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Resistive and magnetic studies of $Nd_1Ba_2Cu_3O_{7-\delta}$ and $Pr_1Ba_2Cu_3O_{7-\delta}$

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We report resistivity, structural, and magnetic susceptibility $[\chi^{\mathrm{spin}}(T)]$ measurements for the compounds $Pr_1Ba_2Cu_3O_{7-\delta}$ and $Nd_1Ba_2Cu_3O_{7-\delta}$. The Nd compound is superconducting with an onset transition temperature of 90 K, while the Pr compound is semiconducting above 4 K. The lattice parameters for these two materials have been determined using x-ray diffraction techniques, and both appear to be tetragonal, although the $Nd_1Ba_2Cu_3O_{7-\delta}$ compound may exhibit some orthorhombic splitting. The high-temperature effective moments in the two systems are within a few percent of the free-ion moments. In each case the presence of significant curvature in the inverse susceptibility versus T behavior on the scale of 100 K suggests the presence of crystalline electric field splittings on the same energy scale. For the Pr compound this is further confirmed by a finite value for $\chi^{\mathrm{spin}}(0)$ and a residual large constant term at high temperatures. The possible origin of semiconducting behavior as compared with superconducting behavior in the Nd and other rare-earth compounds is discussed in terms of differences in charge-carrier density and possible role of valence fluctuations among Pr rare-earth ions.

I. INTRODUCTION

It is now well known that high-temperature superconductivity near 90 K in compounds of the generic form $RBa_2Cu_3O_{7-\delta}$ is almost independent of which trivalent R ion is used from among yttrium and the rare earths.[1-3] Exceptions to this rule are lanathanum,[4] cerium,[1] terbium (for which, as far as we are aware, no 1:2:3 compound has been prepared), and praseodynium (which forms a semiconductor).[5-7] It has been noted that Tb, Ce, and Pr all have a tendency towards valence instabilities (partial tetravalence) which may be related to the difficulties in making superconductors out of these compounds. It should be noted that difficulties with the light lanthanides may arise in part from the larger ionic radius.

These "exceptions" to the independence of the trivalent substitution may play an important role in probing the physics of high-temperature superconductivity. It is therefore prudent to characterize the properties of these materials as thoroughly as for the 90-K superconductors. In this work we will examine the details of resistivity, magnetic susceptibility, and structural measurement on single-phase polycrystalline samples of $Nd_1Ba_2Cu_3O_{7-\delta}$ and $Pr_1Ba_2Cu_3O_{7-\delta}$. To our knowledge these are the first reported detailed magnetic measurements on these materials which differ only by one atomic number. A comparison of the properties of the Nd and Pr compounds enables insight into the origins of high-temperature superconductivity present only in the Nd compound. It is suggested that this results from differences in the charge-carrier density and possible role of valence fluctuations.

Our resistivity measurements reveal the Nd-based sample to be superconducting with an onset temperature of 90 K and zero resistance at 75 K. The resistivity curves are shown in Fig. 1. X-ray diffraction measurements reveal tetragonal or weakly orthorhombic structure. The samples are single phase as revealed by x-ray and scanning electron microscopy (SEM) studies. The effective moment obtained for the Nd compound is $3.57\mu_B$ which compares very well with the value of $3.62\mu_B$ which is calculated for the free ion. Below the superconducting transition temperature, the Nd compound shows a broadened diamagnetic transition[8] now well known to be a characteristic of the granular composite structure of the single-phase samples. In addition, a weak paramagnetic tail is observed well below T_c as in previous work on the magnet-

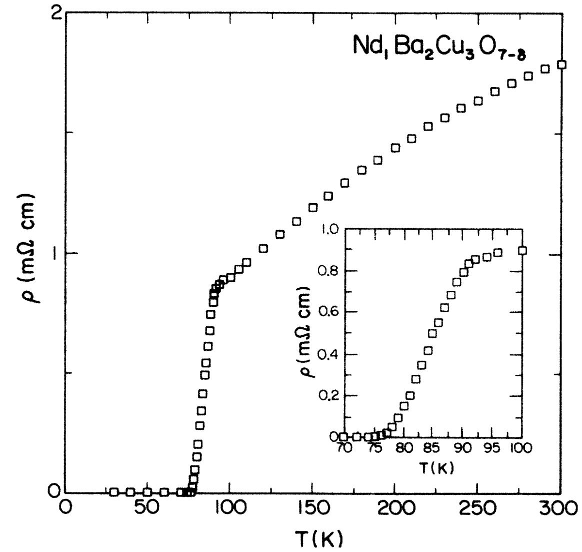

FIG. 1. Resistivity ρ vs temperature T for $Nd_1Ba_2Cu_3O_{7-\delta}$. Inset: ρ vs T near the superconducting transition.

ic ion based 1:2:3 compounds[8] due to the influence of the screened local field on the Nd local moments. The Meissner effect is 26% of $1/4\pi$ at a field of 690 G. The Pr sample, on the other hand, is a semiconductor. Analysis of the magnetic data yields a high-temperature effective moment of $3.35\mu_B$ which is slightly less than that measured for the Pr free ion.[9,10] The susceptibility measurements for the $Nd_1Ba_2Cu_3O_{7-\delta}$ and $Pr_1Ba_2Cu_3O_{7-\delta}$ compounds indicate the role of strong crystal-field splittings in both of these materials. The Pr compound shows pronounced curvature in plots of inverse susceptibility as a function of temperature.

SEM and x-ray diffraction studies of both samples show them to possess a 1:2:3 structure and samples are identified as being single phase. The SEM measurements in particular indicate both the samples as having a grain size of 30 μm. The lattice parameters of the Pr and Nd compounds were determined using x-ray diffraction techniques. Data are consistent with tetragonal symmetry, though there is evidence of some orthorhombic shouldering in the $Nd_1Ba_2Cu_3O_{7-\delta}$ case. The lattice parameters for the $Pr_1Ba_2Cu_3O_{7-\delta}$ are $a=3.8868\pm0.0016$ Å, $b=3.8887\pm0.0022$ Å, and $c=11.654\pm0.0058$ Å. The $Nd_1Ba_2Cu_3O_{7-\delta}$ compound similarly exhibits a tetragonal symmetry albeit with some orthorhombic shouldering and one obtains $a=3.8795\pm0.0021$ Å, $b=3.8745\pm0.0029$ Å, and $c=11.626\pm0.0076$ Å.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The samples used in this study were prepared by a coprecipitation technique described extensively elsewhere.[11,12] The resistivity measurements were carried out using a four-probe technique and results indicate that the sample retains its semiconducting behavior to temperatures as low as 4 K. The Nd compound, on the other hand, exhibits behavior which is consistent with a superconductor. The onset temperature for superconductivity is approximately 90 K. A plot of the resistivity as a function of temperature is shown in Fig. 1. In the inset we note that the resistance exhibits a drop over a region in temperature between 75 and 90 K and since this region is fairly wide, our magnetic data must be interpreted in this context. In Fig. 2 we show a plot of resistivity as a function of temperature for $Pr_1Ba_2Cu_3O_{7-\delta}$. Between 300 and 80 K the resistivity varies approximately as $\exp[(T_0/T)^{1/4}]$ with $T_0=5.4\times10^4$. Below 80 K the resistivity decreases more slowly with decreasing temperature.

The magnetic measurements were performed using a Faraday balance which has been described elsewhere.[13] The 0.015-cm^3 samples were loaded in a 0.99999 pure Al sample holder and the data which was obtained was corrected for the sample holder as well as the core diamagnetism of the sample. (The core diamagnetism was obtained adding the core susceptibilities[14] of the individual constituents in the system; for oxygen content we assumed $\delta=0$.) In Fig. 3 we show a plot of reciprocal spin susceptibility as a function of temperature for the Pr sample; one finds that the susceptibility does not follow a simple Curie-Weiss law. The data in the temperature region between 150 and 300 K can be fit to an expression of the form $\chi^{\rm spin}=A+B/(T-\Theta)$. We obtain a Curie constant of 1.37 which yields an effective moment of $3.35\mu_B$ somewhat reduced from the free-ion value of $3.58\mu_B$.[9,10] In the infinite temperature limit we get a large constant term A of value 2.19×10^{-3} emu/mol which, as has been found previously for the Er- and Ho-based 1:2:3 materials, has been attributed to the Van Vleck contribution arising from the crystal-field splittings.

The susceptibility of the Pr-based compound is qualitatively consistent with the presence of crystal-field splittings of a nominally stable trivalent ion ranging from 10 to 100 K. In support of this claim we note the following. (1) For the tetragonal fields at the rare-earth site, group theoretic considerations show that the $J=4$ Hund's-rule ground multiplet will split into two doublet and five singlet levels. There are therefore a large number of possible nonmagnetic ground states. This is consistent with the

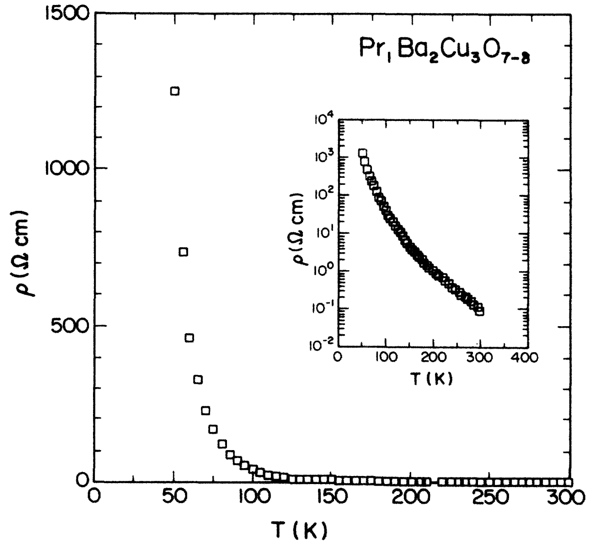

FIG. 2. Resistivity ρ vs temperature T for $Pr_1Ba_2Cu_3O_{7-\delta}$. Inset: ρ vs T plotted on a logarithmic scale.

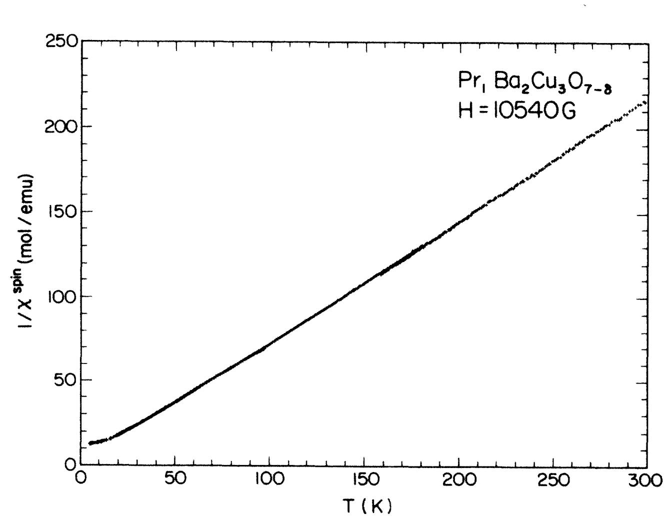

FIG. 3. Reciprocal spin susceptibility $(\chi^{\rm spin})^{-1}$ vs temperature T for $Pr_1Ba_2Cu_3O_{7-\delta}$ at a field of 10540 G.

finite susceptibility as T goes to infinity, which must then be of Van Vleck origin. (2) The inverse susceptibility shows considerable curvature in the region between 100 and 200 K as is common in crystal-field split ionic materials. (3) If one fits the high-temperature behavior by the sum of a Curie-Weiss law plus a constant term, one obtains a Curie constant of 1.37 which is within 5% of the theoretically calculated value, a $\Theta = -5$ K indicating antiferromagnetic interactions and a constant term which is about an order of magnitude greater than either the (nominal) Pauli susceptibility observed in the yttrium based or the free ion Pr^{3+} Van Vleck susceptibility (due to excited spin-orbit multiplets).[10] In view of the latter result, given the comparable sizes of the matrix elements, a ground-state–excited-state splitting one order of magnitude or smaller than the free ion $J=4$ to $J=5$ splitting of about 3000 K (Ref. 15) is consistent with the constant A value used. A quantitative description of the crystal-field effects is not possible at this time due to the large number of (undetermined) parameters necessary for describing the seven different levels.

The Nd sample which was studied was of 0.015 cm^3 dimension. A correction for the demagnetization factor was not taken into account since the dimensions for the material were irregular. Figure 4 shows a plot of the spin susceptibility χ^{spin} as a function of temperature for a field of 5.37 kG. Using the value of the χ^{spin} at the higher temperature regime we obtain an effective moment of $3.57\mu_B$. The theoretical free-ion effective moment of $3.62\mu_B$ (Ref. 9) agrees well with the experimentally obtained value. However, we note that (most probably as a consequence of crystal-field effects again) a fit to the form $\chi^{spin}=A+C/(T-\Theta)$ is not possible. With decreasing temperature one notices the negative curvature in the susceptibility which is characteristic of superconductivity. At a temperature of 20 K one obtains a $\chi=0.003$ emu/mol or about 2.1×10^{-2} emu/cm^3 amounting to about 26% of perfect diamagnetism. The susceptibility for $Nd_1Ba_2Cu_3O_{7-\delta}$ near the transition at low fields is indicative of strong flux penetration. In composite materials such behavior arises if the penetration length is comparable to the scale of the inhomogeneities.[16] In the inset to Fig. 4 we show a plot of the susceptibilities as a function of the temperature for a field of 0.691 kG. The data obtained for the normal state of the Nd sample are qualitatively consistent with crystal-field splittings of the order of 100 K, given the curvature of the inverse susceptibility in this regime. The magnetization M as a function of the applied field H at a temperature of 70 K (not shown here) can be used to estimate H_{c1} as 100 G at 70 K; this compares well with the data obtained for other 1:2:3 superconductors in the range of a few hundred gauss. As mentioned earlier the data at temperatures below 20 K show an upturn in the susceptibility. The data fit a Curie law

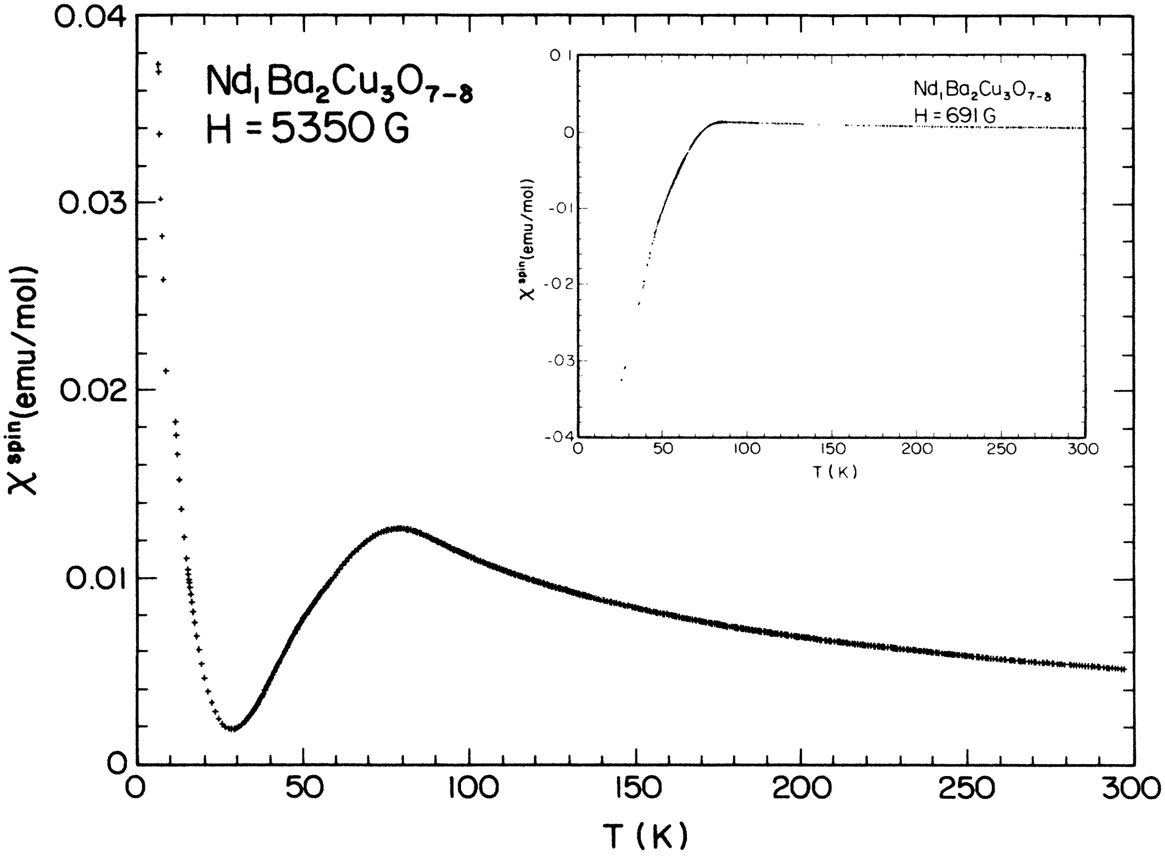

FIG. 4. Spin susceptibility χ^{spin} vs temperature T for $Nd_1Ba_2Cu_3O_{7-\delta}$ at a field of 5350 G. Inset: χ^{spin} vs T at a field of 691 G for the $Nd_1Ba_2Cu_3O_{7-\delta}$ sample.

and one obtains 0.6 spins per formula unit; the reduction in the number of Curie spins has been attributed to screening of the local fields on the localized Nd moments.[8] We note that further evidence for crystal-field splittings in these two compounds comes from the observation of Schottky anomalies in the specific heat.[17]

The origins of the semiconducting behavior in $Pr_1Ba_2Cu_3O_{7-\delta}$ compound are of fundamental interest in determining the origin of the high-temperature superconductivity in other members of this family of compounds. The similarities of the magnetic data with the neighboring compound $Nd_1Ba_2Cu_3O_{7-\delta}$ suggests that the origins lie in the Pr valence fluctuations which make the rare-earth ions slightly tetravalent. A valence of $3+v$ will drive the formal Cu valence towards 2+. In the Y-Ba-Cu-O system, oxygen annealing experiments reveal that when the Cu ions are formally divalent, superconductivity vanishes. This could give a tendency towards insulating behavior since in a Mott-Hubbard picture the divalent Cu ions represent a half-filled band. However, it may be that the dynamics of the spin fluctuations play a role through pair breaking.

To see why valence arguments are insufficient, assume an oxygen deficiency from seven atoms of δ and a nominal Cu valence of 2. Then v from above is given by $2-4\delta$. We expect v to be quite small, assuming a value of 0.1 for v (Ref. 18), δ must equal 0.475. It is unlikely that one would have such a large oxygen deficiency in the presence of excess positive charge. Hence, it may well be that the Pr valence fluctuations play a dynamic pair-breaking or weakening role. Experiments are in progress to test the validity of these theories.

III. SUMMARY

In summary, we have presented comprehensive measurements on the magnetic and structural aspects of the high-T_c superconductor $Nd_1Ba_2Cu_3O_{7-\delta}$ and the insulator $Pr_1Ba_2Cu_3O_{7-\delta}$. The data can be well understood in the framework of existing theory of superconductivity and in the framework of crystal-field effects which are known to exist in these rare earths. The general curvature in susceptibility which is obtained can be well understood on the basis of magnetic behavior of the rare earths. The critical field is estimated to be of order of 100 G at 70 K. The magnetic moments that are obtained agree rather well with the free-ion moments. For the Nd sample we obtain a flux exclusion of 26% of the perfect diamagnetism which is in agreement with what is measured in other magnetic superconductors. The origin of the semiconducting behavior of the $Pr_1Ba_2Cu_3O_{7-\delta}$ may be in the changed carrier density in the Cu-O lattice and effects of the Pr valence fluctuations.

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