# Superconducting and magnetic phase boundaries in $Bi_2Sr_2Ca_{1-x}M_xCu_2O_8$ , with M = Y, Gd, and Pr

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The temperature dependences of the electrical resistivity, magnetic susceptibility, and specific heat have been measured in Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub> $M_x$ Cu<sub>2</sub>O<sub>8</sub>, where M = Y, Gd, and Pr, for concentrations  $0 \le x \le 1.0$  and temperatures 1.6 K  $\le T \le 300$  K. All three dopants substitute a trivalent ion for divalent Ca and cause a depression of  $T_c$  observable in the resistivity and susceptibility. Both Pr and Gd retain their free-ion magnetic moment and appear to cause little, if any, magnetic pair breaking. Instead, the dominant suppression mechanism in all three cases is driven by the filling of the Cu 3d hole by the extra electron and the breaking of the Cu 3d-O 2p hybridization. Consequent localization of Cu 3d holes causes an observable antiferromagnetic ordering of Cu ions within the planes in the case of Y. The evidence for Cu ordering for Gd and Pr is obscured by the large Curie contribution to the magnetic susceptibility due to the rare-earth ions.

### I. INTRODUCTION

The study of the effect of impurities on the physical properties of superconductors has long been recognized as being of great importance. Unlike conventional superconductors, where the addition of a nonmagnetic dopant causes limited changes in the superconducting transition temperature and gap parameter, reflective of changes in electron densities or the removal of anisotropies in the pair coupling, impurities substituted on Cu sites in hightemperature superconductors generally are found to cause a rapid suppression of the superconducting transition temperature. The overwhelming destructive effects of nonmagnetic doping within high- $T_c$  superconductors have been disappointing from a purely technological point of view because doping has not led to enhancements in  $T_c$  or improvement in such quantities as critical current and magnetic shielding through the introduction of pinning sites as with conventional superconducting systems. However, the lack of a clear understanding of the effects of nonmagnetic and magnetic impurities in the new oxide superconductors continues to stimulate much interest.

From extensive studies of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> (Y 1:2:3) system,<sup>1-4</sup> it has been found that while the final result of an impurity doped onto a Cu site may be to lower  $T_c$  (Zn,Ni,Co,Al,Ga), the reasons for this may be both

diverse and subtle, involving charging effects at particular atomic sites, breaking of conduction-electron-level hybridization, and classic Abrikosov-Gorkov pair breaking. Alternatively, substitution of Y by most trivalent rareearth elements (Eu,Gd,Dy,Ho,Er,Tm,Yb) leaves T<sub>c</sub> almost unchanged.<sup>4</sup> The lack of any apparent exchange depairing in most of the rare-earth-doped 1:2:3 oxide superconductors reflects the negligible electronic wavefunction overlap between 4f electrons on the rare-earth site and the  $CuO_2$  hybridized 2p-3d hole states within the copper oxide planes. One exception to this behavior is  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ , where  $T_c$  is depressed rapidly with increasing x and  $T_c \rightarrow 0$  for  $x_{cr} \approx 0.54$ . Specific-heat<sup>5</sup> and other studies<sup>6</sup> suggest that for  $(Y,Pr)Ba_2Cu_3O_7$  there is substantial f-electron hybridization between the 4f electrons on the Pr site and the 2p-3d holes within the Cu-O planes. Such hybridization is not apparent in the other rare-earth-doped 1:2:3 oxides. This hybridization may lead to exchange depairing of the paired electrons (holes) within the Cu-O planes and could account for at least a portion of the depression of  $T_c$  with increasing Pr doping.7 In addition, magnetic-susceptibility and neutrondiffraction studies<sup>8</sup> have suggested that the Pr within Y 1:2:3 may be strongly mixed valent and possibly close to tetravalent. Under such circumstances the doping of Y 1:2:3 with Pr would lead to a depression of  $T_c$  as a result of changes in the charge density within the Cu-O planes

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similar to that observed in oxygen-deficient  $YBa_2Cu_3O_{7-\delta}$ . Such arguments are supported by recent NMR results in (Y,Pr)  $Ba_2 Cu_3 O_7$  (Ref. 9) and studies of  $T_c$  vs x and y in  $(Y_{1-x}Pr_x)_{1-y}Ca_yBa_2Cu_3O_7$ , where the substitution of divalent Ca tends to reverse the depression in  $T_c$  as a result of Pr doping.<sup>10</sup> The controversy associated with the valence state of Pr in (Y,Pr)Ba\_2Cu\_3O\_7 and the interesting and unexpected properties displayed by this system have stimulated the study of other systems with controlled doping.

Doping studies of  $Bi_2Sr_2CaCu_2O_8$  (2:2:1:2) are fewer in number in the literature, but in many ways this material provides a superior medium. All copper sites are equivalent, there being no chain sites as found in 1:2:3.<sup>11</sup> The material is easy to manufacture and does not require the extensive oxygenation procedure of 1:2:3; nor does it show the environmental sensitivity of this material. A number of studies of rare-earth and lanthanide doping of this system have been reported; 12-14 however, these studies have primarily indicated trends of  $T_c$  versus doping and have not included more extensive studies of the thermodynamic, magnetic, and transport behaviors.

In this paper we present measurements of the temperature dependence of the magnetic susceptibility, lowtemperature specific heat, and electrical resistivity along with measurements of the room-temperature lattice constants for the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}(Y,\text{Pr},\text{Gd})_x\text{Cu}_3\text{O}_8$  (2:2:1:2) system and discuss reported behavior for this system in relationship to similar studies reported for the other high- $T_c$ superconductors. In particular, we will contrast the behavior of Pr, one of the few rare-earth ions to cause  $T_c$ suppression in 1:2:3 and believed to be of mixed-valence character in that system, with the effects of Pr doping in 2:2:1:2.

## II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

All the samples used in this study were prepared using a two-stage coprecipitation method.<sup>15</sup> The first stage consisted of the actual powder production; dilute stoichiometric solutions of the specific cations (Bi, Sr, Ca, etc.) were added dropwise to a rapidly stirred solution of NaOH, Na<sub>2</sub>CO<sub>3</sub>, and acetone chilled to  $0^{\circ}$ C. The resulting precipitate was filtered, washed, and dried. The second stage consisted of the subsequent calcination of the dried powder. Because of the large variation in partial pressure of  $CO_2$  with temperature exhibited by metal carbonates, calcination of the powders generally required a longer heat-treatment process than is typical for the production of high- $T_c$  compounds from oxides. The powders were heated in air at 540 °C for 5 h, followed by a longer 780-800 °C bake for 12 h. Sample disks were then pressed from the powder and sintered at 850 °C for. approximately 100 h. Regrinding, sieving, and sintering were repeated as necessary to provide good sample homogeneity. After each reheating and sintering, the samples were examined for phase purity using a  $2\theta$ - $\theta$  automatic x-ray diffractometer. Heat treatments were continued until there was no evidence of second phases within the x-ray powder pattern. The impurity-phase contributions

were estimated from the diffraction patterns using a commercial computer alogarithm, and in all cases the second phase did not exceed 5%, in most cases being <3%, the limits of second phase detection being  $\sim 2\%$ . Pressed pellets of 2-4 g obtained from the final heat treatment were used for the specific-heat measurements with small bars being cut from these for the transport and magnetic-susceptibility measurements.

The room-temperature crystal-structure and lattice constants were determined using Cu  $K\alpha$  radiation and an automated Rigaku D/Max-B series or Siemens  $2\theta$ - $\theta$  x-ray powder diffractometer. A standard dc four-probe technique was used to measure the electrical resistivity on polycrystalline samples from room temperature to 1.25 K. The specific heat was measured using a semiadiabatic heat-pulse technique for the temperature range 1.5-25 K with some of the measurements extended to 250 K. The magnetization was measured for  $1.6 \le T \le 400$  K and  $H \le 5.5$  T using a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

#### **III. RESULTS AND DISCUSSION**

### A. Crystal structure

The crystal structure was found to remain tetragonal for all samples of Y, Pr, and Gd with  $0 \le x \le 1.0$ . Figure 1 shows the variations of the lattice constants *a* and *c* with concentration of dopant *x* for Y, Gd, and Pr. In the case of Y, the basal plane *a* increases very slightly, while the *c* axis shows a contraction consistent with the replacement of a bigger Ca<sup>2+</sup> ion (ionic radius  $r_{\text{eff}}=0.99$  Å) with a smaller Y<sup>3+</sup> ion ( $r_{\text{eff}}=0.89$  Å). However, the contraction appears to have two separate regimes, a linear decrease in *c* for  $x \le 0.7$  and concentration-independent region for  $0.7 \le x \le 1.0$ . We note that a similar magnitude change in *c* with *x* has been observed by other authors in the form of a single smooth decrease.<sup>16</sup> This



FIG. 1. Variations of the tetragonal unit-cell parameters a and c with concentration of dopant x for Y, Gd, and Pr.

nonlinear dependence of c vs x for Y is not as apparent in the other rare-earth-substituted system studied. While such a trend does seem evident, the uncertainties preclude a definitive statement being made. The very slight elongation of a with x indicates that the addition of a smaller ion at the Ca-ion site has little effect on the Cu-O bond length within the planes.

Doping the Ca site of 2:2:1:2 with  $Gd^{3+}$  ( $r_{eff} = 0.93$  Å) or  $Pr^{3+}$  ( $r_{eff} = 1.06$  Å) causes very little change in a, again reflecting the insensitivity of the Cu-O bond length to the size of ion at the Ca site. The similarity of the concentration dependence of a for Y, Pr, and Gd, despite the significant difference in ionic radii for these ions, suggests that the a-lattice-constant variation is a reflection of change in the Cu-O hybridization brought about by the change in the charge density within the Cu-O planes. Changes are observed in the c parameter with Gd and Pr substitution. Doping causes a slight increase in the case of Pr, in keeping with the  $\sim 6\%$  increase in size of the Pr ion. The c lattice constant decreases with Gd doping. The general trends reported here for the x dependence of c are semiquantitatively consistent with the expected behavior based on ionic radii of the dopants relative to that of Ca. As noted above, there also seems to be a slight nonlinearity for Gd similar to that observed in the Ydoped data. The dashed lines in Fig. 1 are a guide to the eye and would suggest an initial linear depression for  $x \le 0.70$  and a lesser rate of decrease of c for  $x \ge 0.70$ . With the present statistics for the c parameter for the Prand Gd-doped materials, we cannot definitively defend such a variation and note that more careful measurements will be required to resolve this issue.

## **B.** Electrical resistivity

The temperature dependence of the electrical resistivity  $\rho(T)$  for Y-doped 2:2:1:2 is shown in Fig. 2. A linear



FIG. 2. Temperature dependence of the electrical resistivity for a number of concentrations of Y in 2:2:1:2.

high-temperature behavior together with a depression of the superconducting transition temperature  $T_c$  is observed for concentrations  $x \leq 0.6$ . For this concentration range, the temperature derivative of the resistivity,  $d\rho/dT$ , for  $T > T_c$  is reasonably independent of Y doping. Samples with  $x \ge 0.7$  show increasing resistance with decreasing temperature, i.e., semiconducting behavior, in full agreement with previous investigations of this material 16-18 and with the behavior reported for many other doped systems where an abrupt change from "metallic" to semiconducting" behavior occurs in the vicinity of the concentration required to depress  $T_c$  to zero. Figure 3 shows the behavior for Gd and Pr doping. In both these materials,  $T_c$  is suppressed with increasing dopant with  $T_c \rightarrow 0$  for  $x \approx 0.5$ , and for concentrations  $x \ge 0.5$ the samples display a semiconductor T dependence. The similarity in  $T_c$  vs x for Pr and Gd is significant in that it suggests that both ions enter the lattice as trivalent ions and that there must be minimal exchange coupling between the rare-earth ions and the conduction holes within the Cu-O planes. If the classic Abrikosov-Gorkov pairbreaking phenomenon<sup>19</sup> due to a magnetic ion was a significant factor in the suppression of  $T_c$  in these materials, it would be expected that the concentration of dopants required for the observed suppression of  $T_c$ would differ greatly in the two cases because of the substantial difference in their paramagnetic moments and total angular momentum, i.e.,  $\mu_{\text{eff}} = 7.9 \mu_B$ ,  $J = \frac{7}{2}$  and  $\mu_{\text{eff}}=3.54\mu_B$ , J=4 for the trivalent Gd and Pr free ions, respectively. The depression would thus be significantly different in the cases of Gd and Pr and substantially different from that reported here for nonmagnetic Y. That this is not apparent strongly suggests that the principal mechanism of suppression is rather a nonmagnetic charging effect due to the extra electron introduced at the Ca site by the dopant. This electron fills the Cd 3d holes (a factor confirmed by Raman spectroscopy<sup>20</sup>) and hence disrupts the Cu 3d – O2p hybridization, believed to be the primary source for the formation of Cooper pairs, thus



FIG. 3. Temperature dependence of the electrical resistivity for a number of concentrations of (a),(b) Gd and (c),(d) in 2:2:1:2.

leading to the observed suppression of superconductivity. This view is supported by recent theoretical discussions, based on the Anderson impurity model,<sup>21</sup> indicating that the electronic states near the Fermi level are itinerant for a large overlap of the Cu 3d and O 2p wave functions, but become localized when this overlap is reduced.

To continue this approach, for the concentrations of dopant that promote semiconducting behavior, the resistivity can be modeled assuming variable-range hopping between localized states, <sup>22,23</sup> giving rise to

$$\rho(T) \propto \exp(T_0/T)^{1/n} , \qquad (1)$$

where n is an integer having a value of 3 for twodimensional localization and n=4 for three-dimensional localization. In the case of all three of these materials for all semiconducting concentrations, the best fit of the data with Eq. (1) is obtained with n=4. shown in Fig. 4 is the logarithm of  $\rho(T)$  vs  $T^{-1/4}$  for the fully doped compounds. Evidence for three-dimensional variable-range hopping for the other nonsuperconducting samples is observed, but the temperature range over which this behavior is apparent is not as extensive. Similar behavior has been seen for other high- $T_c$  oxide systems which have been doped outside the superconducting region, such as  $La_{2-x}Sr_{x}CuO_{4}$  (Ref. 24) and  $YBa_{2}Cu_{1-x}Zn_{x}O_{7-\delta}$ .<sup>25</sup> This result is, however, particularly interesting when viewed in the context of detailed measurements of the electrical resistivity of the superconducting parent compound 2:2:1:2.<sup>26</sup> Analysis of these results for the temperature regime  $109 \le T \le 125$  K in terms of thermodynamic fluctuations of the pair density has shown that the excess conductivity found is in close agreement with that predicted for a two-dimensional superconductor. In addition, the normal-state conductivity for the parent compound Y 2:2:1:2 is extremely anisotropic with metallic behavior in the basal plane and highly resistive behavior perpendicular to this. With doping of Y, the magnitude of the resistivity at any particular temperature  $(T > T_c)$ increases, but the metallic nature is maintained for most



FIG. 4. Electrical resistivity data fit to a three-dimensional hopping model as detailed in Eq. (1).

of the samples within the superconducting concentration regime. As soon as x is increased to the point where  $T_c \rightarrow 0$ , the resistivity switches from this quasi-two-dimensional behavior to a highly resistive state reflective of three-dimensional variable-range hopping.

### C. Magnetic properties

For those samples that remain superconducting, the temperature dependence of the magnetization shows both a systematic suppression of the magnitude of the diamagnetic response and of  $T_c$  with increasing Y-, Gd-, and Pr-dopant concentration. The  $T_c$ 's derived for the magnetic susceptibility  $\chi(T)$  are in full agreement with those obtained from electrical resistivity and similar to the results of work on other systems.<sup>4</sup>

The temperature dependence of  $\chi(T)$  for Y-doped 2:2:1:2 in the temperature range  $80 \le T \le 400$  K (i.e.,  $T > T_c$ ) is shown in Fig. 5. For  $x \le 0.5$  the susceptibility is essentially temperature and concentration independent. At higher concentrations sufficient to depress  $T_c$  to zero,  $\chi(T)$  switches to a Curie-Weiss-like behavior, i.e.,

$$\chi(T) = \chi_0 + \frac{C}{T + T^*}$$
 (2)

In addition, a detailed examination of the hightemperature data for the Y-doped samples reveals weak but clear cusps at 290, 362,and 369 K for x=0.8, 0.9, and 1.0, respectively. See, for example, the anomaly shown for x=1.0 in the inset of Fig. 5. In this insert  $\Delta \chi$  is the difference between the measured  $\chi(T)$  and  $\chi^*(T)$  obtained by fitting  $\chi(T)$  to the curve over an extended temperature range. These cusps are indicative of long-range antiferromagnetic ordering of the Cu<sup>2+</sup> spins as the substitution of Y<sup>3+</sup> for Ca<sup>2+</sup> causes the localization of the



FIG. 5. High-temperature magnetic-susceptibility data for Y-doped 2:2:1:2. Inset shows an example of antiferromagnetic ordering cusp seen for  $x \ge 0.8$ .

Cu 3d electrons. This increase in localization may enhance the antiferromagnetic superexchange interaction between the Cu ions and result in an observable Néel temperatures for these concentrations. This magnetic ordering has been confirmed by muon-spin-resonance measurements.<sup>27</sup>

In Fig. 6 the inverse susceptibility versus T for two concentrations of Pr- and Gd-doped 2:2:1:2 are shown. For the high-concentration nonsuperconducting samples, the  $\chi(T)$  behavior is Curie-Weiss like with  $T^* < 0$ , indicating antiferromagnetic exchange. No explicit cusps indicative of antiferromagnetic ordering similar to those apparent in  $\chi(T)$  for the Y-doped samples are observed. Evidence for an antiferromagnetic ordering temperature of the Cu localized d state in the Pr- and Gd-doped samples is likely obscured by the large Curie-Weiss contribution to  $\chi(T)$  due to the rare-earth moments. The data in Fig. 6 have been fitted to the standard Curie-Weiss-like expression given in Eq. (2), and the effective paramagnetic moments versus x for the Pr- and Gd-doped samples have been extracted and are shown in Fig. 7. It can be seen that for both Gd and Pr the ions retain an effective paramagnetic moment which is nearly independent of x, with average values of these moments being close to the free-ion paramagnetic moments for  $Pr^{3+}$  and  $Gd^{3+}$ , shown by the solid lines in Fig. 7. It is interesting to note, however, that in the case of Pr-doped 2:2:1:2 the effective paramagnetic moment is not the same moment obtained when Pr is substituted for Y in the 1:2:3 lattice, also shown in Fig. 7 for convenience. In 1:2:3 for all values of x, the effective moment has a value consistently closer to the one expected for a  $Pr^{4+}$  ion. This result has caused much discussion in the literature.<sup>8,28</sup> It has been proposed that the apparent tetravalent behavior of Pr in 1:2:3, as reflected by the data in Fig. 7, is due to the improper accounting of crystal electric-field (CEF) effects in the analysis of the high-temperature  $\chi(T)$  data. If this is true, the disparity in the observed effective moment for Pr in 1:2:3 vs 2:2:1:2 remains difficult to understand as one would not expect a large difference in the CEF splitting of the low-lying Pr levels for these two systems. The local environment for the Pr ion in these two systems is



FIG. 6. Inverse susceptibility vs temperature for two concentrations of (a) Gd-doped 2:2:1:2 and (b) Pr-doped 2:2:1:2.



FIG. 7. Effective moment of impurity ions obtained from susceptibility data. Solid lines indicate the values of the free-ion moments for trivalent Gd and Pr in 2:2:1:2 and tetravalent Pr in 1:2:3. Open circles indicate the effective moment developed by Cu ions in Y-doped 2:2:1:2.

very similar; i.e., we would suggest that the lattice position of the substituted Pr ion in both 2:2:1:2 and 1:2:3 at the center of an almost cubic Cu-O array is sufficiently similar to first-order nearest and next-nearest neighbors that it would be both surprising and fortuitous if the splitting could cause this discrepancy in  $\mu_{\rm eff}$ .

It is clear from susceptibility measurements on Pr 2:2:1:2 that while this material exhibits some antiferromagnet exchange, a clear antiferromagnetic transition such as that observed in Pr 1:2:3 at  $\sim 17$  K (Ref. 29) is not in evidence for T > 1.6 K. The large electronic specific-heat contribution seen in Pr 1:2:3 has been associated with strong 4f-conduction-hole hybridization which could drive the ordering of the Pr ions. As discussed next, evidence for such hybridization for Pr 2:2:1:2 is absent and the significantly depressed exchange interaction due to the lack of hybridization could account for the difference in magnetic response between these two systems. No evidence for ordering of the Gd moments is seen for T > 1.5 K, and this should be compared to the  $T_N \approx 2.25$  K due to Gd ordering in GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. It would thus appear that the coupling of the rare-earth ions in rare-earth-doped 2:2:1:2 is depressed relative to that reported for rare-earth-substituted 1:2:3 despite the similarity in the local environment of the ions.

#### D. Specific heat

Examples of specific-heat data for the three materials plotted as C/T vs  $T^2$  are shown in Fig. 8. All of the materials show an almost linear temperature dependence with a slight upturn at low T. The data was fitted for comparison to the standard equation  $C(T)/T = \gamma + \beta T^2$ , giving the values of  $\gamma$  shown in Fig. 9. Also shown in Fig. 9(b) are  $\gamma$  values for Pr-doped 1:2:3. In all cases, as the concentration of impurity is increased,  $\gamma$  also in-



FIG. 8. Temperature dependence of the specific heat for two concentration of impurities (a) Y, (b) Gd, and (c) Pr in 2:2:1:2.

creases. This again supports the suggestion that the substitutions reduce the hybridization of the Cu 3d and O 2plevels, causing a localization of the holes at the Fermi energy and a subsequent increase in the density of states at  $E_F$ . The increase in the electronic contribution to the specific heat is greater by an order of magnitude for Pr doped into 1:2:3 than for the equivalent amount of the



FIG. 9. The concentration dependence of the electronic contribution to the specific heat for (a) Y and Gd and (b) Pr in 2:2:1:2. Also shown for comparison are similar data for Pr in 1:2:3.

material in 2:2:1:2. This has been argued to be a result of the mixed-valence nature of Pr when in the 1:2:3 lattice, <sup>30</sup> causing strong 4f mixing or hybridization with the conduction holes of the Cu-O planes. The slight differences seen between the x dependences of  $\gamma$  for Y, Gd, and Pr must be attributed to differences in Cu-O conduction-hole localization brought about by differences in the lattice constants. The  $\gamma = 33 \text{ mJ/(mol K}^2)$  measured for Gd 2:2:1:2 is similar to that reported for highly correlated *d*-electron systems such as Pd. The upturns seen in C(T) as  $T \rightarrow 0$  could then be due to spinfluctuation effects. Additional measurements of C(T) extended to lower temperature and in a magnetic field would help shed some light on further analysis of the specific-heat data for these systems.

Despite the fact that the C(T) data do not explicitly show additional structure at low temperature, a careful analysis of C(T) for T < 15 K clearly indicates evidence of an excess phonon contribution in the specific heat of Y-doped 2:2:1:2 similar to that observed in the pure material.<sup>26</sup> This additional structure in C(T) is most likely due to low-energy phonon modes and can be accounted for by the inclusion of a low-temperature Einstein contribution to C(T).

As previously stated, specific-heat measurements do not shown any explicit peaks due to magnetic ordering



FIG. 10. Magnetic phase diagrams for (b) Y and (c) Gd and Pr in 2:2:1:2. Also shown is a similar figure for (a) Pr in 1:2:3 with the detail of the crossover region of  $T_c$  and  $T_N$  shown in the inset.

for  $T \ge 1.7$  K for the Pr- or Gd-doped materials. This is somewhat puzzling when compared to  $T_N = 17$  and 2.25 K for Pr 1:2:3 and Gd 1:2:3, respectively.

### **IV. CONCLUSIONS**

The results presented above allow the construction of the phase diagrams of the Y-, Pr-, and Gd-doped 2:2:1:2 materials, shown in Fig. 10 together with the equivalent data for the Pr-doped 1:2:3.<sup>31</sup> The most noticeable aspect is the similarity of the curve of  $T_c$  vs x for the Gd and Pr materials. As mentioned, this highlights the minimal contribution to  $T_c$  suppression of Abrikosov-Gorkov pair breaking, a fact that is surprising when compared with the phase diagram for Pr-doped 1:2:3. The sharp drop in the curve of  $T_c$  for Pr 1:2:3 around x=0.5, highlighted in the inset of Fig. 10(a), is indicative of exchange depairing in this system. Renormalization of  $T_c$ vs x due to exchange effects in the vicinity of crossings between magnetic and superconducting phase boundaries have been frequently seen in magnetically doped conventional superconductors.<sup>32</sup> We note that no such effect is observed for Y- Pr- or Gd-doped 2:2:1:2.

Also shown in Fig. 10(a) is the Néel temperature of the copper ions  $(T_{N1})$ . This curve clearly intercepts the critical temperature curve at  $x \sim 0.5$ , thus raising the possibility of the coexistence of antiferromagnetism and superconductivity. Extrapolation of the  $T_N$  curve for the Y-doped 2:2:1:2 shows the possibility of a similar intercept behavior. However, further measurements on a fine grid of concentrations around x=0.5 are needed.

In conclusion, measurements of some of the transport and thermodynamic properties of Y-, Gd-, and Pr-doped 2:2:1:2 have been presented and discussed. All of these materials substitute a 3+ ion for a 2+ ion at the Ca site, with the consequent introduction of magnetic moments in the cases of Gd and Pr. The dominant superconducting suppression effect in all cases seems to be the filling of the Cu-O holes by the excess charge introduced by the dopant, leading to a breakdown of the hybridization of the Cu 3d - O 2p states within the Cu-O planes. A corre-

lation between  $T_c$  and hole concentration in the Cu-O planes has previously been established in  $La_{1-x}Sr_xCuO_4$ and 1:2:3. 33,34 With the complete suppression of superconductivity, known to be a quasi-two-dimensional phenomenon in these materials, the predominant conductivity mechanism is one of three-dimensional variablerange hopping between localized states, resulting in a macroscopic semiconducting behavior. Localization of the Cu 3d electrons causes an increase in antiferromagnetic exchange between Cu ions and the appearance of antiferromagnetic ordering for concentrations of  $x \ge 0.8$ of Y. In the case of Gd or Pr, this Cu ordering is not observable because of the large Curie-Weiss contribution of the rare-earth moments themselves. In addition, no anomalies that would indicate possible magnetic ordering of the rare-earth moments in fully substituted Gd and Pr 2:2:1:2 are observed in either the magnetic susceptibility or heat capacity for  $T \ge 1.5$  K. The effective moments of Gd and Pr within the materials are very close to their 3+free-ion values, which, in the case of Pr, contrasts with the suspected 4 + value found when doped for Y in 1:2:3. The reason for this is not yet understood.

It is clear from the measurements and discussions presented here that the effect of impurity doping on the physical properties of high-temperature superconductors is far from clear-cut. In particular, the addition of magnetic impurities may not cause the significant changes one may expect from a simple examination of the free-ion moments, this being due to the importance of the lattice position of the impurity and the specific conductionelectron wave-function overlaps. The special case of the so-called mixed-valence impurity is likely to engender much interest and future work.

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