Observation of Pr magnetic order in $PrBa_2Cu_3O_7$

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Neutron-diffraction experiments have been carried out to investigate the magnetic order in $PrBa_2Cu_3O_7$. Our neutron data indicate that the Cu spins order above 300 K. This ordering is not significantly affected at low temperatures, where new magnetic Bragg peaks develop below 17 K that must be associated with the antiferromagnetic ordering of Pr spins, with an ordered moment of $0.79(5)\mu_B$. This rules out the possibility recently proposed by Nehrke and Pieper [Phys. Rev. Lett. **76**, 1936 (1996)] that the new magnetic Bragg peaks arise from a spin reorientation of the Cu spins and that the Pr carries essentially no moment. [S0163-1829(97)50506-6]

The physical properties of $PrBa_2Cu_3O_7$ have been studied extensively[1] in order to understand the absence of superconductivity in this material, as Pr is the only rare earth (R) that forms the $RBa_2Cu_3O_7$ structure and does not superconduct. However, there are contradicting reports on the magnetic properties of the Pr ions in this system. The first neutron-diffraction experiments on powder $PrBa_2Cu_3O_7$ revealed[2] antiferromagnetic ordering of the Pr ions, with an ordered moment of $0.74\mu_B$ and a Néel temperature of 17 K. These observations were in good agreement with magnetic susceptibility and specific-heat measurements. The magnetic ordering of Pr has been studied in detail as a function of oxygen concentration and as a function of Y (and other rare earth) substitution on the Pr site,[1,3,4] and Pr ordering has also been observed in a variety of Pr cuprate compounds.[5] However, recently Nehrke and Pieper[6] have reported an NMR study where they concluded that the Pr ions are in a singlet crystal-field ground state, with only a small induced ordered moment ($0.017\mu_B$) at low T. They speculated that the observed neutron-diffraction peaks originate from a change in the order of Cu plane spins rather than Pr ordering. We have therefore carried out new experiments on polycrystalline $PrBa_2Cu_3O_7$ to address this issue. Our results unambiguously demonstrate the presence of Pr order in $PrBa_2Cu_3O_7$.

Since the original powder-diffraction measurements, new measurements on single crystals have been reported as specimens became available.[7,8] The sensitivity to magnetic order is generally much higher for single crystals, especially in the present system where both the Cu and Pr moments are small. However, these flux-grown crystals have a small contamination from the crucible, whereby some Al ends up on the Cu chain sites in the crystal. This alters the electron doping levels, and in particular induces the Cu-chain spins to order magnetically. The symmetry for this magnetic chain ordering is the same as that reported for the Pr, and so severely complicates the interpretation of the single-crystal data. We have prepared, by the usual solid-state reaction technique,[9] a new 12 g polycrystalline sample to avoid this problem. Neutron diffraction measurements were performed at the Research Reactor at the National Institute of Standards and Technology. High-resolution neutron data were taken on the BT-1 powder diffractometer at room temperature to characterize the sample. For these measurements, a Cu(311) monochromator was used with a wavelength of 1.5396 Å, and the data were analyzed using the GSAS program.[10] The refinement of the room temperature data gave an oxygen concentration of 6.93(2) and the lattice parameters a,b, and c are 3.8632(2), 3.9265(2), and 11.7031(5) Å, respectively. We have also observed $BaCuO_2$ as an impurity at the 5% level, as expected based on the phase diagram for the Pr-Ba-Cu-O system.[11]

For the measurements of the magnetic Bragg peaks a high-intensity/coarse-resolution instrumental configuration must be used to compensate for the weak magnetic scattering. Measurements were therefore taken on the BT-2 triple-axis spectrometer using a pyrolytic graphite PG(002) monochromator and analyzer, and a PG filter to suppress higher-order wavelength contaminations. The incident wavelength was either 2.351 or 2.443 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 collimator was used after the analyzer. A pumped ^{4}He cryostat with a temperature capability between 1.8 and 350 K was used.

With respect to the superconducting and magnetic properties of this class of materials, there is a dramatic difference between Pr and the other rare earths (R). The general magnetic behavior in the $RBa_2Cu_3O_{6+y}$ systems[12] is very interesting as both Cu and rare-earth ions can have magnetic moments. The crystal structure is essentially tetragonal ($a\approx b$) with $c\approx 3a$, and there are three sets of Cu layers. Two of these are equivalent Cu layers that have an oxygen between each Cu ion, and are known as Cu planes. The other type of

Cu layer, which is known as the Cu chain layer, has oxygen ions only along the *b* axis. This oxygen can be readily removed, and in the oxygen-deficient insulator $RBa_2Cu_3O_6$ the Cu spins in the planes order antiferromagnetically with Néel temperatures (T_N) as high as 525 K. The spins lie in the *a*-*b* plane, and the observed magnetic Bragg peaks can be indexed as $(h/2,k/2,l)$, which will be referred to as ''whole-integral'' peaks. With appropriate doping either directly on the chain site, or on the Ba site, the chain spins can also develop an ordered moment at low temperatures (below T_N), and the observed magnetic peaks can be indexed as $(h/2,k/2,l/2)$, which will be referred to as ''half-integral'' peaks. Therefore, if the Cu spins in the chains start to order, the half-integral magnetic peaks increase in intensity while the whole-integral peaks decrease to zero. Adding oxygen has the effect of doping the plane layers with holes, and causes the Néel temperatures to drop to zero at $y \approx 0.4$. Further oxygenation will induce superconductivity, with T_c exceeding 90 K for the fully oxygenated $RBa_2Cu_3O_7$. At very low temperatures the rare-earth ions, which are located in the body-centered position between the two Cu planes, order antiferromagnetically with $T_N \sim 1$ K. The nearest-neighbor rare-earth ions are separated by a distance *a*, and without direct bonding of orbitals the magnetic interactions are very weak. Since the nearest-neighbor distance along the *c* axis is about three times longer than that in the *a*-*b* plane, magnetic interactions in the *c* direction are much weaker than in the *a*-*b* plane and many of the rare-earth ions exhibit two-dimensional behavior in this system.[13]

The observed magnetic peak at 5 K is shown in Fig. 1(a). These data were obtained by subtracting the data taken at high temperatures (25 K) from the data taken at low temperatures, whereby the nuclear Bragg contributions to the intensity subtract out and only the magnetic contributions survive. The data clearly show the development of a new magnetic Bragg peak at the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ position that was originally associated with the Pr order,[2] and the temperature dependence of this peak is shown in Fig. 1(b). For comparison, our old data[2] are also shown in the same plot. The ordered moment we obtain from these data is $0.79(5)\mu_B$, assuming that the Pr ions are ordering with the magnetic structure determined previously. Both sets of data are in excellent agreement, and they show that the magnetic intensities start to increase around 17 K.

These results for the Pr ordering are directly contradicted by a recent NMR study by Nehrke and Pieper,[6] who claimed that the Pr ions in $PrBa_2Cu_3O_7$ have a (nonmagnetic) Γ_1 singlet as a crystal-field ground state and there is (essentially) no ordered magnetic moment. They also reported a much larger splitting of the quasitriplet crystal-field levels than observed directly by inelastic neutron scattering, and concluded that the *a* axis is the magnetic easy axis, again in disagreement with inelastic neutron scattering and magnetic susceptibility measurements.[14–20] They speculated that the new magnetic Bragg peaks that develop below 17 K originate from a change in the spin structure of the Cu planes rather than from Pr ordering.

To address the behavior of the Cu spins, we have measured the temperature dependence of the $(\frac{1}{2},\frac{1}{2},1)$ magnetic Bragg peak associated with the Cu plane ordering, which is shown in Fig. 2. We see that the Cu plane spins order antiferromagnetically above 300 K as expected, and this is in good agreement with Mossbauer[3] and muon data,[21] and with the single-crystal measurements.[7,8] The intensity varies smoothly with temperature into the low-*T* regime, and then we see a small anomaly in the intensity as the Pr spins order. This small anomaly, which is not detectable in integrated intensities (solid squares in Fig. 2), was observed by measuring peak intensities (open circles) with longer counting times.

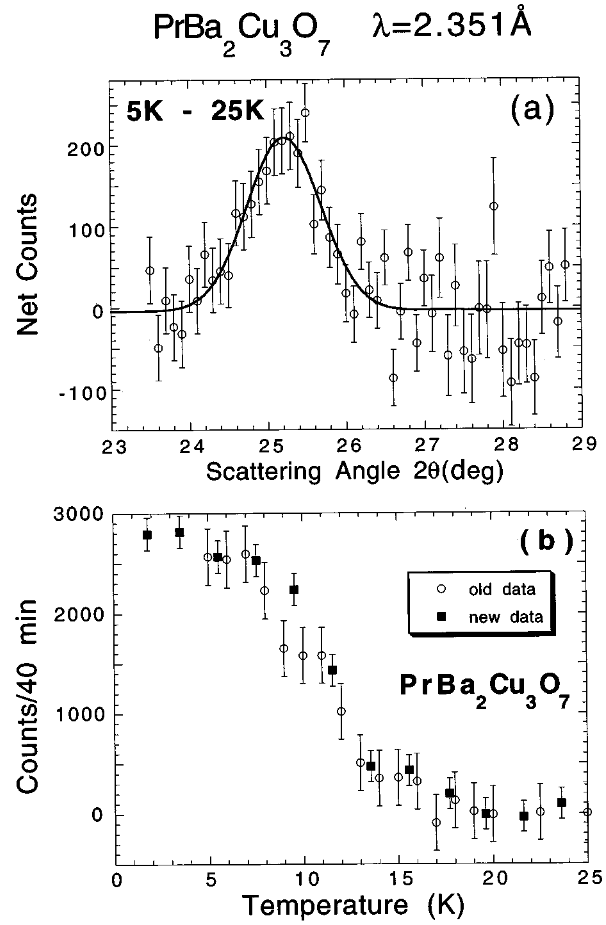

FIG. 1. (a) Magnetic intensity observed at 5 K. These data were obtained by subtracting high-temperature (25 K) data from that at 5 K. The solid curve is a Gaussian fit to the data. (b) Temperature dependence of the Pr magnetic peaks (background is subtracted). Solid squares are for the data taken from this experiment, and these data are compared with our earlier results (Ref. 2).

There are three possible interpretations of these data. Nehrke and Pieper[6] suggested that the additional magnetic peaks below 17 K can be explained in terms of two types of spin reorientations of the plane Cu spins, which are already ordered above room temperature and have their fully saturated moments at low *T*. To accommodate the development of new Bragg peaks, the whole-integral peaks must then decrease proportionately, and are in fact expected to vanish at low *T*. This should reveal itself in the difference pattern of Fig. 1(a) as a very strong negative intensity (about twice as strong as the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ peak) at 27.3°, the position of the $(\frac{1}{2},\frac{1}{2},1)$ reflection.[5,22] The measurements, however, show no significant change at the $(\frac{1}{2},\frac{1}{2},1)$ position at this level of detection. These data, therefore, rule out the possibility of a significant Cu spin reorientation transition.

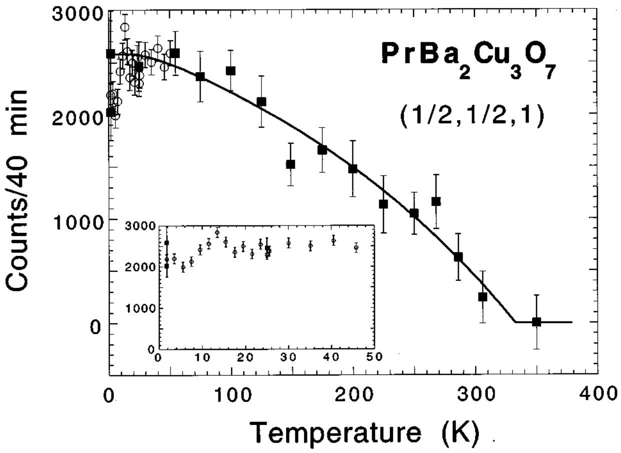

FIG. 2. Temperature dependence of the $(\frac{1}{2},\frac{1}{2},1)$ magnetic Bragg peak originating from the ordering of the Cu plane spins. Solid squares are integrated intensities and open circles are peak intensities. Low-temperature data are shown in the inset. Only a small anomaly is observed below the 17 K transition.

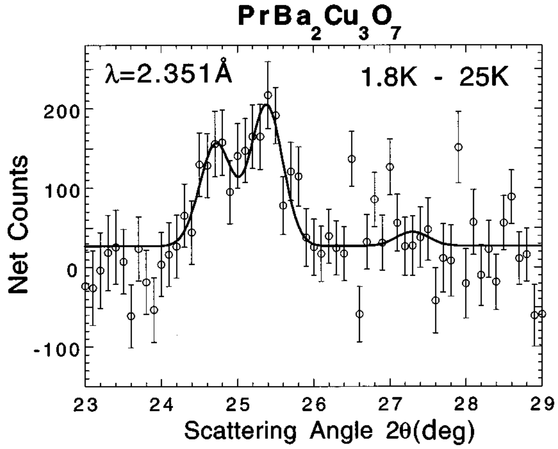

FIG. 3. Magnetic intensity observed at 1.8 K. These data were obtained by subtracting high-temperature (25 K) data from that at 1.8 K. The solid curve is a fit of resolution-limited Gaussian peaks to the data. The two peaks at lower angles correspond to the $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ peaks associated with the Pr order, while there is essentially no change in the intensity of the $(\frac{1}{2},\frac{1}{2},1)$ peak at 27.3° associated with the Cu order.

The second possibility is that the new Bragg peaks originate from an ordering of the Cu spins in the chain layer. The chain spins are not expected to carry a magnetic moment in $PrBa_2Cu_3O_7$, but they do in the Al-doped single crystals.[7,8] However, when the Cu spins in the chain layers start to order, the half-integral peaks increase in intensity while the intensities of the whole-integral peaks decrease to zero. Therefore, there must be a drastic decrease in the $(\frac{1}{2},\frac{1}{2},1)$ magnetic intensity at low temperatures if the Cu chain spins order, and this is ruled out by the data. In addition, the relative intensities of the half-integral magnetic peaks we observe are qualitatively different than the intensities observed when the Cu chain spins order, as described elsewhere.[2,20]

We are therefore left with the third possibility, that the half-integral Bragg peaks that develop below 17 K originate from the ordering of magnetic moments on the Pr ions. The small anomaly in the $(\frac{1}{2},\frac{1}{2},1)$ intensity in Fig. 2 is then the result of weak coupling between the Cu and Pr spins as the Pr orders. The Pr ordering temperature (17 K) is an order of magnitude higher than those of other rare-earth ions in this system,[12] and this behavior originates from f-electron hybridization. This hybridization has been observed directly in inelastic neutron scattering experiments on $PrBa_2Cu_3O_7$, where the crystal-field excitations of the Pr ions showed large linewidths.[15–20] This f-electron hybridization dramatically increases the exchange interaction, which is weak in other rare-earth compounds, and thereby increases the ordering temperature. The high-ordering temperature for the Pr (compared to the other rare earths) and associated exchange interactions explain in a natural way the absence of superconductivity in this system. If Pr were in an isolated singlet ground state as suggested by Nehrke and Pieper,[6] we would expect this material to be a high-temperature superconductor.

We now turn to the data we obtained below 5 K, which is a temperature regime that we had not explored previously. The magnetic Bragg scattering observed at 1.8 K is shown in Fig. 3, and we see that there are two magnetic peaks at 24.7° and 25.3° at this temperature rather than just a single peak. These peaks can be indexed as $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ based on the chemical unit cell, and the solid curve in the figure is the fit of two Gaussians with widths fixed to the instrumental resolution. The data in Fig. 1(a), on the other hand, cannot be fit by two resolution-limited peaks, although the single peak width at this temperature is sowewhat broader than the resolution. This observation is consistent with the results of Longmore *et al.*,[8] where they observed an ordered moment for Pr of $0.5\mu_B$, but with incomplete ordering along the c axis. We note that the simultaneous presence of these two types of peaks, representing ferromagnetic and antiferromagnetic coupling of the rare-earth ions along the c axis, respectively, is not uncommon in the $RBa_2Cu_3O_{6+x}$ systems; the magnetic interactions along the c direction are extremely weak, and subtle changes can give rise to regions in the sample that order one way or the other.[23] This change from antiferromagnetic to ferromagnetic coupling is also consistent with the small anomaly observed in magnetic susceptibility and specific heat.[2] For both of these types of order, though, the in-plane magnetic structure is the same, with nearest-neighbor Pr spins coupled antiferromagnetically in the a-b plane.

The present results demonstrate conclusively that the Pr ions order magnetically in $PrBa_2Cu_3O_7$, although there is still considerable work that needs to be done before a complete and satisfactory description of the Pr magnetic structure and properties is achieved. One aspect concerns the spin direction. Based on the intensities of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ peaks we tentatively assigned the moment direction to be along the c axis,[2] and this is in agreement with magnetic susceptibility measurements.[14] Crystal-field analyses based on the inelastic neutron scattering data also indicate the c axis as the magnetic easy axis.[18,19] The single-crystal study by Longmore *et al.*[8] gave a moment direction 59° away from the c axis, but with an ordering temperature of 11 K. This low ordering temperature and the different moment direction may be due to the Al contamination on the Cu chain site. In order to verify the correct direction of the Pr moment in clean $PrBa_2Cu_3O_7$ and other details of the magnetic structures of Pr and Cu at low *T*, neutron-diffraction measurements need to be performed on high-quality uncontaminated single crystals, which are currently not available. However, the present lack of such details does not detract from the basic conclusion that the Pr ions carry a magnetic moment and order at 17 K.

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[1] For a review, see H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).
[2] W.-H. Li, J. W. Lynn, S. Skanthakumar, T. W. Clinton, A. Kebede, C.-S. Jee, J. E. Crow, and T. Mihalisin, Phys. Rev. B **40**, 5300 (1989).
[3] I. Felner, U. Yaron, I. Nowik, E. R. Bauminger, Y. Wolfus, E. R. Yacoby, G. Hilscher, and N. Pillmayr, Phys. Rev. B **40**, 6739 (1989).
[4] D. W. Cooke, R. S. Kwok, R. L. Lichti, T. R. Adams, C. Boekema, W. K. Dawson, A. Kebede, J. Schwegler, J. E. Crow, and T. Mihalisin, Phys. Rev. B **41**, 4801 (1990).
[5] For a recent review, see J. W. Lynn, J. Alloys Compd. (to be published).
[6] K. Nehrke and M. W. Pieper, Phys. Rev. Lett. **76**, 1936 (1996).
[7] N. Rosov, J. W. Lynn, G. Cao, J. W. O'Reilly, P. Pernambuco-Wise, and J. E. Crow, Physica C **204**, 171 (1992).
[8] A. Longmore, A. T. Boothroyd, C Changkang, H. Yongle, M. P. Nutley, N. H. Andersen, H. Casalta, P. Schleger, and A. N. Christensen, Phys. Rev. B **53**, 9382 (1996).
[9] C.-S. Jee, A. Kebede, D. Nichols, M. V. Kuric, J. E. Crow, T. Mihalisin, G. H. Myer, I. Perez, R. E. Salomon, and P. Schlottmann, Solid State Commun. **69**, 379 (1989).
[10] A. C. Larson and R. B. V. Dreele, General Structure Analysis System, Los Alamos National Laboratory, Los Alamos, NM 87545 (1990).
[11] M. Park, M. J. Kramer, K. W. Dennis, and R. W. McCallum, Physica C **259**, 43 (1996).
[12] J. W. Lynn, in *High Temperature Superconductivity*, edited by J. W. Lynn (Springer-Verlag, Berlin, 1990), p. 268.
[13] J. W. Lynn, J. Alloys Compd. **181**, 419 (1992).
[14] For recent work on this, see S. Uma, T. Sarkar, K. Sethupathi, M. Seshasayee, G. Rangarajan, C. Changkang, H. Yongle, B. M. Wanklyn, and J. W. Hodby, Phys. Rev. B **53**, 6829 (1996).
[15] L. Soderholm, C.-K. Loong, G. L. Goodmann, and B. D. Dabrowski, Phys. Rev. B **43**, 7923 (1991).
[16] G. L. Goodman, C.-K. Loong, and L. Soderholm, J. Phys. Condens. Matter. **3**, 49 (1991).
[17] H. Jostarndt, U. Walter, J. Harnischmacher, J. Kalenborn, A. Severing, and E. Holland-Moritz, Phys. Rev. B **46**, 14 872 (1992).
[18] G. Hilscher, E. Holland-Moritz, T. Holubar, H. Jostarndt, V. Nekvasil, G. Schaudy, U. Walter, and G. Fillion, Phys. Rev. B **49**, 535 (1994).
[19] A. T. Boothroyd, S. M. Doyle, and R. Osborn, Physica C **217**, 425 (1993).
[20] S. Skanthakumar, W.-H. Li, J. W. Lynn, A. Kebede, J. E. Crow, and T. Mihalisin, Physica B **163**, 239 (1990).
[21] W. K. Dawson, J. C. Lam, C. Boekema, R. L. Lichti, D. W. Cooke, and J. E. Crow, J. Appl. Phys. **69**, 5385 (1991).
[22] H. Casalta, P. Schleger, E. Brecht, W. Montfrooij, N. H. Andersen, B. Lebech, W. W. Schmahl, H. Fuess, R. Liang, W. N. Hardy, and T. Wolf, Phys. Rev. B **50**, 9688 (1994).
[23] For example, see T. W. Clinton, J. W. Lynn, J. Z. Liu, Y. X. Lia, T. J. Goodwin, R. N. Shelton, B. W. Lee, M. Buchgeister, M. B. Maple, and J.-L. Peng, Phys. Rev. B **51**, 15 429 (1995).