

Structural, magnetic, and heat-capacity studies on Zn- and Ga-substituted $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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The compound $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is not superconducting and exhibits antiferromagnetic ordering of the Pr moments with Néel temperature T_N of ~ 17 K. We have carried out magnetic, heat-capacity, and neutron-diffraction structural studies on Zn- and Ga-substituted $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The Zn and Ga dopants presumably substitute at the plane and the chain Cu sites, respectively. Our measurements reveal that T_N is reduced in both cases; the reduction being faster for Ga substitution than for Zn substitution. For 10 at. % Zn substitution T_N is ~ 15 – 16 K, while for the same substitution level of Ga it is ~ 12 – 14 K. It is rather unusual that the plane-site substitution has relatively less effect on T_N than the chain-site substitution. From neutron-diffraction studies the cause of such contrasting behavior may be understood in terms of changed planar Cu-O₂ and Pr-O₂ bond lengths. The electronic specific-heat coefficient γ of the substituted samples is found to be large as in the parent $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound.

I. INTRODUCTION

The compound $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Pr:123) exhibits very intriguing behavior (see, for instance, Refs. 1–7). This compound belongs to the orthorhombic family of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R :123) compounds ($R=Y$ or a rare earth) most of which are superconducting with superconducting transition temperature T_c in the 90 K range. However, $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is nonsuperconducting. Further, it shows antiferromagnetic ordering of the Pr moments with Néel temperature T_N of nearly 17 K.^{2,3} The electronic specific-heat coefficient γ of this compound is also very large^{2–5}—of the order of 250 mJ/mol K²—reminiscent of the heavy-fermion systems. The reasons behind the quenching of superconductivity, the relatively high T_N , and the large electronic specific-heat coefficient γ of this compound are still not well understood. Generally, two mechanisms have been advanced in the literature to account for the unusual behavior of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, namely, hole filling or localization of mobile holes in Cu-O₂ planes^{3–6} and/or pair breaking by local Pr moments. In these anisotropic quasi-two-dimensional high- T_c cuprate systems, the superconductivity is presumed to reside basically in the Cu-O₂ planes. In the hole-filling model, the Pr ion in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is assumed to be in a valence state higher than 3+. Thus the extra electron contributed by Pr relative to other trivalent rare-earth ions fills/neutralizes the holes in the planar Cu-O₂ network, which are very important for the occurrence of superconductivity. The intermediate value of the magnetic moment of Pr in this compound between that of Pr^{3+} and Pr^{4+} is consistent with this suggestion. However, the view of hole filling is contradicted by the energy-loss spectroscopy results where

the total hole concentration in Pr:123 has been reported to be nearly the same as in other R :123 compounds.⁷ Further, the intermediate Pr moment value can also be understood on the basis of crystal-field effects without invoking the mixed-valent nature of the Pr ion. In another model, the Pr 4*f* electrons are presumed to hybridize with the electrons in the planar Cu-O₂ network. This may lead to a strong interaction between the Pr 4*f* moments and the conduction electrons which can result in a nonsuperconducting system with an unusually high T_N and large electronic specific-heat coefficient. The model proposed by Fehrenbacher and Rice⁸ (FR) and improved and extended by Liechtenstein and Mazin⁹ appears to be the most satisfactory and explains a great body of data on Pr:123 compounds including the rare-earth dependence of the suppression of superconductivity in $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds.¹⁰ In this model, the holes from the Cu-O₂ band are presumed to be taken up by the FR state. The FR state is a mixture of $4f^1$ and $4f^2\bar{L}$ orbitals, where \bar{L} is a ligand hole in the O 2*p* orbital in the original model⁸ but forms a dispersive band in the modified FR model.⁹ The transfer of holes to the FR state leads to a nonsuperconducting and insulating ground state.

It has been reported that complete chain-site substitutions in Pr:123 lead to a lowering of T_N in this compound.^{11,12} Moreover, oxygen stoichiometry in Pr:123 also influences the antiferromagnetic ordering of the system.^{13,14} In the case of oxygen-deficient Pr:123, it has been suggested¹⁴ that the changed Cu-O bond lengths in Cu-O₂ planar networks may be responsible for bringing down the value of T_N . Increased bond lengths in adjacent Cu-O₂ planes may reduce the hybridization of Pr with Cu-O, as a result of which T_N may decrease. It is of interest to examine different possibilities of

suppressing the magnetic ordering of the Pr moments in Pr:123 systems without affecting the number of conduction holes in the parent system. With this in mind, we have carried out a detailed study of structural, magnetic, and specific-heat behavior of Zn- and Ga-substituted Pr:123. The results of these studies are reported in this paper.

II. EXPERIMENTAL DETAILS

The $\text{PrBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ samples ($M = \text{Ga}$ and Zn and $x = 0.0-0.1$) were prepared by the usual ceramic technique by heating stoichiometric amounts of thoroughly mixed powders of Pr_6O_{11} , BaCO_3 , CuO , ZnO , and Ga_2O_3 at 930°C for 24 h with intermediate grinding. The resulting product was pulverized and resintered and this process was repeated at least three times. The final sintering was carried out in flowing oxygen and the samples were cooled slowly to room temperature. Samples were characterized for phase purity by powder x-ray diffraction studies using a JEOL x-ray diffractometer equipped with $\text{Cu } K_\alpha$ radiation. Neutron-diffraction measurements were carried out at room temperature on both the Zn- and Ga-substituted samples with $x = 0.1$ at the Missouri University Research Reactor Center. Magnetic susceptibility measurements were carried out on a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design) in the temperature range 2–300 K. The heat-capacity measurements were made on some of the samples in an adiabatic heat-pulse calorimeter in the temperature range 2–20 K.

III. RESULTS AND DISCUSSION

Powder x-ray diffraction studies showed that the $\text{PrBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ samples ($M = \text{Ga}$ and Zn and $x = 0.0-0.1$) are essentially single-phase materials. From earlier x-ray and neutron-diffraction studies on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, it has been established that the Zn atoms substitute at the plane-site Cu while the Ga atoms substitute at the chain-site Cu.^{15,16} Rietveld refinement of our present neutron-diffraction patterns on 10% Zn- and Ga-substituted $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples is consistent with this assignment. Details of the structural analysis and other experimental results are given below.

A. Structural aspects from neutron-diffraction studies

The Pr:123 compound is isostructural to other R :123 compounds and crystallizes in the orthorhombic structure (space group $Pmmm$). This structure of R :123 compounds has a unique rare-earth site, two copper sites, and five oxygen sites. The structure may be thought to consist of layers of $\text{BaO}/\text{CuO}_2/\text{R}/\text{CuO}_2/\text{BaO}$. The Cu(2) atoms form puckered Cu(2)-O_2 planes with oxygen sites labeled O(2) and O(3). The oxygen atoms in the Ba-O plane are designated as O(4). The Cu(1)-O(1) atoms form chains along the b -axis direction. The O(5) sites are along the a -axis direction in a plane containing Cu(1) sites. The orthorhombicity of R :123 compounds is found to be due to the missing oxygen atoms at the O(5) sites along the shorter a -axis direction. When O(1) and O(5) sites are equally occupied, the system transforms to a tetragonal structure (space group $P4/mmm$) in which O(2) and O(3) sites also become equivalent.

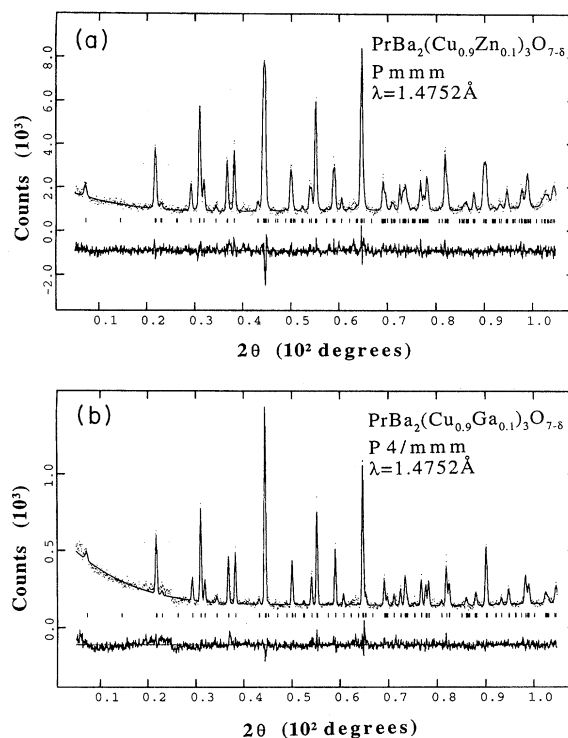


FIG. 1. (a) Observed and fitted neutron-diffraction pattern of $\text{PrBa}_2(\text{Cu}_{0.9}\text{Zn}_{0.1})_3\text{O}_{7.8}$. (b) Observed and fitted neutron-diffraction pattern of $\text{PrBa}_2(\text{Cu}_{0.9}\text{Ga}_{0.1})_3\text{O}_{7.8}$.

The least-squares structural refinements were made using the computer program GSAS,¹⁷ which employs a full-profile Rietveld analysis.¹⁸ The pseudo-Voigt peak profile, as described by Thompson, Cox, and Hastings,¹⁹ was used. The Zn and Ga atoms were assumed to occupy Cu(1) and Cu(2) sites, respectively. However, a model in which Zn randomly occupies both the Cu sites was also investigated (see below). The O(2) and O(3) sites were taken to be completely filled. It has been observed earlier that, in addition to O(1) sites, there is also a small occupancy of the O(5) sites in orthorhombic Pr:123.¹⁴ Therefore, we have performed the analysis of neutron-diffraction data of pure and Zn-substituted Pr:123 both with and without the O(5) site occupancy. The Ga-substituted sample shows a tetragonal structure (see below) in which O(1) and O(5) sites are equally occupied. Analysis of the neutron-diffraction data showed materials nearly free of impurity phases consistent with x-ray diffraction results. The observed and fitted neutron-diffraction data for $\text{PrBa}_2[\text{Cu}_{1-x}(\text{Zn,Ga})_x]_3\text{O}_{7-\delta}$ compounds with $x = 0.1$ are shown in Figs. 1(a) and 1(b) and the structural parameters are summarized in Tables I–IV.

For $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the results of the analysis of neutron-diffraction data are summarized in Table I. We obtain lattice parameters $a = 3.8604(4)$ Å, $b = 3.9250(4)$ Å, and $c = 11.7015(13)$ Å. Oxygen content of the sample, without the O(5) site occupancy, is refined to be 6.96(3). An analysis with the O(5) site occupancy gave nearly the same lattice parameters but slightly higher oxygen content of 7.01(5) [with occupancies of O(1)=0.83(3) and O(5)=0.18(2)] for the same compound. In fact, inclusion of the O(5) occupancy

TABLE I. Structural parameters for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (space group $Pmmm$): Atomic positions (x, y, z), fractional site occupancies, and isotropic thermal parameters (U_{iso}). Lattice parameters are $a = 3.8604(4)$ Å, $b = 3.9250(4)$ Å, and $c = 11.7015(13)$ Å. $wRp = 0.0930$, $Rp = 0.0742$, $\chi^2 = 1.255$.

Atom	Space group position	x	y	z	Fractional occupancy	$100 \times U_{\text{iso}}$ (Å ²)
Pr	1 <i>h</i>	0.5	0.5	0.5	1	0.14(24)
Ba	2 <i>t</i>	0.5	0.5	0.18136(57)	1	0.97(14)
Cu(1)	1 <i>a</i>	0	0	0	1	1.07(17)
Cu(2)	2 <i>q</i>	0	0	0.34963(36)	1	0.78(10)
O(1)	1 <i>e</i>	0	0.5	0	0.957(28)	2.82(42)
O(2)	2 <i>s</i>	0.5	0	0.37142(30)	1	0.89(10)
O(3)	2 <i>r</i>	0	0.5	0.37142(30)	1	0.89(10)
O(4)	2 <i>q</i>	0	0	0.15820(55)	1	1.68(17)
O(5)	1 <i>b</i>	0.5	0	0		

yields a slightly better fit to the data in the present situation, with wRp and χ^2 changing from 0.0930 and 1.255 without O(5) occupancy to 0.0917 and 1.233 with O(5) site occupancy. We have observed that the O(5) site occupancy in Pr:123 varies from sample to sample, ranging from almost zero, as in other $R:123$ compounds, to the presently observed value. There are two possible explanations for the occupancy of O(5) sites in this system, namely, (i) presence of mixed-valent Pr and/or (ii) the intermixing of Pr and Ba atoms in the system. Unfortunately, the neutron-scattering cross sections of Pr and Ba are very similar, preventing an analysis of the neutron data in terms of an intermixing model.

For the Zn-substituted $x=0.1$ sample, we noted that the analysis of the neutron-diffraction data, without the inclusion of O(5) sites, led to inferior fits and low oxygen occupancies. Therefore the analysis was performed with variable O(5) site occupancy. The Zn was assumed to occupy the planar Cu(2) site. The observed and fitted neutron-diffraction patterns for this compound are shown in Fig. 1(a) and the results of the analysis are given in Table II. The lattice parameters obtained are $a = 3.8825(7)$ Å, $b = 3.9175(7)$ Å, and $c = 11.7016(20)$ Å. The total oxygen content of this sample is refined to be 6.97(9). In the case of other $R:123$ compounds, the oxygen content and the cell parameters have been found to be nearly unchanged on Zn substitution at the

Cu sites.^{15,16} In the present situation also the changes are nominal. The large occupancy of the O(5) site in the Zn-substituted sample, compared to that in pure Pr:123, is rather unexpected. If Zn substitutes only at the planar Cu(2) site, then the O(5) occupancy should not be affected. Therefore the possibility exists that Zn substitutes randomly at both the Cu sites in this compound and has a tendency to modify the oxygen occupancies to yield a tetragonal structure without increasing the overall oxygen content. Analysis of the neutron-diffraction data on this model yielded Zn occupancies of 0.18(7) at the Cu(1) site and 0.06(3) at the Cu(2) site. Though the improvement in wRp and χ^2 is marginal, this model can account for the large O(5) site occupancy.

The Ga-substituted $x=0.1$ compound crystallizes in the tetragonal structure with lattice parameters $a = 3.9014(2)$ Å and $c = 11.6712(10)$ Å. Unfortunately, the neutron-scattering cross section of Ga and Cu are very similar and, therefore, preferential substitution of Ga at the chain-site Cu cannot be directly confirmed. However, it is confirmed indirectly, since tetragonal symmetry is a consequence of octahedral coordination of Ga atoms. In addition, the oxygen content of the system, which is refined to be 7.12(5), is consistent with the fact that Ga atoms are randomly distributed and do not form clusters. The observed and fitted neutron-diffraction patterns are shown in Fig. 1(b) and the results of refinement are given

TABLE II. Structural parameters for $\text{PrBa}_2(\text{Cu}_{0.9}\text{Zn}_{0.1})_3\text{O}_{7-\delta}$ (space group $Pmmm$): Atomic positions (x, y, z), fractional site occupancies, and isotropic thermal parameters (U_{iso}). Lattice parameters are $a = 3.8825(7)$ Å, $b = 3.9175(7)$ Å, and $c = 11.7016(20)$ Å. $wRp = 0.0954$, $Rp = 0.0738$, $\chi^2 = 1.328$.

Atom	Space group position	x	y	z	Fractional occupancy	$100 \times U_{\text{iso}}$ (Å ²)
Pr	1 <i>h</i>	0.5	0.5	0.5	1	0.34(29)
Ba	2 <i>t</i>	0.5	0.5	0.18061(68)	1	1.42(16)
Cu(1)	1 <i>a</i>	0	0	0	1	1.28(21)
Cu(2)	2 <i>q</i>	0	0	0.35069(40)	0.85	0.35(12)
Zn	2 <i>q</i>	0	0	0.35069(40)	0.15	0.35(12)
O(1)	1 <i>e</i>	0	0.5	0	0.625(44)	2.84(57)
O(2)	2 <i>s</i>	0.5	0	0.37159(34)	1	0.94(12)
O(3)	2 <i>r</i>	0	0.5	0.37159(34)	1	0.94(12)
O(4)	2 <i>q</i>	0	0	0.15730(68)	1	2.47(24)
O(5)	1 <i>b</i>	0.5	0	0	0.346(44)	2.84(57)

TABLE III. Structural parameters for $\text{PrBa}_2(\text{Cu}_{0.9}\text{Ga}_{0.1})_3\text{O}_{7-\delta}$ (space group $P4/mmm$): Atomic positions (x, y, z), fractional site occupancies, and isotropic thermal parameters (U_{iso}). Lattice parameters are $a = 3.9014(2)$ Å and $c = 11.6712(10)$ Å. $wRp = 0.0856$, $Rp = 0.0671$, $\chi^2 = 1.645$.

Atom	Space group position	x	y	z	Fractional occupancy	$100 \times U_{\text{iso}}$ (Å ²)
Pr	1d	0.5	0.5	0.5	1	0.12(29)
Ba	2h	0.5	0.5	0.18349(75)	1	1.42(17)
Cu(1)	1a	0	0	0	0.7	1.47(23)
Ga	1a	0	0	0	0.3	1.47(23)
Cu(2)	2g	0	0	0.35165(46)	1	0.85(13)
O(1)	2f	0	0.5	0	0.562(25)	3.95(65)
O(2)	4i	0.5	0	0.37164(41)	1	1.14(13)
O(4)	2g	0	0	0.15575(84)	1	3.03(28)

in Table III. In the case of other Ga-substituted $R:123$ compounds with comparable doping, tetragonal structure (space group $P4/mmm$) with increased oxygen content is observed.^{15,16} It has also been observed that Ga, Fe, Co, and Al substitution at the Cu site in other $R:123$ systems results in an increased oxygen content and a decreased carrier concentration in the system.^{15,16} Increased oxygen fills the O(5) sites and, hence, at a critical concentration x of the substituent, the O(5) site occupancy becomes equal to the O(1) site occupancy and the system becomes tetragonal. [In the tetragonal structure, the O(2) and O(3) sites also become equivalent.] It, therefore, appears that, as far as the lattice parameters and oxygen content values are concerned, the results for Ga- and Zn-substituted Pr:123 follow the same trend as observed earlier in other $R:123$ systems (see, for instance, Refs. 15 and 16). Selected bond distances in the compounds discussed above are given in Table IV. The large thermal factors for some of the oxygen sites seen in Tables I–III are partly due to their incomplete occupancies and consequential disorder at these sites, and partly due to the influence of disorder at the neighboring Cu sites caused by the random substitution of Zn and Ga. Further, possible occupancy of Pr ions at the Ba site will have the effect of displacing/moving some of the nearby oxygen atoms, thereby contributing to their thermal factors.

B. Magnetic studies

The magnetic ordering in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and related compounds manifests itself as a small break in the magneti-

TABLE IV. Selected bond distances (Å) in $\text{PrBa}_2[\text{Cu}_{1-x}(\text{Zn}, \text{Ga})_x]_3\text{O}_{7-\delta}$.

Bond	$x = 0.0$	$x_{\text{Zn}} = 0.1$	$x_{\text{Ga}} = 0.1$
Cu(1)–O(1)	1.9625(2)	1.9587(4)	1.9508(1)
Cu(1)–O(4)	1.851(6)	1.841(8)	1.818(10)
Cu(1)–O(5)	1.9302(2)	1.9412(4)	
Cu(2)–O(2)	1.9459(7)	1.9566(8)	1.9646(9)
Pr–O(3)	2.4473(21)	2.4548(24)	
Pr–Cu(2)	3.2669(23)	3.2646(25)	3.2571(29)
Pr–O(2)	2.4729(21)	2.4687(24)	2.4597(29)
Ba–O(1)	2.869(5)	2.870(6)	2.897(6)
Ba–O(2)	2.966(6)	2.972(7)	2.937(8)
Ba–O(4)	2.7659(11)	2.7712(13)	2.7777(17)

zation (M) versus temperature (T) curve and is best seen through the plot of dM/dT as a function of temperature. Figure 2 shows such a plot for the Ga-substituted samples. The Néel temperature T_N is defined as the temperature of a relative minimum in the dM/dT versus T curve. As can be seen from this figure, the antiferromagnetic ordering temperature T_N decreases slightly with increasing Ga substitution in the system. The dM/dT versus temperature curves for the Zn-substituted samples are shown in Fig. 3, where there is very little change to be seen in the T_N of the system with progressive Zn substitution; T_N decreases only by 1–2 K for the $x = 0.1$ sample compared to that of the parent compound. This is in agreement with the results reported earlier²⁰ on the same system.

In the case of Ga-substituted Pr:123 samples, we observe a considerably smaller decrease in T_N than that reported in Ref. 20. On examining the structural parameters of the samples employed in Ref. 20 with those of Ga-substituted $R:123$ compounds as well as Ga-substituted Pr:123 compounds used in the present study, we note several important differences. As mentioned above, Zn and Ga substitution in $R:123$, including the present Pr samples, gives rise to disordering of the O(1) and O(5) site oxygen occupancies, leading

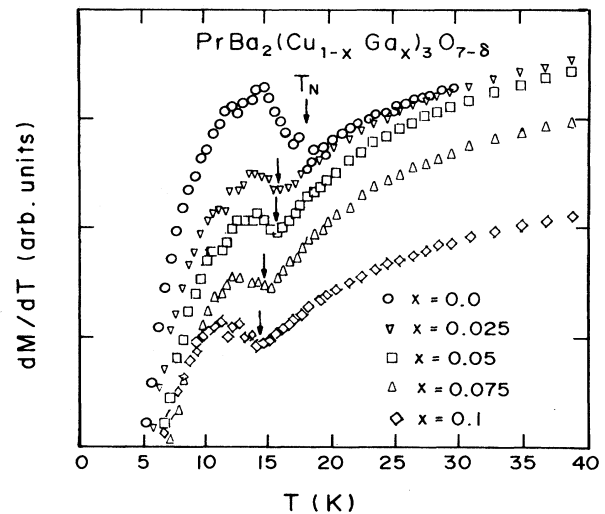


FIG. 2. Temperature (T) derivative of magnetization (dM/dT) versus T for the system $\text{PrBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_{7-\delta}$.

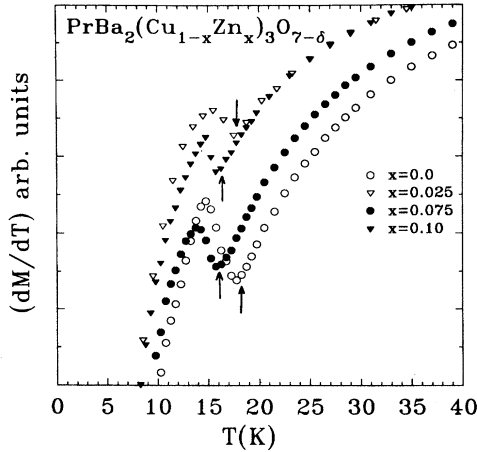


FIG. 3. Temperature (T) derivative of magnetization (dM/dT) versus T for the system $\text{PrBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$.

to reduced orthorhombicity. Eventually the material transforms to a tetragonal structure with about 10% Ga substitution, but continues to be orthorhombic—albeit with reduced orthorhombicity—for the Zn substitution. In the case of Ga substitution, the c lattice parameter either remains unchanged or decreases a little, consistent with the fact that the mismatch between the Cu ionic size and that of Ga is very small. However, the samples of Ref. 20 tend to become tetragonal for both Zn and Ga doping and also show a large increase in the c lattice parameter. It is also known that a decrease in overall oxygen content in the $R:123$ compounds leads to an increase in the c lattice parameter.²¹ It has also been observed that T_N of Pr:123 depends on the oxygen stoichiometry and decreases with decreasing oxygen content^{13,14} and the same is probably true in the substituted samples. It is, therefore, possible that the Ga-substituted samples of Ref. 20 are deficient in oxygen and part of the decrease in T_N is a consequence. Unfortunately, the oxygen content of the samples employed in Ref. 20 is not known. Further, even with complete replacement of chain-site Cu by Nb and Ta, the T_N of Pr:123 falls to only about 12 and 11 K, respectively. In that respect, our results for T_N on Ga-substituted samples appear reasonable.

From the magnetic-susceptibility and heat-capacity (see below) results of both Zn- and Ga-substituted Pr:123 compounds, it appears that the antiferromagnetic ordering temperature T_N is affected somewhat more by Ga substitution than by Zn substitution. Since Zn is presumed to go to the planes and Ga to the chains, the above results imply that substitution in adjacent Cu-O planes has less deleterious effects on the T_N of Pr moments in Pr:123 than substitution in the rather distant Cu-O chains. In fact, on distorting Cu-O chains either by removing the oxygen from them, or by putting substituents there, the T_N decreases.¹¹⁻¹⁴ This looks unusual considering that in the superconducting $R:123$ compounds carriers in the Cu-O plane are presumed to play a major role, and may point towards other factors which may influence T_N (see below).

In the paramagnetic state, the susceptibility (χ) of all the compounds follows Curie-Weiss behavior given by

$$\chi = C/(T - \theta_p) + \chi_0, \quad (1)$$

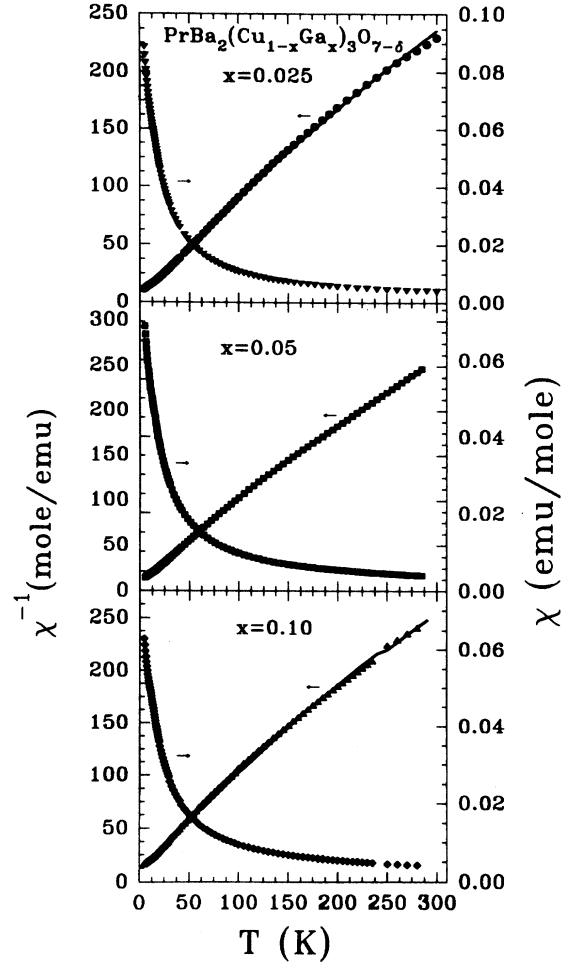


FIG. 4. Susceptibility versus temperature and inverse susceptibility versus temperature for some of the compounds in $\text{PrBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_{7-\delta}$ series.

where C is the Curie constant which is related to the effective paramagnetic moment (μ_{eff}), θ_p is the paramagnetic Curie temperature, and χ_0 is the temperature-independent susceptibility. Figures 4 and 5 show a plot of χ and χ^{-1} as a function of temperature for some of the samples. The temperature-independent susceptibility χ_0 is small and nearly the same in all the compounds. The values of μ_{eff} and θ_p obtained from the fit of data to Eq. (1), are given in Table V. These do not show any systematic trends. However, the negative θ_p values are consistent with the antiferromagnetic ordering of Pr moments. The μ_{eff} values are again found to be intermediate between those of free-ion Pr^{3+} and Pr^{4+} values.

C. Heat capacity

Figure 6 shows the results of heat-capacity measurements on the parent and the 10% Zn- and Ga-substituted compounds. The heat-capacity data confirm reasonably the T_N values obtained from the magnetic-susceptibility results. These measurements also reveal a large value of the electronic specific heat coefficient γ . The γ values are 265 and

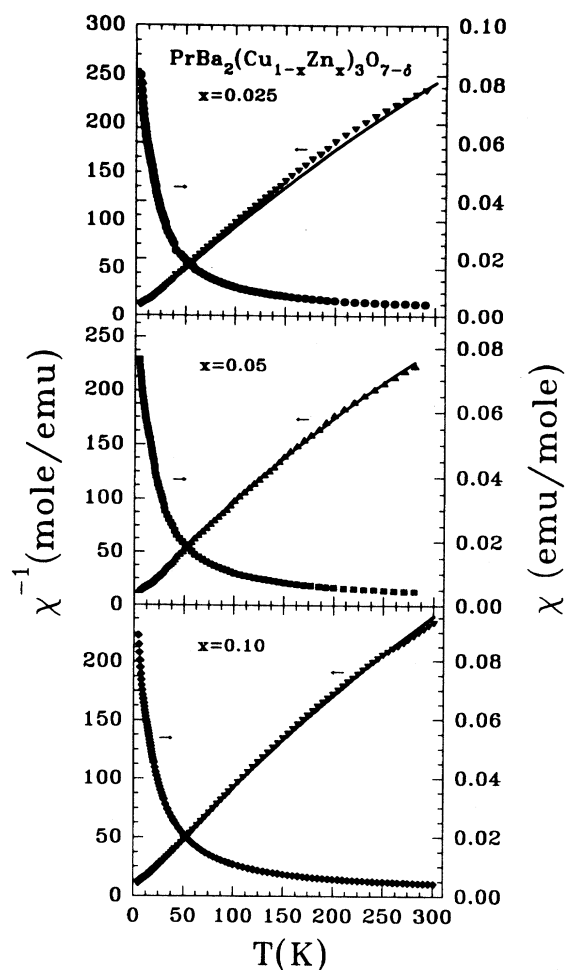


FIG. 5. Susceptibility versus temperature and inverse susceptibility versus temperature for some of the compounds in the $\text{PrBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$ series.

285 mJ/mol K^2 for Ga- and Zn-substituted samples, respectively. These values are quite comparable to that obtained for the pure Pr:123 compound^{2,3,5} and seem to have the same origin.

D. Bond distances, carrier density, and T_N

Various bond lengths in pure and Zn- and Ga-substituted Pr:123 compounds are given in Table IV. The Cu(1)-O(1) distance in the Cu-O chains is found to decrease with Ga substitution in comparison to that in the pristine and the Zn-substituted samples. The reason for this is that the O(1) and the O(5) oxygen sites in the Ga-substituted sample are equally occupied. For the Zn-substituted sample, the change in the Cu(1)-O(1) chain distance is minor. Changes in the bond distances in Cu-O chains with Zn and Ga substitution in Pr:123 are consistent with similar changes in other R :123 systems for the same substitutions (see, for instance, Refs. 15 and 16). The Cu-O₂ plane distance between the ions, e.g., the Cu(2)-O(2) distance, increases for both the Zn- and the Ga-substituted samples compared to that in the pristine sample. The relative increase in Cu(2)-O(2) distance is

TABLE V. Effective paramagnetic moment (μ_{eff}), paramagnetic Curie temperature (θ_p) and Néel temperature (T_N) from dM/dt , unless otherwise specified, for $\text{PrBa}_2[\text{Cu}_{1-x}(\text{Zn,Ga})_x]_3\text{O}_{7-\delta}$ compounds.

x	μ_{eff} (μ_B)	θ_p (K)	T_N (K)
x_{Ga}			
0.0	2.85	-6.0	17
0.025	3.03	-4.7	16
0.05	2.77	-6.1	15
0.1	2.77	-9.9	12 ^a , 14
x_{Zn}			
0.025	2.95	-4.3	16
0.05	2.77	-3.2	17
0.1	2.98	-4.4	15 ^a , 16

^aFrom heat capacity data.

more for the Ga-substituted sample than that for the Zn-substituted sample. Increase in the Cu(2)-O(2) distance reflects a possible decrease in the number of carriers in the Cu-O₂ planes.²¹ This result is also in agreement with that in other R :123 compounds, where a decrease in the number of carriers with Ga substitution has been observed.^{15,16} The only point of difference is that in the case of the Zn-substituted Pr:123 sample the carriers also seem to decrease, which has not been the case in other R :123 compounds with the same substitution.^{15,16} It is noteworthy that the change in carrier concentration, reflected through Cu(2)-O(2) bond distances, is relatively more in the case of Ga substitution than in the Zn-substituted samples. These findings are consistent with the FR model^{8,9} discussed earlier. Another important distance in the Pr:123 compounds, often discussed, is the Pr-O(2) distance which may influence the hybridization of Pr 4*f* electrons with the carriers in the adjacent Cu-O(2) planes. The Ga-substituted sample is found to be tetragonal and hence the O(2) and O(3) sites become identical in this sample. In order to compare the Pr-O distances, we have taken the mean of Pr-O(2) and Pr-O(3) distances for the pristine and the Zn-substituted samples and compared the two

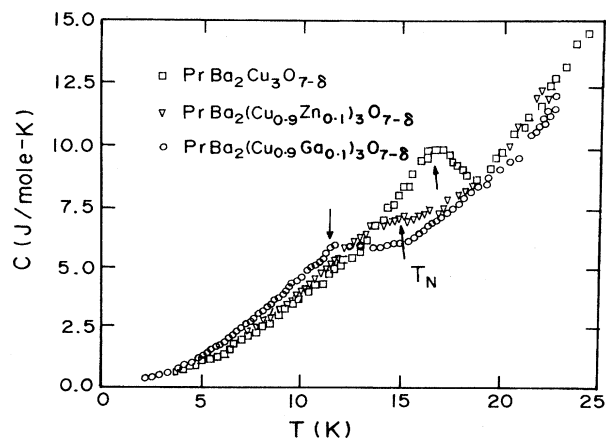


FIG. 6. Heat capacity (C) versus temperature (T) for $\text{PrBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ system: $M=\text{Zn}$ and Ga and $x=0$ and 0.1 .

with the Pr-O(2) distance for the Ga-substituted sample. Considered in this way, it appears that the average Pr to Cu-O(2) plane distance changes very little for both Zn- and Ga-substituted samples.

As remarked earlier, the unusually high T_N of Pr in Pr:123 decreases slightly with Ga substitution at the Cu site in the Pr:123 system. In all the R:123 compounds, Ga substitution increases the oxygen content with a decrease in the number of conduction holes of the system.^{15,16} In high- T_c cuprates, it is believed that the conduction holes reside in the Cu-O₂ planes only. Any change in the number of holes in R:123-type high- T_c systems is accompanied by a modification of the in-plane Cu-O bond lengths.^{14,21} In the case of Pr:123 or related compounds, a change in Cu-O bond lengths may modify the strength of hybridization of Pr 4*f* electrons with the Cu-O conduction holes and, as a result, alter the T_N . In fact, the expected decrease in the number of holes due to Ga substitution at the Cu site increases the in-plane Cu-O bond lengths. In the present work we find that for 10 at. % Zn and Ga substitution in Pr:123, the average Pr-O distance [average of Pr-O(2) and Pr-O(3) distance] is nearly the same as the corresponding distance in undoped Pr:123, which cannot explain the reduction in T_N on Zn and Ga substitution in terms of the reduced hybridization mentioned above. At this juncture it appears that the hybridization of Pr 4*f* electrons with the Cu-O conduction band (and hence the T_N , assuming it arises due to the above hybridization) is affected both by the separation of the Pr 4*f* from the Cu-O₂ planes and by the density of hole carriers in the Cu-O₂ planes.

IV. SUMMARY AND CONCLUSIONS

The main results may be summarized as follows. The antiferromagnetic ordering temperature T_N of Pr:123 decreases with Zn and Ga substitution, as revealed through both magnetic-susceptibility and heat-capacity measurements, though the decrease in T_N is slightly faster for Ga substitution. The in-plane Cu(2)-O(2) bond length increases for both the Ga and the Zn substitutions compared to that in undoped Pr:123. The average Pr-O₂ distance remains nearly the same for both Zn and Ga substitutions. Therefore it seems that, besides the Pr-O distances, the planar Cu-O distances are also important in deciding the strength of Pr 4*f* hybridization with the Cu-O conduction band. While the former (Pr-O bond length) is a measure of the distance of Pr from the Cu-O network, the latter (Cu-O bond length) reflects the hole carrier density in the Cu-O₂ planes. Despite different T_N values for Ga- and Zn-substituted samples, the electronic specific-heat coefficient γ of these compounds continues to be high as in parent Pr:123 and most likely has the same origin.

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