Incommensurate Magnetism in non-Superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{6.92}$

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Abstract

We report the discovery of incommensurate magnetic order in non-superconducting single crystals $\text{PrBa}_2\text{Cu}_3\text{O}_{6.92}$. Resonant x-ray magnetic scattering at the Pr L_{II} and L_{III} edges and high resolution neutron diffraction were used to characterise the magnetic order on the different magnetic sublattices. The data reveal that the Pr sublattice orders at a temperature of 19 K in an incommensurate structure with ordering wavevector $(0.5 \pm \delta, 0.5, 0)$ or $(0.5, 0.5 \pm \delta, 0)$, $\delta \approx 0.006-0.008$. A spin reorientation in the Pr sublattice to a commensurate antiferromagnetic structure with ordering wavevector $(0.5, 0.5, 0.5)$ takes place at a temperature close to 9 K.

Introduction

$\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ exhibits surprising and anomalous properties in comparison with isostructural compounds containing other trivalent rare earth ions [1]. Polycrystalline and flux grown single crystal samples of $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ do not superconduct for any value of x , but single crystals grown by the floating zone method have been reported to superconduct below a transition temperature T_c of up to 85 K [2]. Evidence for superconductivity has also been found in some thin film samples [3]. An explanation of these observations would be of interest both to those attempting to understand the basic physics of cuprate superconductors, and also to the applied superconductivity community who frequently use $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ as a non-superconducting spacer layer in thin film applications.

This paper addresses the unusual magnetic ordering properties of $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$. One aspect of this is antiferromagnetism of the Cu sublattice that sets in at temperatures in the vicinity of room temperature throughout the entire range of oxygen stoichiometries between $x = 0$ and 1 [4], in contrast to $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, for which the Cu antiferromagnetism is lost once the level of doping x exceeds 0.4. In the present paper, however, we concentrate upon the temperature regime below approximately $T_{\text{Pr}} = 20$ K in which magnetic ordering of the Pr sublattice occurs in addition to Cu antiferromagnetism. The value of T_{Pr} is in itself anomalous in comparison to the rare earth (R) sublattice magnetic ordering in isostructural $\text{RBa}_2\text{Cu}_3\text{O}_{6+x}$ compounds which is typically 0–2 K, and the magnetic structures observed in this phase have been the subject of a number of previous investigations [5–8].

The key results of our recent studies [9, 10] are the confirmation of a substantial ordered moment on the Pr ions, and the observation of incommensurate magnetic order involving on the Pr and Cu sublattices. In this paper we review our latest work and present new results on the incommensurate phase.

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Experimental details

We have used a combination of high resolution neutron diffraction and resonant x-ray magnetic scattering to investigate the magnetic structures. Both techniques were crucial to this investigation. Neutron diffraction is good for establishing the ordering wavevectors of magnetic structures and for determining the size and orientation of the moments within an assumed model for the magnetic structure, while the x-ray resonant technique unambiguously identifies which elements contribute to a given order parameter. The incomparable wavevector resolution available at synchrotron x-ray sources permits the observation of magnetic structures with long period modulations. One other distinction between neutron and x-ray scattering is the penetrating power of the radiation. Neutrons probe distances into the sample of order several cm, whereas x-rays are sensitive only to the near surface region (typically $\sim \mu\text{m}$).

The neutron experiments were performed on triple-axis spectrometers at the DR3 reactor of the Risø National Laboratory, and the synchrotron x-ray scattering employed the X22C and X25 beamlines of the National Synchrotron Radiation Facility at Brookhaven National Laboratory and the ID20 station at the European Synchrotron Radiation Facility in Grenoble.

The single crystal samples used in all the experiments were prepared by the flux growth method described in ref. [11] with MgO crucibles. Crystals for the x-ray work were small ($1.5 \times 1.5 \times 0.1 \text{ mm}^3$), but had an excellent mosaic of typically 0.03° FWHM in rocking curves. Larger crystals (approximately $2 \times 2 \times 0.7 \text{ mm}^3$) from the same batch were used for most of the neutron measurements. All the results presented in this paper refer to crystals with an oxygen stoichiometry of $x = 0.92$.

Results

Magnetic ordering of the Pr sublattice occurs in our crystals at $T_{\text{Pr}} = 19$ K, and in a previous paper [7] we deduced from an analysis of neutron diffraction data that the magnetic structure below T_{Pr} includes not only antiferromagnetism of the Pr moments, but also a noncollinear arrangements of the bilayer Cu spins as shown in Fig. 1. Also shown in Fig. 1 is the AFI antiferromagnetic structure of the Cu spins that is observed above T_{Pr} up to the Néel temperature (276 K in this crystal). It has been argued [12, 13] that an anisotropic, pseudodipolar Pr–Cu exchange interaction may be responsible for the observed noncollinearity in the Cu ordering, and a symmetry analysis of the AFI and AFIII structures has been presented [12].

One limitation of neutron magnetic scattering is that the strength of the scattering from an individual magnetic moment of a given magnitude and orientation does not depend on which atom or isotope carries the moment. With more than one magnetic species present it can be hard to separate the scattering from each magnetic sublattice. Any ambiguities can be resolved, however, by the use of resonant x-ray magnetic scattering which takes advantage of the enhancements in scattering when the x-ray energy is tuned to an atomic absorption edge. In the case of $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$, therefore, it is possible to examine the Pr and Cu magnetic sublattices independently by this technique.

Our first resonant x-ray magnetic scattering studies were performed with the incident x-ray energy tuned to the peak of the Pr L_{II} dipole resonance (6441 eV). To our surprise, these revealed incommensurate magnetic ordering below T_{Pr} . To illustrate this we show in Fig. 2(a) a contour plot of the intensity measured in the $(h,k,0)$ plane centred on the $(0.5, 0.5, 9)$ antiferromagnetic point at $T = 12$ K. The four satellites centred at $(0.5 \pm \delta, 0.5, 9)$ and $(0.5, 0.5 \pm \delta, 9)$ are displaced from the antiferromagnetic point by only $\delta = 0.007$ r.l.u., as may be seen from the cut shown in Fig. 2(b), corresponding to a modulation of the antiferromagnetic structure with a long periodicity of

approximately 600 Å. Furthermore, from the width of the peaks a correlation length of at least 1000 Å may be inferred.

To confirm that the scattering is magnetic in origin we performed energy scans through the Pr L_{II} resonance with the spectrometer fixed in reciprocal space. Fig. 3(a) shows such a scan at $(0.5, 0.5+\delta, 9)$. These data prove that the scattering is resonant and originates from magnetic order of the Pr sublattice. Subsequent neutron diffraction measurements in a high resolution configuration also resolved the satellites (just! See Fig. 1(b) of ref. [9]), and this confirms (a) that the incommensurate order is present throughout the bulk of the crystal, and (b) that the ordering is static on a timescale of $\sim 10^{-12}$ s set by the neutron energy resolution.

On lowering the temperature below 9 K we observed a decrease in the intensity of the incommensurate satellites, and a corresponding appearance of peaks at $(0.5, 0.5, l+0.5)$, l integer, positions in reciprocal space. This change signifies a reorientation of the Pr sublattice ordering from an incommensurate to a commensurate structure, with an associated doubling of the magnetic unit cell in the c direction. Uma *et al* [8] also observed a c axis doubling of the magnetic order, but the resolution of their scans was not sufficient to observe the incommensurate splitting in the high temperature phase. Our own neutron measurements on the same crystal as used in the x-ray experiments did not reveal the transition, and we conclude from this that the reorientation in our crystals takes place only in the near surface region probed by the x-rays. More details of our observations on this reorientation may be found in ref. [9], but we remark that the change from an incommensurate to a commensurate magnetic structure on doubling the magnetic unit cell along c could indicate that the incommensurability arises from some feature of the c axis coupling, perhaps due to interactions with the Cu-O chains.

Despite the reorientation transition described above, the incommensurate satellites do not vanish entirely below 9 K. Fig. 4 shows a sequence of scans along the $(1, 1, 0)$ direction in reciprocal space through the point $(0.5, 0.5, 7)$ at different temperatures between 4.4 K and 16.7 K. The scans were made with an experimental configuration that had relatively poor resolution perpendicular to the scattering plane, and hence

the satellites are observed even though the scan trajectory does not pass through the centre of the satellites. Fig. 5 shows the variation of the incommensurate splitting δ as a function of temperature. For much of the temperature range the incommensurability increases linearly with temperature at a rate $d\delta/dT = 2.2 \times 10^{-4}$ (r.l.u.) K⁻¹.

The L_{II} x-ray resonance shown in Fig. 3(a) is dominated by dipole $2p \leftrightarrow 5d$ transitions, and so strictly speaking the x-rays are detecting a Pr $5d$ ordered moment. This is most likely induced by a large ordered moment on the Pr $4f$ electrons, but to show this directly we searched for the quadrupole $2p \leftrightarrow 4f$ resonance which is usually found to be stronger at the L_{III} edge than at the L_{II} edge. Figure 3(b) shows an energy scan through the Pr L_{III} resonance (5967 eV). The main peak is from the dipole transitions, but the scan also reveals a weak peak approximately 8 eV below the dipole resonance. We observed this peak at several different magnetic Bragg peaks, and it closely coincides with a quadrupole feature identified in the x-ray magnetic circular dichroism spectrum of Pr [14]. We believe, therefore, that the weak peak at 5959 eV is in all probability a $2p \leftrightarrow 4f$ quadrupolar excitation, thus confirming directly the existence of magnetic ordering of the Pr $4f$ moments.

All the x-ray measurements reported so far have been made at or near the Pr L_{II} and L_{III} resonance energies. From Figs. 3(a) and (b) it is clear that if one moves well away from the resonance then the scattering intensity reduces considerably, and is in fact indistinguishable from the background. This means that the contribution to the observed signal from non-resonant Cu (or, indeed, non-resonant Pr for that matter) is negligible, and so the peaks we have observed truly reflect the magnetic ordering of the Pr sublattice. In order to investigate selectively the magnetic order on the Cu sublattice by a similar x-ray resonance method it is necessary to use x-ray energies in the vicinity of the Cu K edge (8979 eV). The resonant enhancement effect is much weaker for Cu than for Pr, but we have recently succeeded in observing the Cu resonant magnetic scattering, and have carried out a study of the Cu sublattice magnetic ordering. These results will be the subject of a forthcoming paper [10]. Our

main conclusions are that the Cu ordering is commensurate above T_{Pr} , but has both commensurate and incommensurate components below T_{Pr} . The incommensurate scattering associated with the Cu ordering occurs at the same wavevector as that for the Pr ordering, strongly suggesting a coupled magnetic structure.

Discussion and Conclusions

In recent years it has become apparent that incommensurate structures due to the formation of charge stripes separated by antiferromagnetic regions are a fundamental property of doped transition metal oxides. These structures have been observed in cuprates that anomalously do not exhibit superconductivity, such as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, with $x = 0.125$ [15]. There are several differences, however, between the incommensurate order that we have observed in non-superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{6.92}$, and that in other doped oxides. Firstly, in the present system the incommensurate wavevector is very small compared with other systems that have comparable doping levels. Second, a commensurate component of the Cu magnetism remains even in the incommensurate phase below T_{Pr} . Finally, the incommensurate modulation vanishes below the reorientation transition associated with a doubling of the magnetic periodicity along c . It seems most likely, therefore, that the incommensurate order in $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ does not have the same origin as that observed in other cuprates.

The observation of x-ray magnetic resonant scattering from Pr below T_{Pr} confirms unambiguously the existence of an ordered moment on the Pr sublattice. This finding is in accord with many other experimental results, but conflicts with the interpretation of data from an NMR investigation [16] in which the Pr ordered moment was deduced to be only $0.017 \mu_B$. It is improbable that such a small moment would produce the strength of signal observed in our x-ray measurements.

By contrast, the AFIII model of coupled Pr-Cu magnetic ordering with ordered moments $\mu_{Pr} \approx \mu_{Cu} \approx 0.6 \mu_B$ proposed in ref. [7] appears to give a consistent description of all the x-ray and neutron scattering results. The main feature of this model is a

non-collinear arrangement of the Cu spins on the bilayers either side of the ordered Pr sublattice, as depicted in Fig. 1. This local arrangement of spins can exist in both Pr structures observed below T_{Pr} . In the commensurate phase, with periodicity $2c$, the stacking sequence for the Cu rotation angle ϕ_{Cu} is $(-,+)(+,-)(-,+)$, etc, whereas for the incommensurate phase, periodicity c , the stacking is $(-,+)(-,+)(-,+)$, etc. In the latter sequence, however, the neighbouring Cu spins separated by a chain layer are not antiparallel, and this configuration may be inherently frustrated. It is possible that this frustration is responsible for the incommensurability.

These experiments have revealed a complex magnetic structure in $PrBa_2Cu_3O_{6.92}$, and efforts to understand the observed features of the ordering should be rewarded with greater insight into the interaction between the electrons on the Pr ions and the states on the adjacent CuO_2 layers. It is hoped that this detailed information on the magnetic couplings will help to provide a better understanding of the unusual electronic properties of $PrBa_2Cu_3O_{6+x}$.

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Figure captions

Figure 1. The upper drawing shows the collinear AFI antiferromagnetic arrangement of Cu spins. The lower drawing depicts the AFIII noncollinear magnetic structure of $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$ observed below T_{Pr} [7]. Part of one magnetic unit cell is shown, including the two CuO_2 planes either side of the Pr layer. The axes of the Cu spins on each plane are rotated by $\pm\phi_{\text{Cu}}$ relative to their direction in the collinear antiferromagnetic phase above T_{Pr} . θ_{Pr} is the angle of the Pr moments away from the CuO_2 plane. In $\text{PrBa}_2\text{Cu}_3\text{O}_{6.92}$ at $T = 4.2$ K we find $\phi_{\text{Cu}} = 30^\circ \pm 5^\circ$ and $\theta_{\text{Pr}} = 55^\circ \pm 20^\circ$.

Figure 2. Incommensurate x-ray resonant magnetic scattering from $\text{PrBa}_2\text{Cu}_3\text{O}_{6.92}$ measured with the x-ray energy tuned to the Pr L_{II} dipole resonance. (a) Contour plot of the intensities measured in the $(h,k,0)$ plane in the neighbourhood of the $(0.5, 0.5, 9)$ antiferromagnetic point in reciprocal space. (b) Cut through the satellites at $(0.5 \pm \delta, 0.5, 9)$, $\delta = 0.007$. The scan direction is shown in the inset.

Figure 3. Scans of the x-ray energy measured at a satellite of the $(0.5, 0.5, 9)$ antiferromagnetic position at a temperature of 12 K. (a) The Pr L_{II} resonance, and (b) The Pr L_{III} resonance. The main peak is dominated by $2p \leftrightarrow 5d$ dipole transitions, but the inset in (b) shows the weak $2p \leftrightarrow 4f$ quadrupolar feature.

Figure 4. Series of scans through the incommensurate satellites around $(0.5, 0.5, 7)$ at temperatures between 4.4 K and 16.7 K. The vertical lines are a reference for the peak positions at 4.4 K.

Figure 5. Temperature variation of the incommensurate splitting measured from the separation of the satellite peak positions near $(0.5, 0.5, 7)$. The points were obtained from Gaussian fits to the satellites peaks. The rate of increase of the splitting indicated by the straight line is $d\delta/dT = 2.2 \times 10^{-4}$ (r.l.u.) K^{-1} .

AFI phase

AFIII phase

Fig. 2(a)

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(b)

Fig 2(b)

Boothroyd et al. 1992, p. 100

Fig. 3

$(\xi, \xi, 7)$

Fig 4
Intensity of ξ vs ξ

Fig. 5

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