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Magnetic order of Pr in $PrBa_2Cu_3O_7$

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The magnetic order of Pr in nonsuperconducting $PrBa_2Cu_3O_7$ has been studied by specific-heat, susceptibility, and neutron-diffraction measurements. The basic ordering consists of a simple antiferromagnetic arrangement, with a saturated moment of $0.74\mu_B$ and a Néel temperature T_N of ~ 17 K, which is two orders of magnitude higher than expected from either dipolar or Ruderman-Kittel-Kasuya-Yosida interactions alone. The small moment, along with the large value of the low-temperature electronic specific-heat coefficient γ of 196 mJ/mole K^2, suggests that there is substantial f-electron character at the Fermi level.

Some of the very first experiments on the $Y_{1-x}R_xBa_2Cu_3O_7$ (R is a rare-earth element) system showed that the superconducting transition temperature did not depend significantly on x, the concentration of trivalent rare-earth elements in the material (e.g., Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb), indicating that the rare-earth and copper sublattices are electronically decoupled for all practical purposes.[1] An important exception to this behavior is Pr, which forms[2] the same orthorhombic structure but is thought to be strongly mixed valent, and close to the tetravalent ionic state. The superconducting transition temperature T_c is found to be strongly suppressed as a function of Pr concentration,[3-6] in a manner which is consistent with the classical Abrikosov-Gorkov depairing theory.[7] The superconductivity is lost for Pr concentrations $x \geq 0.6$. In the present paper we report the nature of the magnetic order of the Pr in $PrBa_2Cu_3O_7$. A simple commensurate antiferromagnetic order is observed below $T_N \approx 17$ K, with a moment direction along the orthrohombic c axis but with a low-temperature value of the moment of only $0.74\mu_B$. In comparison with the isostructural compound $GdBa_2Cu_3O_7$, which orders at $T_N \approx 2.2$ K, the Pr ordering temperature is 2 orders of magnitude higher than would be expected if one scales the T_N for $GdBa_2Cu_3O_7$ assuming either purely dipolar interactions, or Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange. Moreover, the electronic coefficient determined from the low-temperature specific-heat measurements for $T < T_N$ is $\gamma \sim 196$ mJ/mole K^2, which is comparable to many heavy-fermion systems. These observations indicate that the f electrons in this material are strongly hybridized, and play an essential role in the electronic properties.

The polycrystalline samples were prepared by the usual solid-state reaction technique, starting from high-purity powders of Pr_6O_{11}, $BaCO_3$, and CuO. Details of the sample preparation technique can be found elsewhere.[6] Both x-ray diffraction and high-resolution neutron-profile-refinement measurements were used to characterize the samples prepared for these measurements. From the neutron measurements, the nominal oxygen concentration was determined to be 7.00 ± 0.08, and the measured lattice parameters of $a = 3.8793(3)$ Å, $b = 3.9129(3)$ Å, and $c = 11.6617(11)$ Å at 78 K are in good agreement with previous data.[6] Any impurity phases were found to be less than 1% of the sample.

To determine the nature of the Pr ordering, neutron-diffraction measurements were taken on a standard triple-axis spectrometer at the National Institute of Standards and Technology (formerly National Bureau of Standards) Research Reactor. A pyrolytic graphite PG(002) monochromator was employed, with a PG filter to suppress higher-order wavelength contaminations. The wavelength was 2.355 Å, and the angular collimations before and after the monochromator and after the sample were 60′-20′-20′ (full width at half maximum), respectively. No analyzer crystal was used in these measurements.

Figure 1 shows two magnetic Bragg peaks found in this system at low temperatures. These data were obtained by subtracting[8] data taken at high temperatures from data taken well below T_N. In the situation where there is no significant structural distortion, which is usually the case for these low-temperature magnetic phase transitions, only the magnetic contribution to the scattering will survive the subtraction procedure. The data exhibited in Fig. 1 are a portion of a complete powder diffraction pattern. Data taken at 25 K serve as background, and have been subtracted from data taken at 6 K where the system is well ordered. The observed magnetic Bragg reflections may be indexed as $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\}$ and $\{\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2}\}$ reflections, respectively, on the orthorhombic chemical unit cell. Since all three Miller's indices are half-integer, the magnetic unit cell is just double the chemical unit cell along all three crystallographic directions as shown in the inset in Fig. 2. Hence the underlying magnetic structure consists of nearest-neighbor spins in all three directions which are aligned antiparallel, and is the same type of structure as has been found for the Dy (Ref. 9), Gd (Ref. 10), and Nd (Ref. 11) systems.

In addition to the basic spin configuration, which is

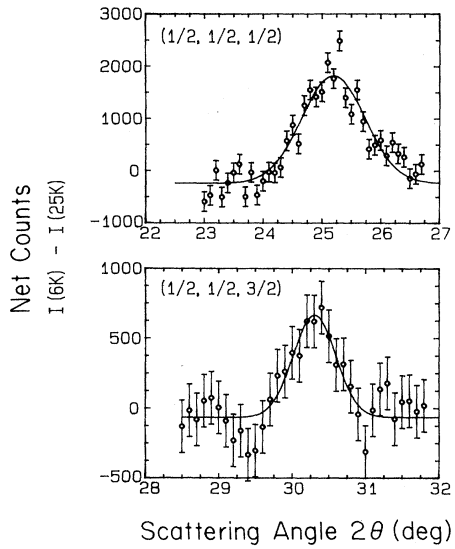

FIG. 1. Magnetic intensities observed in nonsuperconducting $PrBa_2Cu_3O_7$ at $T=6$ K. The two peaks may be indexed as the $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\}$ and $\{\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2}\}$ Bragg reflections, indicating a three-dimensional antiferromagnetic ordering of Pr ions with a magnetic unit cell which is doubled along all three crystallographic directions. The solid lines are Gaussian fits to the data.

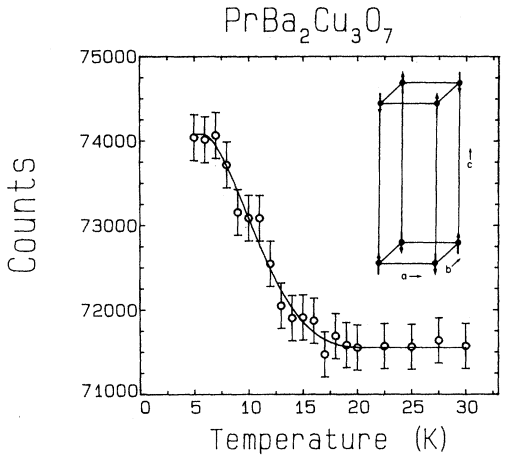

FIG. 2. Temperature dependence of the $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\}$ peak intensity, showing the variation of the square of the staggered magnetization with temperature. The Néel temperature for this system is ~17 K, based on these data as well as the specific-heat data. The solid curve is a guide to the eye. The inset shows the magnetic configuration of the Pr spins.

given by the angular positions of the magnetic Bragg peaks, we can also determine the spin direction and the value of the ordered (staggered) moment of the Pr. The scattering intensity for a collinear magnetic structure is given by[8,12]

$$I_m = C\left(\frac{\gamma e^2}{2mc^2}\right)^2 [\mu_z]^2 f^2(\tau)[1-(\hat{\tau}\cdot\hat{\mathbf{M}})^2] \times \frac{M_{hkl}}{\sin(\theta)\sin(2\theta)}, \quad (1)$$

where M_{hkl} is the multiplicity of the powder reflection, C is an instrumental constant, and 2θ is the scattering angle for the reciprocal lattice vector τ. The constant in the parenthesis is -0.27×10^{-12} cm, $f(\tau)$ is the magnetic form factor, $[\mu_z]$ is the thermal average of the aligned magnetic moment of the Pr, $\hat{\tau}$ and $\hat{\mathbf{M}}$ are unit vectors in the direction of τ and the spin direction, respectively, and the orientation factor $[1-(\hat{\tau}\cdot\hat{\mathbf{M}})^2]$ must be calculated for all possible domains. For the two peaks shown in Fig. 1, the scattering angles are not very different, and hence the angular factor and the form factor in the above equation should not differ much between the two reflections. Hence the intensity ratio is controlled primarily by the orientation factor $[1-(\hat{\tau}\cdot\hat{\mathbf{M}})^2]$. The considerably weaker intensity for the $\{\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2}\}$ peak then suggests that the moment direction in the system is predominantly along the c-axis direction, as was also found to be the case for the Gd, Dy, and Nd systems. However, in the present case there are only two observable peaks due to the small value of the magnetic moment (as discussed below), and hence we should only consider this spin direction as tentative. An additional feature is that the relative intensity of the $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\}$ peak to the $\{\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2}\}$ peak associated with the Cu chain ordering in oxygen-deficient Y-Ba-Cu-O is $\frac{1}{20}$ whereas in the present case this ratio is 2.[13] Therefore, the relative intensity is suggestive that the magnetic scattering is due to an ordering of the Pr ions.

To determine the absolute value of the magnetic moment in the system, we need to ascertain the instrumental constant C. The standard method used to evaluate C involves measuring the intensities of several nuclear Bragg peaks.[8] The low-temperature ordered moment we obtain from our data is $[\mu_z]=(0.74\pm0.08)\mu_B$. This value is smaller than the free-ion moment of $2.14\mu_B$ for Pr^{4+} ($J=\frac{5}{2}$) or $3.18\mu_B$ for Pr^{3+} ($J=4$). Crystal-field (CF) effects may be important in reducing the value of $[\mu_z]$ below the free-ion result, and an ordered moment of $0.71\mu_B$ would be expected for the most likely CF ground state ($|\pm\frac{1}{2}\rangle$ doublet) of Pr^{4+}.[5-7] For Pr^{3+}, on the other hand, the orthorhombic distortion would totally remove the ninefold degeneracy,[14] concomitantly reducing T_N, the ordered moment, and the entropy removal at T_N, which is inconsistent with our data. We believe that the reduced moment ($0.74\mu_B$), along with the large electronic contribution to the specific heat as discussed below, indicates that there is a significant hybridization of the $4f$ electrons due to the mixed-valent nature of Pr in this system.

Figure 2 shows the temperature dependence of the $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\}$ peak intensity, and reveals a typical order parameter with a Néel temperature of $T_N\simeq17$ K. The temperature dependence of the specific heat $C(T)$ for this compound is shown in Fig. 3(a), where a clear anomaly in the vicinity of 17 K is evident. The magnetic entropy associated with this transition is ~5.0 J/mole K,[6] and is somewhat smaller than the expected entropy change due to the ordering of a CF doublet ground state, i.e., 5.7 J/mole K. In addition to the magnetic transition in the vicinity of 17 K, there is another weak anomaly near 5.2 K which is ap-

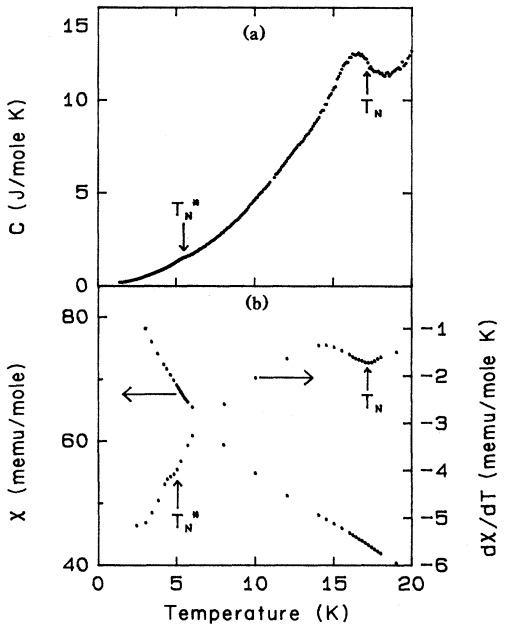

FIG. 3. (a) Measurements of the specific heat at low temperatures for $PrBa_2Cu_3O_7$ showing the magnetic transition at $T_N = 17$ K. (b) Measurements of the magnetic susceptibility $\chi(T)$ (in milliemu/mole) and temperature derivative $d\chi/dT$ for $PrBa_2Cu_3O_7$.

parent in $C(T)$ and $d\chi/dT$. The nature of this anomaly is not known at present, and further studies are planned.

The electronic specific-heat coefficient γ obtained by fitting $C(T)/T$ to $\gamma + BT^2 + \alpha T^4$ for $T > 17$ K, $5.2 < T < 17$ K, and $T < 5.2$ K, all yield large values of γ characteristic of relatively strong f-electron hybridization at the Fermi energy (heavy mass behavior).[15] The γ value obtained for $T > 17$ K is in excess of 300 mJ/moleK^2, while γ for $5 < T < 17$ K is 196 mJ/moleK^2, and γ is 114 mJ/moleK^2 for $T < 5$ K. The γ value for $T > 17$ K must be considered with some caution because of the limited temperature range used in the fit.

The temperature dependence of the magnetic susceptibility $\chi(T)$ and $d\chi/dT$ for $PrBa_2Cu_3O_7$ is shown in Fig. 3(b). The behavior is different from that expected based on the simple structure observed in the neutron data. For $GdBa_2Cu_3O_7$, for example, $\chi(T)$ decreases below T_N, whereas for this sample $\chi(T)$ monotonically increases with decreasing temperature and only displays a change in slope at 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 indicated by neutrons. The anomalous increase of $\chi(T)$ for $T < T_N$ cannot be attributed to impurity phases or multiple site occupancy of the Pr. As indicated earlier, both x-ray and neutron-diffraction studies indicate that the impurity phases are less than 1% of the sample. In addition, neutron-refinement analysis clearly shows that the Pr resides on the Y-site. Because of the small moment and consequent weak Bragg scattering, additional magnetic Bragg peaks which would indicate a modulated structure or spin canting could be hidden. However, the basic underlying spin structure is that shown in the inset of Fig. 2. Measurements on single crystals would be helpful in resolving this issue.

The essential difference in the magnetic ordering between the present nonsuperconducting $PrBa_2Cu_3O_7$ system and the trivalent superconducting $RBa_2Cu_3O_7$ systems is their Néel temperatures T_N, and the values of the ordered moment. The T_N's for R=Yb (Ref. 16), Nd (Ref. 11), Er (Ref. 17), Dy (Ref. 9), and Gd (Ref. 10) in $RBa_2Cu_3O_7$ were found to be 0.35, 0.5, 0.5, 1.0, and 2.2 K, respectively.[18] If we scale these temperatures with respect to either the size of the (free-ion) magnetic moment of Pr, or $(g-1)J(J+1)$ as one would expect for an RKKY exchange interaction, then we would expect a transition temperature for $PrBa_2Cu_3O_7$ which is an order of magnitude smaller than T_N for $GdBa_2Cu_3O_7$. The observed transition is of course about an order of magnitude larger than these trivalent rare earths. In addition, the ordered moments for the heavy rare-earth materials Er, Dy, and Gd were found to be 4.9, 7.2, and 7.4μ_B, respectively, while the Pr moment is only 0.74μ_B.[19] Thus the higher ionic state for the Pr affects not only the electronic and superconducting properties of the Cu-O layers (e.g., the suppression of T_c), but also the electronic and magnetic properties of the Pr sublattice. The present specific-heat and neutron-diffraction data taken together indicate that the $4f$ level for the Pr ions hybridizes strongly with the electrons at the Fermi level.[20]

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[19]The ordered moment for the Nd compound is $1.07\mu_B$, but the ordering temperature is 0.5 K (see Ref. 11).

[20]We have obtained some preliminary inelastic neutron-scattering data on this system which show a broad energy distribution of magnetic scattering typical of a mixed-valent system.