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Anomalous magnetic ordering in $\text{PrBa}_2\text{Cu}_4\text{O}_8$ and $\text{CmBa}_2\text{Cu}_3\text{O}_7$

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A review of temperature-dependent magnetization data for nonsuperconducting $\text{PrBa}_2\text{Cu}_4\text{O}_8$ and $\text{CmBa}_2\text{Cu}_3\text{O}_7$ suggests that the failure of each to superconduct is related to the presence of Pr and Cm on their respective Ba sites. This defect is manifested, in each case, by short c -axis lattice parameters and anomalous high-temperature magnetic ordering which has been incorrectly attributed to ordering of the entire magnetic sublattice. Instead, it is shown that the anomalous high-temperature ordering as seen in the magnetization data is consistent with the ordering of magnetic ions substituted on the Ba site.

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INTRODUCTION

The anomalous nonsuperconducting behavior of $\text{PrBa}_2\text{Cu}_4\text{O}_8$ (Pr124) (see Fig. 1) has been frequently attributed to the hybridization of spatially extensive Pr wave functions with neighboring cuprate plane oxygen¹ or, in other views, to the presence of Pr^{4+} providing for hole filling. These views were also applied to the apparent lack of superconductivity in Pr123, which as predicted² can be overcome by proper synthesis³⁻¹⁰ to minimize the substitution of Pr on the Ba site (Pr_{Ba}). The authors of Ref. 2 advanced the proposal that pair breaking by Pr_{Ba} is responsible for the typical lack of superconductivity in Pr123. Their model is the only one which successfully explains both the frequent lack of superconductivity in Pr123 and its appearance. The size of the c -axis lattice parameter for both nonsuperconducting Pr123 and Pr124 is anomalously short¹¹ and dependent upon specific preparation conditions. This is a direct indication of the substitution of a variable content of a smaller Pr ion for larger Ba. In addition, BaCuO_2 is detected by electron spin resonance;¹¹ formation of this impurity phase results from the substitution of Pr for Ba. Similar results³ were obtained for nonsuperconducting Pr123. Adachi *et al.* argue, on the basis of lattice parameter size, that Pr^{4+} can be excluded from consideration in Pr124.¹² However, a Pr moment, reduced in size from the expected free-ion value, has motivated arguments for some content of lower-moment Pr^{4+} . Staub¹³ *et al.* show that in $\text{Pb}_2\text{Sr}_2\text{PrCu}_3\text{O}_8$, crystal field effects, acting on Pr^{3+} , can reduce the effective moment from the free-ion value to $\sim 2.72\mu_B$, without consideration of lower-moment Pr^{4+} . In addition, the pressure dependence of the superconducting transition temperature¹⁴ demonstrates that the hybridization model certainly does not apply to Pr123. Since the environment of Pr in Pr124 is essentially identical to that of Pr in Pr123 (as well as in $\text{Pb}_2\text{Sr}_2\text{PrCu}_3\text{O}_8$), it seems unreasonable to suppose that either hybridization or hole-filling models could successfully apply to Pr124. While neutron diffraction would typically identify

the presence of out-of-place ions (substitutional defects), the scattering lengths of Ba and Pr are nearly identical, and this method fails to identify the substitution of Pr for Ba. On the other hand, polarized neutron diffraction¹⁵ identified the presence of magnetic ions on the Ba site, uniquely identifying the defect Pr_{Ba} in nonsuperconducting Pr123. From the magnetization density plot of Changkang *et al.*, we estimate that their crystal contained $\sim 20\%$ Pr_{Ba} . In nonsuperconducting Pr123, antiferromagnetic order is detected at ~ 17 K, while typically in $L123$ (L =lanthanide, Y), the magnetic L order near 2 K. We know of no evidence for anomalous magnetic ordering in superconducting Pr123. Nearly the same high-temperature ordering was found in Pr124 as in nonsuperconducting Pr123. While a variety of proposals

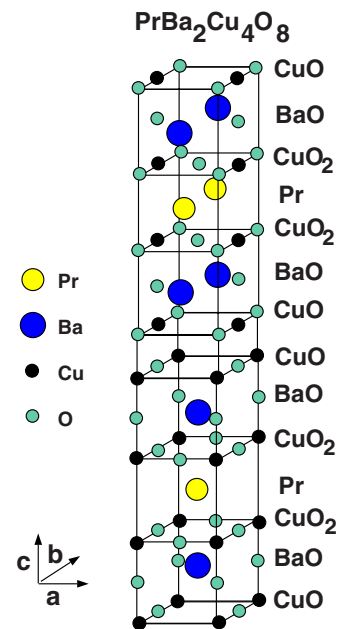


FIG. 1. (Color online) Structure of ideal Pr124. There is a "glide" of $b/2$ in the connecting double-chain layers.

have been advanced to explain the apparent lack of superconductivity in Pr124, none of these has addressed the anomalous temperature-dependent magnetization. The 17-K transition is manifested by a small peak or shoulder in an otherwise paramagnetic response. Below T_N the susceptibility rises at nearly the same rate as immediately above T_N , indicating that only a small fraction of the total magnetic moments are ordered at T_N . This rather obvious feature is readily accessible to any laboratory with superconducting quantum interference device (SQUID) capability and has been reported in several papers. However, its implications have been largely ignored in the literature.

$\text{CmBa}_2\text{Cu}_3\text{O}_7$ (Cm123) has been synthesized and, like typical Pr123, also fails to superconduct,¹⁶ while exhibiting the same anomalous temperature-dependent magnetic response. Due to the radioactivity of the actinide Cm, Cm123 is less well studied than its L homologue Gd123. Cm and Gd have similar magnetic properties: both are S -state ions with $J=7/2$. Cm has a larger ionic radius; as a result, it may tend to substitute more readily for Ba (Cm_{Ba}). The c axis of Cm123 is shorter than would be anticipated¹¹ for stoichiometric-site occupancy. This suggests that the reported Cm123 has the same type of defect as does nonsuperconducting Pr123. In addition, the material is found to exhibit antiferromagnetic ordering at ~ 22 K. Solderholm *et al.*¹⁶ argued that the $5f$ wave functions of Cm are spatially more extensive than the corresponding $4f$ wave functions of Pr, and as a consequence, hybridization with cuprate-plane oxygen would be more pronounced.

While this sample exhibited no sign of superconductivity, it remains to be determined if defect-free Cm123 could superconduct. We suggest that if *defect-free* $\text{Pb}_2\text{Sr}_2\text{Cm}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$ can be synthesized, it would be likely to superconduct, just as the Pr homologue does.¹⁷ Such a synthesis would provide a penetrating test of the hybridization model. In this case, the structure does not appear to provide a site for an additional oxygen adjacent to the Sr site, necessary to lower the potential on the Sr site sufficiently to ionize Pr_{Sr} or Cm_{Sr} to the 3+ state, preventing the formation of the critical defect.

MAGNETIZATION STUDIES

The susceptibility data of Li¹⁸ *et al.* on a well-characterized sample of Pr124 are presented in Fig. 2, along with susceptibilities computed using the Weiss model for the paramagnetic susceptibility:

$$\chi = \frac{c}{T + \Theta_W}.$$

Here Θ_W is the (positive) Weiss parameter which measures the strength of the effective exchange, T is the temperature, and the constant c absorbs several parameters. The model was fit to the low- and high-temperature asymptotes, determining c and Θ_W for Pr_{Pr} and Pr_{Ba} , and the difference was determined by subtraction of the contribution of the Pr on the Pr site from the total. While there is a clear indication of antiferromagnetic ordering at $T_N \sim 17$ K, it is evident that only a few percent of the sample's Pr ions participate in the

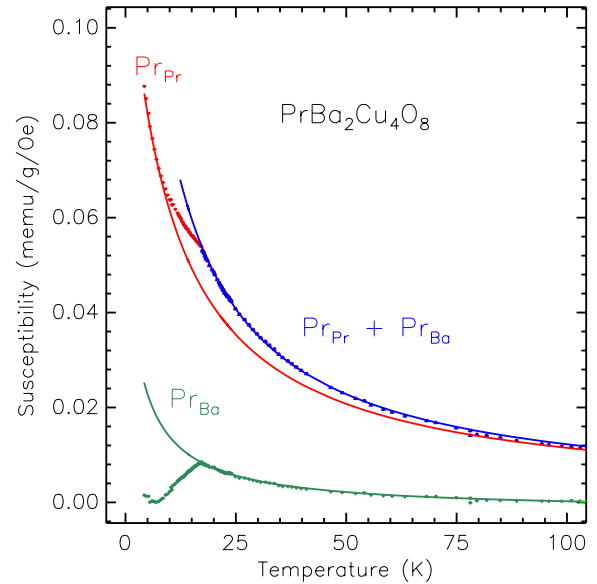


FIG. 2. (Color online) Magnetization data from Ref. 18. Here the data are separated into contributions from two sublattices, one which orders antiferromagnetically at ~ 17 K (blue, upper) and one which orders at a much lower temperature (red, middle). The bottom (green) data is the difference; the minority sublattice is attributed to Pr_{Ba} .

ordering. This was directly confirmed by neutron diffraction which found only a fraction of the moment determined from the paramagnetic susceptibility [$2.74(5)\mu_B$, which is indistinguishable from the value reported by Staub *et al.*¹³] below the Cu ordering temperature. Since for an antiferromagnet the perpendicular susceptibility is temperature independent and the parallel susceptibility falls rapidly with decreasing temperature and is expected to vanish at $T=0$, the *polycrystalline average susceptibility cannot continue to increase for $T < T_N$, as is seen in Fig. 2, if the system is fully ordered.* This means that there are at least two magnetic sublattices whose constituents have large moments. The value of the moment determined from neutron diffraction and the fit of the magnetization data imply that approximately 15% of the Pr order at 17 K. Li *et al.* reported another magnetic transition at a temperature typical of magnetic L123, near 1.5 K.¹⁹ It seems likely that this second ordering is the Pr on the Pr site and the high-temperature ordering is that of the Pr_{Ba} .

Magnetization data as a function of temperature¹⁶ for Cm123 are given in Fig. 3, along with Weiss model calculations carried out as above. While this sample is less well characterized, it also had an unexpectedly short c -axis parameter and the magnetization continues to rise below the nominal 22 K= T_N temperature. Again, the graphical constructions indicate that approximately 15% of the Cm order at T_N . The data deviate systematically from the fitted curve for temperatures above and below ~ 150 K; this may indicate the antiferromagnetic ordering of the Cu sublattice. The sample reported was too small to have permitted neutron diffraction studies.

NEUTRON DIFFRACTION

Li *et al.* have reported neutron diffraction¹⁸ results on the Pr124 system. The data suggest that $(1/2, 1/2, l)$ peaks ap-

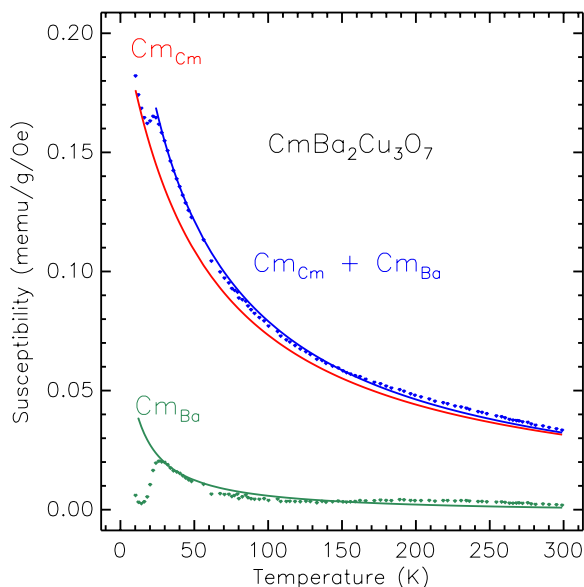


FIG. 3. (Color online) Magnetization data from Ref. 16. The data are separated into contributions from two sublattices, one which orders antiferromagnetically at ~ 22 K and one which may order at a much lower temperature. In this case, the minimum temperature for which measurements are available is 10 K. The bottom (green) data are the difference, attributed to Cm_{Ba} . The solid red, blue, and green lines are computed using the Weiss model for paramagnetic magnetization.

pear with both integer and $1/2$ integer index l , and their models are able to generate both types of reflections and provide a reasonable fit to the data. However, there appears to be a serious problem with the best-fit model of Li *et al.*, which the authors (reasonably) dismiss. This model produces one Pr sublattice with axial moments and a second Pr sublattice, generated from crystallographically equivalent sites, showing pronounced canting. However, their final model has a similar problem. Again, there are two inequivalent Pr sublattices, generated from crystallographically equivalent Pr atoms, one of which has antiferromagnetic coupling along the c axis, while the other shows ferromagnetic coupling. This appears quite unlikely. It appears that no simple structure can produce both types of reflections $(1/2, 1/2, l)$ (l integer and l half-integer) since these imply unit cells of different dimensions. The model of Li *et al.*, however, appears to approximate a two-dimensional magnetic model; i.e., the moments are correlated in the planes, but do not show long-range order along the c direction. Thus, alternating layers may be either parallel or antiparallel. This gives rise to a diffraction pattern that rises steeply at the $(1/2, 1/2, 0)$ position and then falls smoothly above that position. A similar scattering pattern may be expected for two-dimensional ordering of Pr_{Ba} , although it is likely that pairs of BaO planes in each half of the unit cell are coupled, leading to the weak modulation of the two-dimensional (2D) pattern, as reported by Li *et al.* This modulation caused Li *et al.* to dismiss a pure 2D model, which may now be explained by the Pr_{Ba} ordering in pairs of planes. No correlation between Pr_{Ba} in the two half cells is expected since the shift by $b/2$ leads to strong frustration; the atoms in the upper half cell see equal numbers of

near-neighbor spins with opposite signs in the lower half cell (and vice versa). The moment extracted by Li *et al.* is, however, likely to be similar for the 3D model employed and for the 2D model, since it is proportional to the total scattering in the angular range considered. The assumption of a $3\text{-}\mu\text{B}$ Pr moment for Pr_{Ba} leads to roughly 12% Pr on the Ba sites, in agreement with the estimates from the susceptibility data. However, single-crystal neutron data would be very useful for testing this model against other alternatives of Pr_{Ba} - and Pr-site ordering. If these studies were to include polarized neutron measurements for temperatures above the anomalous ordering temperature, the presence of Pr_{Ba} could be definitively established. Conventional neutron scattering, continued to ~ 1 K, should easily confirm the expected ordering of the Pr_{Pr} . Thus, continued studies could eliminate the remaining uncertainties.

Pr_{Ba} MAGNETIC ORDER

Ordering of randomly substituted Pr_{Ba} in an insulating host for which indirect exchange by carriers is probably unavailable²⁰ presents a challenge to understanding. Superexchange appears to be the only available exchange coupling. Since the superexchange paths coupling randomly substituted Pr_{Ba} will be of variable length, it seems surprising that order occurs. However, there is a constant feature providing a uniform exchange coupling for all Pr_{Ba} : the cuprate (CuO_2) planes order at a temperature much higher¹⁸ than that of the Pr and provide eight superexchange coupling paths from the ordered Cu through the O(2), O(3), and O(1) oxygen sites. The shortest superexchange paths are: $Cu(2)\text{-}O(2)\text{-}Pr_{Ba}$, $Cu(2)\text{-}O(3)\text{-}Pr_{Ba}$, and $Cu(2)\text{-}O(1)\text{-}Pr_{Ba}$. Since the Pr_{Ba} are located either above or below the center of the CuO_2 planes, if the Cu are ordered with a simple antiferromagnetic structure in the a - b plane, these eight coupling channels would exactly cancel. Li *et al.* did not claim detection of simple antiferromagnetic CuO_2 plane ordering at high temperatures, although these authors found evidence for such peaks below the threshold of detectability; the signal/noise ratio¹⁸ was insufficient to conclude that such reflections were detected. Simple antiferromagnetic ordering would have been exhibited by the presence of magnetic reflections for which the $(1/2, 1/2, 1/2)$ and $(1/2, 1/2, 3/2)$ are the lowest order and highest intensity. Nevertheless, the existence of Cu antiferromagnetic order is not in dispute. A possible explanation for the absence of expected antiferromagnetic peaks is an alternative structure in which the CuO_2 planes are ordered in ferromagnetic layers which are stacked antiferromagnetically. The magnetic reflections will be coincident with the nuclear reflections and very difficult to observe with a small Cu moment. This is the only configuration we have found which presents a very small cross section. We have recently demonstrated four^{21–25} examples of materials with such CuO_2 order: $YSr_2Cu_{2.1}Nb_{0.9}O_{8-\delta}$, $YSr_2Cu_{2.1}Ru_{0.9}O_{8-\delta}$, $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$, and $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$. In these materials cuprate plane magnetic resonances are observed. Similar resonance was observed¹¹ in $PrBa_2Cu_4O_8$, but we have not detected any such resonance in materials with simple antiferromagnetic order, such as in nonsuperconduct-

ing Pr123. This suggests to us that the CuO_2 order in $\text{PrBa}_2\text{Cu}_4\text{O}_8$ is similar to that in the above-named materials. Fujiyama *et al.*,²⁶ using NMR, concluded that the ordered Cu magnetic moments of Pr124 lie within a few degrees of the cuprate planes, but whether or not the moments are ordered as in the two materials named above is unknown. On the other hand, simple planar antiferromagnetic Cu order should have been easily seen by Li *et al.* Thus, the most probable Cu spin configuration is ferromagnetic cuprate planes stacked antiferromagnetically; this structure provides for *net* magnetic coupling between Pr_{Ba} moments and the cuprate planes, and is the likely root of the Pr_{Ba} magnetic order. The antiferromagnetic order of the Pr moments apparently arises from $\text{Pr}_{\text{Ba}}\text{-Pr}_{\text{Ba}}$ coupling, perhaps moderated (superexchange) by the ordered CuO_2 planes. It is to be noted that at $\sim 15\%$ occupancy, the average $\text{Pr}_{\text{Ba}}\text{-Pr}_{\text{Ba}}$ first-neighbor distance is small as compared to the axial $\text{Pr}_{\text{Pr}}\text{-Pr}_{\text{Pr}}$ distance.

DISCUSSION

The previously published data for Pr124 and Cm123 demonstrate that in each there are at least two magnetic sublattices consisting of large moment ions, one of which orders at a temperature well above the nominal ordering temperature of its homologues. Li *et al.* also discuss specific heat and resistivity measurement evidence for a magnetic transition occurring at a temperature near 2 K in Pr124. These authors conclude that any such transition is not associated with the Pr spin system. Of course, the *L* sublattices in the magnetic *L* 123 are well known to order near 2 K. In either Pr124 or Cm123, the material fails to exhibit superconductivity and the ordered sublattice consists of a fraction of paramagnetic moment determined at high temperature. Since the Pr and Cm materials show similar behaviors, it is possible to exclude crystal field effects as an origin of the small ordered moment in Pr124. This is a consequence of the *S*-state character of the Cm ion, in which crystal field effects are not

expected. In contradiction to the conclusion of Li *et al.*, regarding the 2-K transition, we suggest that the anomalous high-temperature magnetic ordering is associated with Pr (at ~ 17 K) (or Cm at ~ 22 K) residing on the Ba site, as substitutional defects. Pair breaking by magnetic ions substituting on the Ba site has been proposed as the mechanism by which the superconductivity is suppressed.² In this sense, magnetic ions on the Ba site have served as probes of the superconducting condensate, while the same ions on the *L* site have no known impact on the transition temperatures of the *L* 123 materials. It is also well known that substitution of nonmagnetic La^{3+} on the Ba site of La123 slowly depresses the superconducting transition temperature of that material,²⁷⁻³¹ while substitution of Nd^{3+} on the Ba site of Nd123 has a dramatic effect.^{32,33} What is new here is that the magnetic ions substituted on the Ba site also serve as a probe of the magnetic exchange on the Ba site. It is perhaps surprising that relatively dilute concentrations of magnetic ions on the Ba site exhibit magnetic order. However, the estimated Pr_{Ba} concentration is not far below the 3D percolation limit. Thus, the addition of second- and higher near-neighbor interactions may be sufficient to provide coupling sufficient to drive long-range order. It should be noted that there are two spacings between the BaO planes, approximately 4 Å and 8 Å, both of which are shorter than the distance between Pr planes. The magnetization anomalies of Pr124 and Cm123 have been widely ignored, but point to a common origin for the lack of superconductivity in these compounds. Thus, the model considering pair breaking by alkaline-earth-site magnetic ions² now also accounts for the anomalous magnetic order, the shortened *c*-axis length, and the (complete) depression of the superconducting transition temperature. What remains to be explained is the resultant lack of conductivity which may be due to charge localization.¹¹ As is frequently the case, more can be learned from irregular behavior than from regular behavior.

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