probably different in nature.

It has been shown that the Pr-doping effect on the superconducting $RBa_2Cu_3O_{7-y}$ (R denotes rare earth) is similar to oxygen-depleted $YBa_2Cu_3O_{7-y}$ (Ref. 21) and Zn-doped $YBa_2Cu_3O_{7-y}$.[14] Although the mechanism for the disappearance of superconductivity in $PrBa_2Cu_3O_{7-y}$ is being debated[1-8] with the quenching of mobile holes in the Cu-O_2 planes via either the hole-filling[3,7] or the localization of states due to disorder,[5] all the remaining charges of $PrBa_2Cu_3O_{7-y}$ reside in the Cu-O chains. This point

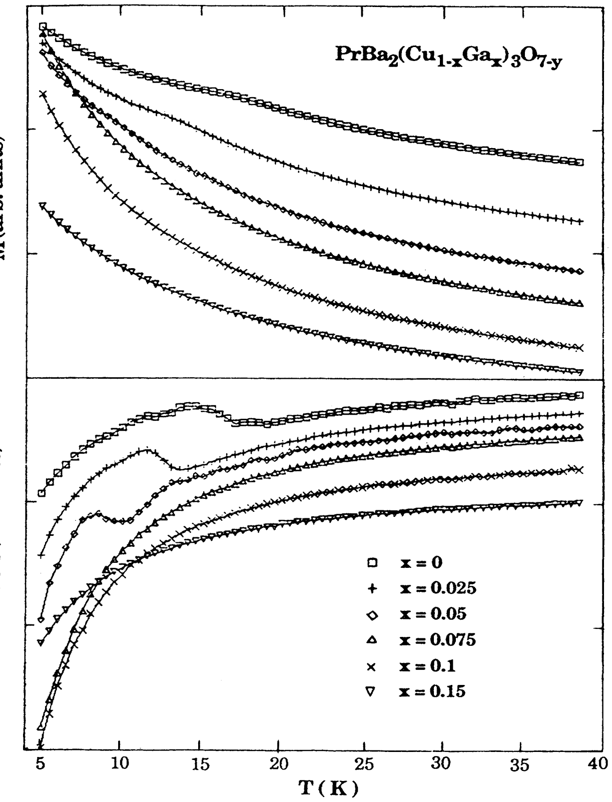

FIG. 3. Low-temperature magnetization $M(T)$ and the temperature derivative of magnetization dM/dT vs temperature for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ with $x=0$, 0.025, 0.05, 0.075, 0.1, and 0.15.

of view is supported by the room-temperature resistivity measurements[22] that the $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$ system is more insulated than $PrBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ due to the destruction of Cu-O chains by the Ga substitution. Xiao *et al.*[14] also found a similar electrical behavior in the $YBa_2(Cu_{1-x}M_x)_3O_{7-y}$ (M=Zn, Ga) systems. Due to the frozenness of plane conductivity in $PrBa_2Cu_3O_{7-y}$, it provides an excellent chance to isolate and study the chain

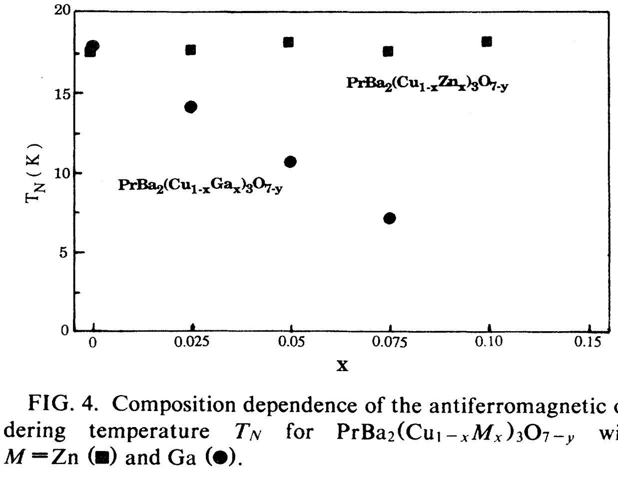

FIG. 4. Composition dependence of the antiferromagnetic ordering temperature T_N for $PrBa_2(Cu_{1-x}M_x)_3O_{7-y}$ with M=Zn (■) and Ga (●).

transport specifically. The fact that whether the chain transport is related to the magnetism of Pr needs further investigation. No magnetic ordering of the Pr moments is observed[23] above 1.5 K in the parent compound Pr_2CuO_{4-y}, where there is no Cu-O chain and only Cu-O_2 planes. This suggests some speculations. From the charge transfer aspect, it would be of interest to study the pressure effect on T_N of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-y}$. For $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$, the disappearance of superconductivity and the appearance of antiferromagnetism in the Pr sites at $x \sim 0.6$ is probably associated with the strong hybridization of Pr 4*f* electrons and conduction electrons in the Cu-O_2 planes.[9] Since the Zn substitution has no significant effect on the T_N of $PrBa_2Cu_3O_{7-y}$, it may indicate that the conduction electrons in the Cu-O_2 planes have been completely localized. This is consistent with Ref. 6, where the quenching of superconductivity in $PrBa_2Cu_3O_{7-y}$ is ascribed to the strong hybridization between Pr 4*f* electrons and conduction holes in the Cu-O_2 planes inducing a localization of the mobile holes. Nevertheless, it is still difficult to understand the reason why the T_N of $PrBa_2Cu_3O_{7-y}$ is as high as 17 K and is strongly dependent on the Ga substitution. Felner *et al.*[9] found that T_N is lowered by the presence of Fe in $PrBa_2(Cu_{0.9}Fe_{0.1})_3O_{7.1}$, probably due to some frustration caused by the strongly magnetic iron. Neutron-diffraction data[11] indicate the dominance of superexchange mechanism involving Cu-O_2 planes in determining Pr magnetism in $PrBa_2Cu_3O_{7-y}$. Based on the persistence of magnetic order of Gd at dilute concentrations and faster depression of T_N of Pr sublattice with dilution in $Pr_{1-x}Gd_xBa_2Cu_3O_7$, Das *et al.*[13] suggest a short-range (superexchange) mechanism in $PrBa_2Cu_3O_{7-y}$ and of long-range (dipolar) interactions in $GdBa_2Cu_3O_{7-y}$. For a successful mechanism to explain the quenching of superconductivity and magnetic order in $PrBa_2Cu_3O_{7-y}$, the apparent dopant dependence of T_N must be accommodated.

In summary, the magnetic properties of Zn and Ga doped $PrBa_2Cu_3O_{7-y}$ have been studied and compared to those in $GdBa_2Cu_3O_{7-y}$. In contrast to $GdBa_2Cu_3O_{7-y}$, the T_N of $PrBa_2Cu_3O_{7-y}$ remains essentially unchanged with Zn substitution and is suppressed dramatically with Ga substitution. It indicates that the magnetic interactions in $GdBa_2Cu_3O_{7-y}$ and $PrBa_2Cu_3O_{7-y}$ are probably different in nature. Moreover, the chain transport or the oxygen-vacancy order may play a significant role in $PrBa_2Cu_3O_{7-y}$ magnetic ordering.

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