Incommensurate magnetism in $PrBa_2Cu_3O_{6.92}$

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We report resonant x-ray magnetic scattering and high-resolution neutron-diffraction studies of the Pr site magnetism in high quality single crystals of $PrBa_2Cu_3O_{6.92}$. These studies reveal that the Pr sublattice orders at 19 K in a well correlated, long period incommensurate structure with probable wave vector $(0.5\pm\delta,0.5,0)$ or $(0.5,0.5\pm\delta,0)$ with $\delta=0.006$ r.l.u. The observed x-ray scattering results from dipole transitions, demonstrating the existence of an ordered $5d$ Pr moment and implying a large $4f$ moment at the Pr site. A spin reorientation transition to a commensurate antiferromagnetic structure of wave vector (0.5,0.5,0.5) is observed at lower temperatures. [S0163-1829(98)07041-6]

One strategy for elucidating the mechanism of high-temperature superconductivity is to study compounds in which the superconductivity is anomalously suppressed. The absence of superconductivity in $La_{2-x}Ba_xCuO_4$ at $x=0.125$,[1] for example, has been found to be associated with the pinning of incommensurate charge and spin stripe correlations,[2,3] which may form the basis for a pairing mechanism in the cuprate superconductors.[4]

Similarly, nonsuperconducting $PrBa_2Cu_3O_{6+x}$ has attracted a great deal of interest as an anomalous member of the $(RE)Ba_2Cu_3O_{6+x}$ series, where RE=Y or rare earth. Although the suppression of superconductivity in $PrBa_2Cu_3O_{6+x}$ is usually discussed in terms of $Pr(4f)$-$O(2p)$ hybridization models[5,6] rather than stripe correlations, the physical properties of $PrBa_2Cu_3O_{6+x}$ (Ref. 7) are sufficiently intriguing, and poorly understood, that other mechanisms cannot yet be ruled out. Of particular significance is the observation[8] that the hole densities in the CuO_2 planes and CuO chains are very similar to those found in the superconducting members of the series. Despite this, $PrBa_2Cu_3O_{6+x}$ is an insulator which exhibits Cu antiferromagnetism for all x, with $T_N(x)=250-350$ K.[9–11] In addition, it appears that the Pr sublattice orders magnetically at an unexpectedly high temperature; $T_{Pr}=10-20$ K compared with other members of the series, for which $T_{RE}=0-2$ K.

The large value of T_{Pr} suggests that the Pr-Pr magnetic coupling is enhanced by electronic interactions with the CuO_2 planes, perhaps as a result of the proposed hybridization schemes.[5,6] In any case, the anomalous Pr magnetism and the suppression of superconductivity in this compound very likely share a common origin, and therefore a better knowledge of the Pr magnetic ordering could help to explain the absence of superconductivity.

Several neutron-diffraction studies[10–13] have been devoted to the magnetic ordering in $PrBa_2Cu_3O_{6+x}$. The consensus from these works is that the Pr sublattice exhibits an antiferromagnetic (AF) structure below T_{Pr}, with a saturated moment of $0.5–0.7\mu_B$. In sharp contrast, recent NMR results[14] were interpreted as evidence for a Pr moment of only $0.017\mu_B$. In addition, the NMR work concluded that the ordered moment lay in the a-b plane, while neutron determinations find it to be closer to the c axis. Boothroyd, Longmore, Andersen, Brecht, and Wolf[11] found it to be tilted out of the plane by $55°\pm20°$, consistent with Mössbauer results,[15] and also found substantial Pr-Cu coupling.

In this paper, we report results of resonant magnetic x-ray scattering measurements on well characterized single crystals of $PrBa_2Cu_3O_{6+x}$. By tuning the incident photon energy to the Pr L_{II} edge we were able to study preferentially the magnetic order on the Pr sublattice with negligible contribution from the Cu order. Our x-ray study, supported by new high-resolution neutron data, confirms the existence of a large ordered Pr moment, and reveals a static, long period incommensurate modulation in the Pr sublattice ordering.

The x-ray experiments were performed at beamline X22C at the National Synchrotron Light Source. A Ge(111) double bounce monochromator, with an energy resolution of ~5 eV, was utilized with a Ge(111) analyzer. The neutron work was carried out at the cold source beamline TAS 7, at Risø National Laboratory. An incident energy of 3 meV was used, with collimation 40′-monochromator-37′-sample-

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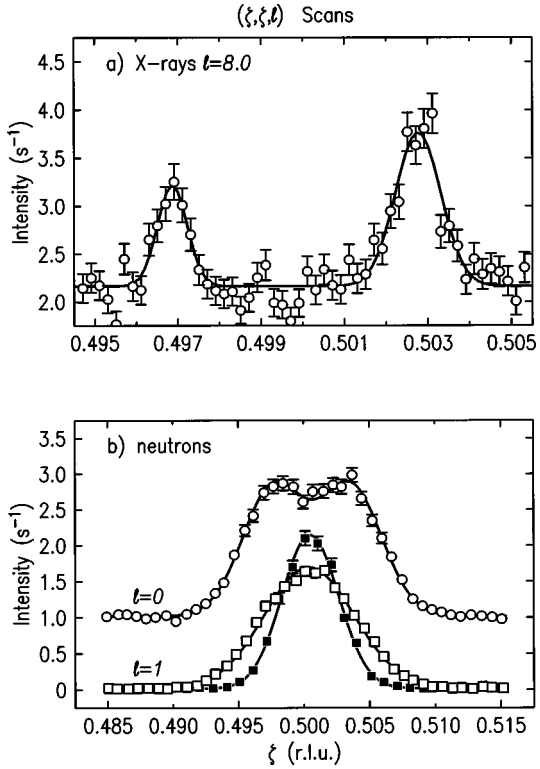

FIG. 1. (a) X-ray scan through the (0.5,0.5,8) antiferromagnetic point with $\hbar\omega = 6441$ eV, revealing incommensurate magnetic order of the Pr sublattice at $T = 10$ K. (b) Neutron scans through (0.5,0.5,l) at $T = 10$ K (open symbols) and 20 K (closed squares). The $l = 0$ data are offset vertically. Lines are fits to Gaussian functions to ascertain the peak positions and widths. Note that the horizontal scale is three times larger for the x-ray data.

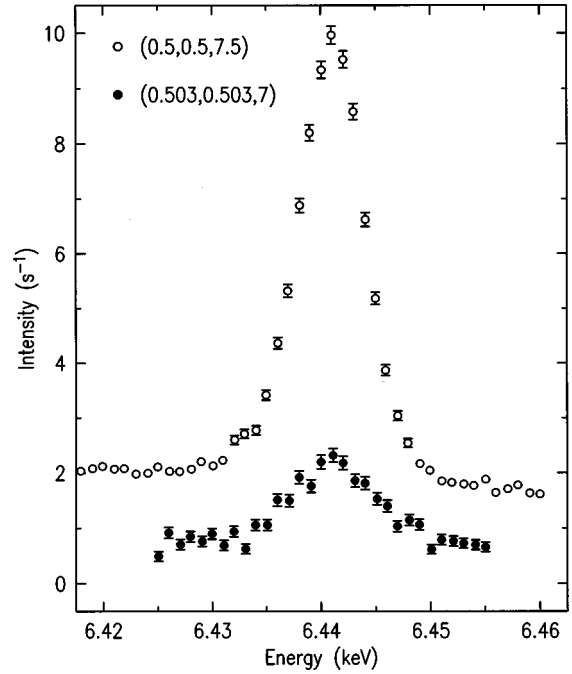

FIG. 2. Incident photon energy dependence of the magnetic scattering at (0.5,0.5,7.5) at $T = 5$ K and (0.503,0.503,7) at $T = 11$ K. Data are offset vertically for clarity.

30′-analyzer. Pyrolytic graphite monochromator and analyzers were utilized, with a Be filter to suppress higher order contamination in the incident beam. The samples were mounted such that peaks of the form (h,h,l) were accessible in the diffraction plane. The reciprocal space resolution [full width at half maximum (FWHM)] of the two spectrometers for scans parallel to $(h,h,0)$ was $\delta h = 5.5\times10^{-3}$ r.l.u. for neutrons and $\delta h = 8.4\times10^{-4}$ r.l.u for x rays.

The crystals studied here are from the same batch as those of Ref. 11. They were grown in MgO crucibles and have very low impurity levels, the most significant being Sr (0.7 at.%) and Mg (0.1 at.%). The oxygen content was $x = 0.92$. The samples were platelets with surface areas of a few mm^2 and a c-axis normal. Mosaic spreads were $\approx 0.05°$ (FWHM). For the x-ray work, two different crystals were studied, each gave identical results.

X-ray resonant magnetic scattering utilizes the enhancements in the magnetic scattering cross section obtained when the incident photon energy is tuned to an atomic absorption edge.[16,17] For the rare-earth elements, large enhancements are observed at the $L_{II,III}$ edges. In the present work, the incident photon energy is tuned to the Pr L_{II} edge. The combination of large enhancements in the scattering from the Pr moments and extremely weak nonresonant scattering from the Cu moments ensures that the observable signal is entirely due to any ordered Pr moment. In contrast, the neutron cannot distinguish between moments of the same size on different elements, and this renders magnetic structure determination in samples with more than one magnetic ion more difficult. The high reciprocal space resolution of x-ray scattering was also crucial in the present experiment.

In accord with earlier single-crystal neutron diffraction results, magnetic scattering was observed below T_{Pr} in the vicinity of (0.5,0.5,l), l integer, positions in reciprocal space, corresponding to a structure in which neighboring Pr moments are oppositely aligned in the a and b directions, but parallel along the c axis. An x-ray scan across the (0.5,0.5,8) antiferromagnetic Bragg point, taken at $T = 10$ K, is shown in Fig. 1(a). Remarkably, however, the data reveal that the scattering is not commensurate, as previously believed, but is comprised of two peaks, symmetrically displaced from the antiferromagnetic point. Similar satellites were seen at all accessible, symmetry related positions.

There are two possibilities for the modulation wave vector that could give rise to the scattering observed in Fig. 1. These are $(0.5+\delta/2, 0.5+\delta/2, 0)$ and $(0.5+\delta, 0.5, 0)$ with $\delta = \pm 0.006$ r.l.u. If one takes into account the crystallographic twinning and a distribution of magnetic domains then these wave vectors each give a pattern of four spots rotated by 45° with respect to each other. However, the out-of-plane resolution is relatively coarse (0.006 r.l.u. FWHM) and were the $(0.5+\delta/2, 0.5+\delta/2, 0)$ ordering to be present, significant intensity would be expected at the commensurate position, in contrast to what is observed. We therefore conclude that the most probable wave vector is $(0.5\pm\delta, 0.5, 0)$ or $(0.5, 0.5\pm\delta, 0)$. A similar pattern was found in Ref. 2.

The x-ray data of Fig. 1 were taken with the incident photon energy at the peak of the Pr L_{II} resonance (6441 eV). A scan of the incident energy taken at the incommensurate wave vector is shown in Fig. 2. These data demonstrate that the scattering is indeed resonant, confirming its magnetic origin, and that any contribution from the Cu order is negligibly small. The data of Fig. 1(a) alone, therefore, require the ex-

istence of long-range antiferromagnetic Pr order, without any recourse to modeling of intensities.

The incommensurability is small, and corresponds to a long period modulation, of wavelength ~ 600 Å. In addition, the structure is highly ordered. The half-width of the observed scattering corresponds to a magnetic correlation length of $\xi_{110} \geqslant 900$ Å along the (110) propagation direction, and $\xi_l \approx 300$ Å in the $(00l)$ direction. The incommensurability increases slightly with temperature, by approximately 10% from $T=5$ K, to $T_{Pr}=19$ K.

High-resolution neutron-scattering measurements were carried out on one of the x-ray crystals, and on a larger (20 mg) sample taken from a different batch. Both samples showed identical behavior in all respects. A neutron scan through the (0.5,0.5,0) Bragg point is shown in Fig. 1(b). The solid line is a fit to two resolution limited Gaussians[18] with a separation of 0.0059 r.l.u. Although the peaks are not fully resolved, the data are clearly consistent with such a splitting. These data serve to confirm that the incommensurate behavior observed by x rays is characteristic of the bulk of the crystal. They further determine that the magnetic modulation is static on a time scale $\sim 10^{-12}$ s set by the energy resolution of the neutron spectrometer. Neutron measurements made under identical experimental conditions on a reduced crystal ($x \approx 0.2$) from the same batch did not resolve any splitting of the (0.5,0.5,0) peak, and put an upper limit of $\delta \approx 0.001$ r.l.u. on any incommensurability.

As mentioned earlier, there has been some controversy concerning the size of the Pr ordered moment. The possibility for debate arises because the neutron-scattering data from the Pr and Cu sublattices cannot be easily separated, and one is forced to rely on model structure factor calculations to interpret measured intensities in terms of ordered sublattices. Thus, while the AFI phase[10] CuO_2 bilayer structure factor forbids scattering at $l=0$, explanations other than an ordered Pr moment are possible for the (0.5,0.5,0) peak, including ordering of the Cu chain sites, ordering of moments on the holes, or structural scattering. However, taken together the present x ray and neutron data unambiguously rule out these alternatives; the resonant x rays confirm the Pr origin of the scattering and justify the earlier neutron analysis of integrated intensities, which obtained an ordered moment of $\langle \mu(\mathrm{Pr}) \rangle = 0.6\mu_B$, e.g., Ref. 11.

The L_{II} resonance shown in Fig. 2 is dominated by dipole $2p \leftrightarrow 5d$ transitions, and thus the x rays are in fact probing the Pr $5d$ polarization, which is most likely to be the result of a large $4f$ moment on the Pr ion.

An important question is whether the incommensurate magnetism is a feature of the Pr sublattice alone, or whether it affects the Cu sublattice as well, below T_{Pr}. We addressed this point by measuring, with neutrons, the (0.5,0.5,1) Cu bilayer antiferromagnetic Bragg peak above and below T_{Pr}, at 20 K and 10 K, respectively. These data are included in the lower part of Fig. 1(b). Although the 10 K scan is broader than the 20 K scan, it does not exhibit the double-hump structure characteristic of the (0.5,0.5,0) reflection. This strongly suggests that the (0.5,0.5,1) scattering is comprised of both commensurate and incommensurate peaks. The presence of a commensurate peak at $l=1$, but not at $l=0$, is in accordance with the AFI phase structure factor, and indicates that the AFI bilayer spin arrangement persists below T_{Pr}. This conclusion is consistent with the AFIII model,[11] because in the AFIII structure the x and y components of the bilayer Cu spins order in different modes: the x component remains in the AFI structure, while the y component couples to the Pr moments and adopts the same symmetry as the in-plane Pr sublattice ordering. Hence the y Cu spin component is expected to be incommensurately ordered below T_{Pr}, while the x component remains commensurate.

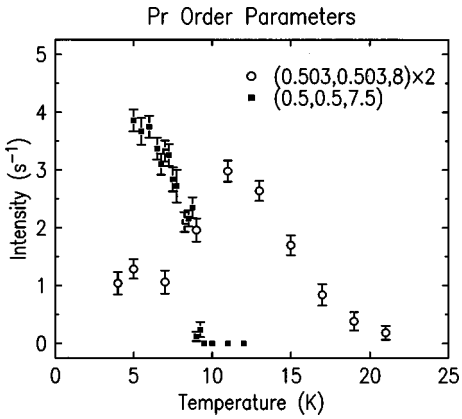

FIG. 3. Temperature dependence of the two observed Pr order parameters. The intensity of the incommensurate modulation is multiplied by 2 to give an approximate indication of the relative intensities of the two structures.

On reducing the temperature we observed a spin reorientation transition near $T_2=9$ K with x rays. The reorientation was signaled by the appearance of peaks of the form $(0.5,0.5,l+0.5)$, l integer, corresponding to a structure which alternates along the c axis as well as along the a and b axes. A simultaneous reduction in the intensity of the magnetic peaks near $(0.5,0.5,l)$ occurred, as may be seen in Fig. 3 on which the peak intensities for both ordering wave vectors are plotted as a function of temperature. Both data sets were taken on warming. A scan of the incident energy (Fig. 2) confirms that this new scattering also originates from Pr moments. Similar reorientation behavior has been reported very recently[13] in neutron experiments on a single crystal of $PrBa_2Cu_3O_{6+x}$ essentially free of ($BaZrO_3$) crucible contamination. In that experiment, the reorientation transition occurred at $T_2=11$ K, on cooling, and was first order and hysteretic. We did not observe this transition in any of our neutron measurements, suggesting that the low-temperature phase occurs in our crystals only in the near-surface region probed by x rays (~ 1 μm), and that the bulk differs slightly in chemical composition. Note that the transition does not go to completion, and that even at 4 K, there was still some incommensurate scattering present, presumably because not all of the volume probed by x rays undergoes this transition. Nevertheless, the fact that our x-ray data reveal almost the same reorientation behavior as was observed by Uma *et al.*[13] in their very high-purity crystal suggests that the surface region is not strongly affected by the small amounts of Sr and Mg impurities in our crystals, and therefore the incommensurate splitting, which is a feature of both surface and bulk in our crystals, is very likely an intrinsic property of $PrBa_2Cu_3O_{6+x}$. Perhaps the most interesting feature, though, of the reorientation transition is that in doubling

the magnetic unit cell, an incommensurate structure is replaced by a commensurate one.

The observation of static incommensurate magnetic order has caused a great deal of excitement recently in connection with the absence of superconductivity in $La_{1.875}Ba_{0.125}CuO_4$. Following our observation of a static incommensurate phase in hole doped $PrBa_2Cu_3O_{6+x}$ it is natural to ask whether the same mechanism might explain the suppression of superconductivity in both compounds. If what we have observed in $PrBa_2Cu_3O_{6+x}$ is due to stripe correlations, however, then there are a number of differences that need to be explained. First, the incommensurate wave vector is very small, which is seemingly inconsistent with the claim that the hole density (which controls the stripe period[2,3]) is the same as in compounds with superconducting planes. However, if in fact the majority of the holes are in orbitals orthogonal to the Cu-O bonds, as proposed by Fehrenbacher and Rice,[5] then it is conceivable that a longer stripe period could be supported. Second, our neutron results indicate that there is still a commensurate component to the bilayer Cu ordering that coexists with the incommensurate structure observed below T_{Pr}, which is difficult to reconcile with stripe correlations. Finally, it is hard to understand within the stripe picture why the incommensurability should disappear below T_2 when the magnetic unit cell doubles in the c direction.

The latter observation tends to suggest alternative explanations centered around the way the Pr ions are coupled in the c direction. One possible factor is frustration arising from the Pr-Cu coupling identified in the AFIII model,[11] which could drive an incommensurate instability. A related possibility concerns magnetic interactions with the CuO chains. When the magnetic repeat along the c direction is $2c$, any magnetic coupling to the chains vanishes by symmetry, whereas when it is c, such a coupling is allowed.[19] Magnetic or electronic features in the chain layers could, therefore, influence the ordering. In order to explore this and other possible explanations further, more information on the c-axis coupling is required, including the role played by any Pr ions on the Ba site. The observation of incommensurate fluctuations on the chains in $YBa_2Cu_3O_{6+x}$ (Refs. 20 and 21) may be of some relevance. Finally, the rather weak temperature dependence of the incommensurate splitting, also observed in the stripe phases of the nickelates,[22] must be accounted for.

The use of resonant magnetic x-ray scattering to probe the Pr magnetic behavior directly, complemented by neutron diffraction from both the Pr and Cu moments, has enabled us both to clarify and to provide new insights into the low-temperature magnetic phases of $PrBa_2Cu_3O_{6+x}$. These findings are important in the field of cuprate superconductivity because of the likelihood that a common interaction is responsible for both the enhanced Pr magnetism and the anomalous absence of superconductivity in $PrBa_2Cu_3O_{6+x}$. The observation of incommensurate magnetism is reminiscent of the spin-charge separation model, but the character of the modulation observed here appears quite different. Other explanations that link the various magnetic couplings with the unusual electronic structure of $PrBa_2Cu_3O_{6+x}$ may need to be sought.

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