Magnetic susceptibility studies on $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ single crystals in the insulating regime

B. Jayaram and H. Srikanth
Materials Science Program, Department of Physics, University of Nebraska at Omaha, Omaha, Nebraska 68182-0266
B. M. Wanklyn and C. Changkang
Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, United Kingdom
E. Holzinger-Schweiger and G. Leising
Institut für Festkörperphysik, Technische Universität Graz, Petersgasse 16, 8010 Graz, Austria
(Received 17 January 1995)

We have performed magnetic-susceptibility measurements on single crystals of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ with $0.4 \leq x \leq 1$, in the temperature range 5–300 K. The susceptibility at low temperature is nonlinear, however, above 100 K it is found to follow the Curie law. The values of the effective moment deduced is attributed to Pr in a 3+ valency state. This interpretation is consistent with the theoretical models that take into account the crystal-field effects on the trivalent Pr. The magnetic anisotropy studies indicate that the susceptibility along the *c* axis is greater than that along the *ab* plane in the entire temperature region 5–300 K. This observation favors the crystal-field schemes that have a ground state of Γ_4 or Γ_2 symmetry.

The pseudoquarternary compounds of the form $RBa_2Cu_3O_{7-\delta}$, except for R =Pr, Ce, and Tb, show a superconducting transition in the vicinity of 92 K.[1] The $PrBa_2Cu_3O_7$ system (henceforth referred to as PBCO) is distinct because of the absence of superconductivity even though its crystal structure is identical to other rare-earth 123 compounds. In the $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ (PYBCO) system superconductivity is rapidly suppressed as Pr content is increased and there is a transition from superconductor to an antiferromagnetic insulator at $x \sim 0.5$. The PBCO and PYBCO systems have been a subject of extensive experimental and theoretical investigations to unravel the principal role of Pr ions in the T_c suppression.

Two basically different points of view have been proposed to account for the absence (suppression) of superconductivity in the PBCO (PYBCO) system. From one point of view, it has been argued that Pr is in a mixed valent state with a valency more than 3+.[1–3] In this scenario, the extra electrons are thought to fill the hole states in the conduction band and thus inhibit superconductivity. A decrease in the number of mobile holes with increasing Pr content, determined by Hall-effect measurements and the magnitude of effective moment, determined from the temperature dependence of the susceptibility seem to favor this conclusion.[3,4] The other point of view is that Pr retains a valency of 3+ and a strong magnetic interaction between the Pr^{3+} ions and the conduction electrons in the CuO_2 planes has a deleterious effect on superconductivity.[5,6] A large mass of recent results, including inelastic neutron scattering, valence-band photoemission, and electron energy-loss spectroscopy measurements support the second scenario.[7–9]

It is crucial to probe the magnetic state of Pr in PYBCO as it is purported to play a major role in the suppression of superconductivity. A majority of the normal-state magnetic-susceptibility measurements that have been made to date to determine the Pr valency, are on polycrystalline materials.[1] The susceptibility data is often shown to follow the Curie-Weiss behavior. Furthermore the data for high Pr concentration (x) shows an anomaly in the vicinity of 17 K, which represents T_N, the temperature corresponding to antiferromagnetic ordering of Pr moments. The polycrystalline data also shows a clear shift in T_N with the variation of x.

In the case of PBCO, because of the enhanced *s-f* interaction and large crystal-field effects involved, Soderholm *et al.*[7] have argued that it is incorrect to compare the effective moment deduced from the normal-state susceptibility data with that of free ion values of Pr 3+ and 4+. They have developed a self-consistent approach to obtain the full set of crystal-field parameters for PBCO which scales with the corresponding parameters for various rare-earth 123 compounds. With this scheme and taking a Pr valence state of 3+ they have calculated the magnetic susceptibility (χ) using the van Vleck formalism. The temperature variation of susceptibility predicted by these calculations deviates significantly from that found in the case of polycrystalline materials. Furthermore the calculations assume that the *c* axis is the easy axis of magnetization. It is essential to make measurements on good quality single crystals to unravel the intrinsic characteristics of magnetic susceptibility of Pr in the $YBa_2Cu_3O_{7-\delta}$ system. In this report we present a systematic study of the magnetic susceptibility of well-characterized single crystals of PYBCO in the insulating regime. We determine the effective moment (μ_{eff}) from the temperature-dependent susceptibility $\chi(T)$ and also study the variation in magnetic anisotropy as the Pr content is changed.

The single crystals of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ (PYBCO) with $0.4 \leq x \leq 1$, were grown from a flux of BaO and CuO.[10] The mixture of the starting materials was heated in an alumina crucible up to 1040 °C at a rate of 75 °C h^{-1}, held at that temperature for 5 h and slowly cooled down to 960 °C at a rate of 0.5 °C h^{-1}. Single crystals in rectangular form with sizes up to $5 \times 5 \times 0.4$ mm^3 have been obtained. The Pr concentration of the

crystals was determined by electron-probe microanalysis. The magnetic-susceptibility measurements were performed using a Quantum Design superconducting quantum interference device magnetometer operating at a magnetic field of 1 T and temperatures ranging from 5 to 300 K.

The temperature-dependent magnetic susceptibility $\chi(T)$ for three single crystals of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ (PYBCO) with x values 0.4, 0.7, and 0.9 are shown in Fig. 1. These three concentrations are chosen as they are representative of the insulating regime from just above the superconductor-insulator transition ($x=0.4$) to well into the insulating region ($x=0.9$). It is to be noted that the superconductor-insulator transition occurs at a lower Pr concentration in these single crystals compared to polycrystalline samples in which the transition takes place typically in the range $x\sim 0.5$ to 0.6. The reason for this could possibly be ascribed to a slight discrepancy in the estimation of actual Pr content in the polycrystalline grains which can be different from that of the starting nominal composition. The $\chi(T)$ curves show a clear trend that the low-temperature susceptibility increases by nearly three orders of magnitude as x is increased from 0.4 to 0.9. This is indicative of the expected enhancement in the ordering of Pr moments as the Pr content is increased in the PYBCO system. The three curves shown in Fig. 1 are for B parallel to ab plane.

One of the anomalous features in the PYBCO system is that though the specific heat shows a fairly prominent Schottky anomaly at the magnetic ordering temperature of Pr moments, the magnetic susceptibility even in the case of single crystals does not show the characteristic cusp at the Néel temperature (T_N).[5,11] In fact in several earlier studies on polycrystalline samples, there is only a weak slope change at 17 K which has been associated with Pr ordering and this shows up as a distinct feature when the derivative ($d\chi/dT$) is plotted.[5,12] This is in conflict with the conventional manifestation of antiferromagnetic order in the bulk susceptibility where a peak occurs at T_N and the susceptibility decreases for $T<T_N$. The increase in $\chi(T)$ below T_N could be due to the small moment in this system or it may indicate that the magnetic structure is more complicated than presently understood. In Fig. 2 we present the derivative of χ with inverse temperature for the three Pr concentrations. A cusp is seen in $d\chi/d(1/T)$ at a temperature which is close to the Pr ordering temperature of 17 K. However, in contrast to the observations made in polycrystalline samples where T_N is found to shift to lower temperatures with the Pr concentration approaching the superconducting regime,[5] as shown in Fig. 2, in single crystals T_N remains invariant for Pr concentration ranging from 0.4 to 0.9. Many of the anomalous features associated with the magnetic ordering could be attributed to the hybridization effects. Cooper has discussed magnetic ordering in Pr-rich PYBCO in terms of cooperative valence fluctuations of the Cu ions mediated through hybridization effects.[13] The Pr ions are hybridized with the conduction electrons and the magnetic ordering is orbitally driven rather than spin driven. In our opinion, the insulating nature of PBCO along with the anomalous magnetic properties of this system is a direct consequence of its unusual electronic properties.

The main panel of Fig. 3 shows the magnetic-susceptibility data for the single crystal ($x=0.7$) with the applied field (B) parallel to the ab plane as well as the c axis. We shall describe the field orientation with respect to the ab plane, as it contains the copper-oxygen planes that are crucial for high-temperature superconductivity, and assign the symbols χ_{ab} (for susceptibility with B parallel to the ab plane) and χ_c (for susceptibility with B parallel to the c axis). Anisotropy in magnetic susceptibility is seen in all the single crystals with $\chi_c>\chi_{ab}$ in the temperature region 5–300 K. In the inset of Fig. 3 we have plotted the difference in susceptibility $\Delta\chi=\chi_c-\chi_{ab}$ at 5 K as a function of Pr concentration. This difference consistently increases as seen in the inset and one can infer that the Pr moments order with a preferred orienta-

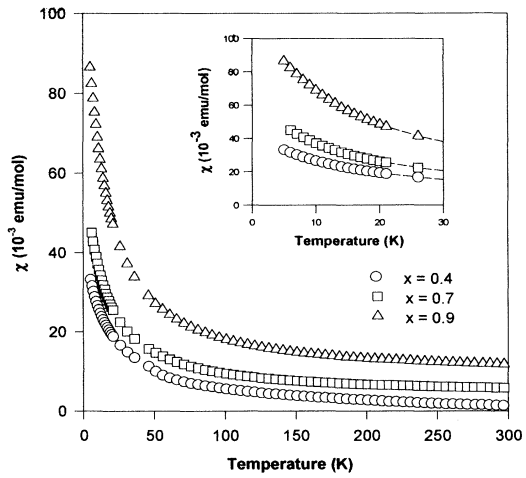

FIG. 1. The temperature-dependent normal-state susceptibility $\chi(T)$ (with B parallel to ab plane) of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ single crystals with $x=0.4$, 0.7, and 0.9 in the temperature range 5–300 K. The inset shows the expanded region, 5–30 K, for the same data. A cusp is expected below 17 K corresponding to the Pr ordering temperature.

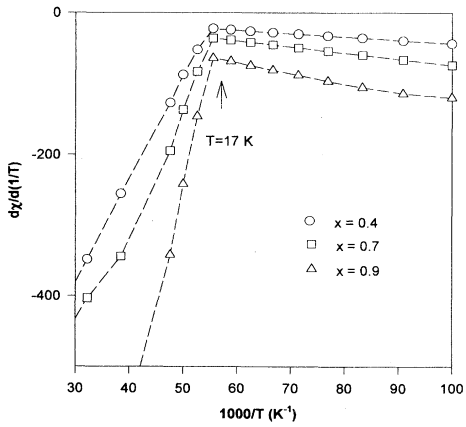

FIG. 2. The derivative of susceptibility plotted as a function of inverse temperature for three compositions of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ crystals. The arrow marks the Néel temperature of Pr ordering ($T_N\sim 17$ K).

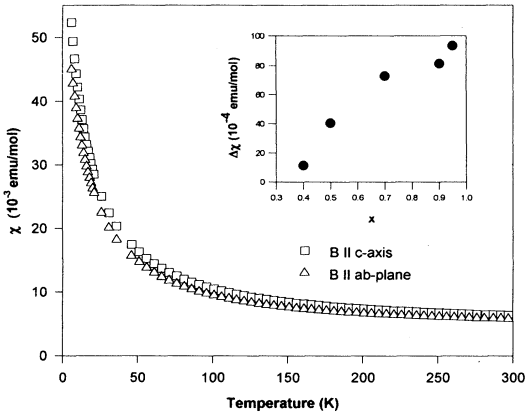

FIG. 3. The temperature-dependent normal-state susceptibility of single crystal $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ ($x=0.7$) for the two field orientations B parallel to the c axis and B parallel to the ab plane. Inset shows the difference in susceptibility $\Delta\chi$ ($=\chi_c-\chi_{ab}$) at 5 K for Pr content (x) ranging from 0.4 to 0.95.

tion along the c axis.

Recently the magnetic nature of Pr in $YBa_2Cu_3O_{7-\delta}$ lattice is probed in great detail by inelastic neutron-scattering measurements accompanied by crystal-field calculations to resolve the controversy regarding its valence state.[5,7,11,14] All these studies unambiguously conclude that Pr is in 3+ state following a satisfactory agreement between the observed and the calculated energies and intensities of the crystal-field transitions. There are, however, inconsistencies pertaining to the symmetry assignments for these levels. The overall energy span of the crystal-field splitting corresponds to 1200 K. Therefore $\chi(T)$ measurements should be performed above this temperature to see the effect of all these levels on susceptibility. However the single-crystal susceptibility data collected over the temperature range of 5–300 K should provide crucial evidence for the correct order of the low-energy levels ($\Gamma_1,\Gamma_2,\Gamma_4$). There exist four different crystal-field schemes, which can be grouped into two models that assign Γ_1 symmetry to the ground state and the others that give Γ_4 or Γ_2. Models with a Γ_1 ground state predict that $\chi_c<\chi_{ab}$ for temperatures below 100 K.[7] On the other hand models with a Γ_4 or Γ_2 ground state predict that $\chi_c>\chi_{ab}$ independent of temperature.[11,14] As depicted in Fig. 3 in the insulating regime χ_c is found to be greater than χ_{ab} over the temperature range 5–300 K. This observation clearly supports the latter crystal-field models with the symmetry assignments Γ_4-Γ_2-Γ_1 with Γ_2-Γ_4-Γ_1 to the ground state and the next-nearest excited states.

Another point of interest in Fig. 3 is that the anisotropy shows a characteristic temperature dependence, that is the anisotropy is maximum at 5 K and reduces as the temperature is increased to 300 K. Physical significance of this is not apparent at this point of time as we are not aware of the functional form with which the anisotropy is expected to change with temperature. It is however evident that the low-temperature (that is $T<50$ K) susceptibility calculations that attempt to make realistic predictions should take into account the exchange coupling that leads to antiferromagnetic ordering of the Pr ions and the considerable lifetime broadening of the crystal-field levels.

Figure 4 shows the temperature dependence of the inverse magnetic susceptibility of $Pr_{0.7}Y_{0.3}Ba_2Cu_3O_{7-\delta}$ single crystal with B parallel to the ab plane as well as the c axis. All other compositions also display this typical behavior. From Fig. 4, it is apparent that the temperature variation is nonlinear and that the susceptibility data does not follow the Curie-Weiss law. As a result the susceptibility data is plotted as a function of inverse temperature in an attempt to fit it to the simple Curie law (inset of Fig. 4). Once again the susceptibility variation in the low-temperature region is highly nonlinear, however the data above 100 K seem to adhere to the Curie law very well. This is clearly seen in Fig. 5 where the data corresponding to the temperature region 100–300 K is replotted. The solid lines are the fits to the Curie law:

$$\chi=\chi(0)+C/T\ , \tag{1}$$

where $\chi(0)$ is the temperature-independent term and C is the Curie constant which is related to the effective moment $\mu_{\rm eff}$ by

$$C=(N\mu_{\rm eff}^2)/3k_B \tag{2}$$

with N representing the Avogadro number and k_B the Boltzmann constant. The inset in Fig. 5 gives a plot of the effective moments extracted in this fashion as a function of Pr concentration for the three single crystals. It is seen that the value increases from about 2 to $3\mu_B$ as the Pr content goes up from 0.4 to 0.9. The effective moment with the field orientation B parallel to the c axis is larger than that with B parallel to the ab plane for all the cases and the difference is roughly the same about $0.2\mu_B$.

In order to understand the above results we return to the discussion on the theoretical analysis of inelastic neutron-scattering measurements by Boothroyd, Doyle, and Osborn,[14] Hilscher *et al.*,[11] and Soderholm *et al.*[7] These groups have calculated the variation of the magnetic susceptibility over a temperature range 5–300 K us-

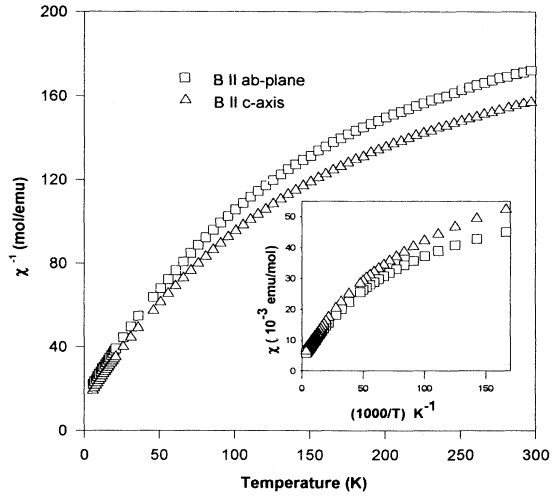

FIG. 4. A plot of $(1/\chi)$ versus T for $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ ($x=0.7$) single crystal. A simple Curie-Weiss behavior is clearly not observed. Inset shows the same data plotted as χ versus $(1/T)$.

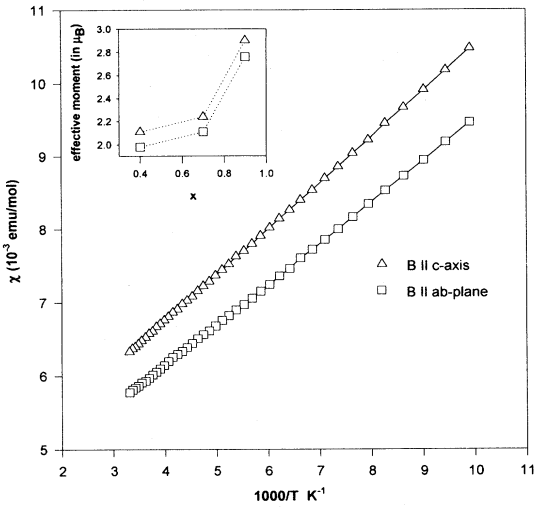

FIG. 5. An expanded view of the high-temperature portion of the data [from 100 to 300 K] shown in the inset of Fig. 4. The solid line is the fit generated using the Curie expression given by Eq. (1) in the test. Inset shows the effective moment (μ_{eff}) extracted using Eq. (2) for both field orientations B parallel to the c axis and B parallel to the ab plane for the three Pr concentrations $x=0.4$, 0.7, and 0.9. The dotted line is a guide to the eye.

ing the consistent set of eigenfunctions and eigenvalues for Pr^{3+} in $PrBa_2Cu_3O_{7-\delta}$, obtained by fitting scaled crystal-field parameters to the crystal-field transitions, observed by inelastic neutron scattering. The inverse susceptibility versus temperature plots of Refs. 14 and 11 suggest that the susceptibility follows the Curie-Weiss law. In contrast the calculations of Soderholm *et al.*[7] indicate nonlinear variation of susceptibility at low temperature. In the high-temperature region the susceptibility is shown to follow the Curie law. The susceptibility data of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ single crystals depicted in Figs. 4 (inset) and 5 agree well with the predictions of this model. Based on the observed agreement between the single-crystal susceptibility data and the theoretical calculations, and the agreement of the μ_{eff} values deduced with that of published values, we strongly believe that Pr enters the $YBa_2Cu_3O_{7-\delta}$ lattice in the 3+ state. Further evidence for this contention is provided by Hilscher *et al.*[11] They have calculated the magnetic susceptibility of Pr in both 3+ and 4+ states. The results show that the room-temperature susceptibility of tetravalent Pr in Pr123 is twice as much as that of trivalent Pr. The room-temperature susceptibility of single crystals is very close to that predicted for the trivalent Pr.

In conclusion, we have studied the magnetic susceptibility of insulating $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ single crystals with x values ranging from 0.4 to 0.95. The relation between inverse susceptibility and the temperature is nonlinear, therefore the data does not follow the Curie-Weiss behavior. Above 100 K, we have found that the data fits well to the simple Curie law. The values of effective moments extracted from the high-temperature $\chi(T)$ data range from 1.9 to $2.9\mu_B$. The observed magnitude of the susceptibility and the temperature dependence agrees well with the theoretical calculations that take in to account the crystal-field effects on Pr^{3+} in $YBa_2Cu_3O_{7-\delta}$ lattice. Furthermore the observed room-temperature susceptibility value agrees well with the calculated value for Pr in the 3+ state. Following the excellent agreement found between our single-crystal results and various theoretical calculations, we can unequivocally substantiate the earlier conclusion, that Pr is in the 3+ state, arrived at by the theoretical analysis of the inelastic-scattering measurements. The magnetic-susceptibility anisotropy measurements indicates that $\chi_c > \chi_{ab}$, which implies that the c axis is the easy axis of magnetization. A notable consequence of this result is, it facilitates to distinguish between various crystal-field schemes. The fact that $\chi_c > \chi_{ab}$ supports the crystal-field scheme proposed by Boothroyd, Doyle, and Osborn.[14] In spite of an excellent agreement between the experimental data and the theoretical predictions, we note a simple discrepancy in our approach, in that, while our magnetic anisotropy results favor the crystal-field scheme of Boothroyd, Doyle, and Osborn,[14] the temperature dependence of the single-crystal susceptibility data is not compatible with the Curie-Weiss behavior predicted by this model. On the other hand the data agrees well with the Curie law as demonstrated by Soderholm *et al.*,[7] who suggest a different crystal-field scheme. This discrepancy may be attributed to the possible aluminum contamination in the crystals, as they are grown in alumina crucibles. This contamination may also explain why a slope change in $\chi(T)$ is barely seen at the Pr ordering temperature (T_N).

This work was supported in part by the NSF through the EPSCoR (Grant No. OSR-925525) and the DOE through the Midwest Superconductivity Consortium (Grant No. DE-FG02-90ER45427). The crystal-growth program at the University of Oxford is supported by the Science and Engineering Research Council. B.J. and H.S. thank Professor J. R. Hardy, J. W. Flocken, and R. A. Guenther for their encouragement.

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