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# Neutron and X-ray scattering studies of magnetism in non-superconducting $PrBa_2Cu_3O_{6+x}$

A.T. Boothroyd*

*Department of Physics, University of Oxford, Oxford OX1 3PU, UK*

**Abstract**

I give a short review of neutron and X-ray scattering experiments undertaken to study the magnetic properties of non-superconducting $PrBa_2Cu_3O_{6+x}$. The measurements have confirmed the magnetic ordering of the Pr sublattice at temperatures below $T_{Pr}\approx 20$ K, and have revealed an incommensurate magnetic structure with a long period (~600 Å) involving both the Pr and Cu spins. The Cu spins in this Pr ordered phase are found to be non-collinear. Taken as a whole, the results provide strong evidence for a substantial magnetic coupling of the pseudodipolar type between the Pr and Cu ions. The effect of this coupling is also evident in the spectrum of low energy magnetic excitations determined by neutron inelastic scattering. 

*Keywords:* High-$T_c$ superconductors (A); Magnetically ordered materials (A); Exchange and superexchange (D); Spin dynamics (D); Neutron scattering (E); X-ray magnetic scattering (E)

## 1. Introduction

One of the most intriguing problems that has emerged from the study of cuprate high $T_c$ superconductors is the suppression of superconductivity that occurs when Pr is incorporated into certain compounds. The effect was first characterised systematically in the series $(Pr_yY_{1-y})Ba_2Cu_3O_{6+x}$ [1–3], and the anomalous electrical and magnetic properties of the end member $PrBa_2Cu_3O_{6+x}$ in comparison with isostructural compounds containing other trivalent rare earth ions have been well documented [4]. Interest in this problem has been heightened by recent reports of superconductivity in single crystals grown by the floating zone method [5,6] and some thin film samples [7,8], and this development emphasises the need to understand why samples of $PrBa_2Cu_3O_{6+x}$ prepared by standard methods do not superconduct (for any value of $x$).

A number of ideas have been put forward to explain why Pr has this adverse effect on superconductivity. A common theme is the valence state of the Pr ions. The rare earth site in the $YBa_2Cu_3O_{6+x}$ structure (see Fig. 1) is normally occupied by ions with a 3+ oxidation state, but if Pr were more highly ionised, as occurs in some other compounds such as $PrO_2$, then holes in the $CuO_2$ planes could be neutralised and the number of mobile charge carriers reduced below the level needed to sustain superconductivity. Early suggestions of a stable 4+ oxidation

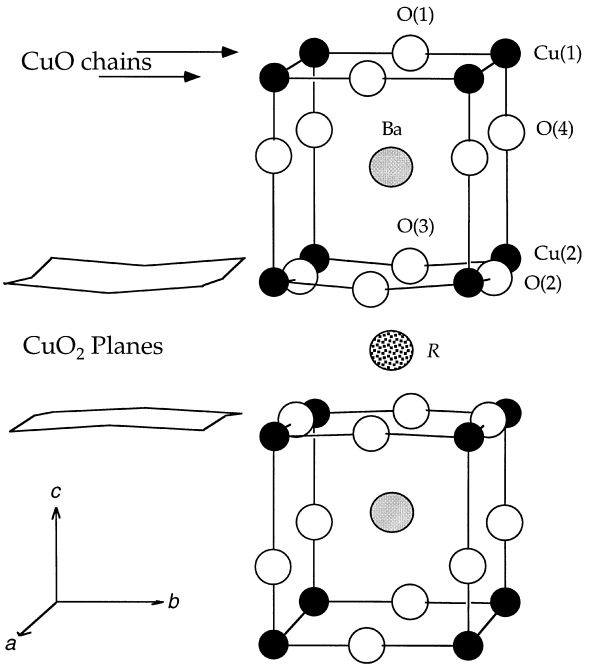


Fig. 1. Unit cell of $RBa_2Cu_3O_{6+x}$ (R=Y, rare earth) showing the different atomic positions.

*Tel.: +44-1865-27-2376; fax: +44-1865-27-2400.

*E-mail address:* a.boothroydl@physics.ox.ac.uk (A.T. Boothroyd)

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state ($4f^1$) for Pr have largely been refuted by spectroscopic data, but the idea of an electronic state in which the Pr ions exist for at least some of the time with a charge greater than 3+ has steadily grown in popularity. The most influential work has been that of Fehrenbacher and Rice [9] who proposed a hybrid state containing stable $Pr^{3+}$ and an intermediate valence Pr(IV) state made from a linear combination of $Pr^{4+}$ and $Pr^{3+}\underline{L}$, where $\underline{L}$ denotes a ligand hole in the neighbouring O 2*p* orbitals. According to Fehrenbacher and Rice the average charge on the Pr ions in this model is ~3.2+.

Alternative, less well-developed explanations have focussed (i) on the presence of a small amount of $Pr^{3+}$ ions on the $Ba^{2+}$ sites performing a similar hole-filling role to that described above [10], and (ii) on the possibility that magnetic pair-breaking might take place due to magnetic coupling between moments on the Pr ions and the spins of the superconducting quasiparticles [11,12].

In this paper I will review only one aspect of the problem, namely the unusual magnetic properties of $PrBa_2Cu_3O_{6+x}$. The magnetic interactions of the Pr ions with their surroundings are clearly of direct relevance to the pair-breaking hypothesis, but the detailed magnetic behaviour is also likely to reflect features of the electronic structure of $PrBa_2Cu_3O_{6+x}$ in a more general sense. Thus, either directly or indirectly, magnetism is of great importance in this compound. In Section 2 I describe what has been found out about the magnetic ordering, and in Section 3 preliminary measurements of the magnetic dynamics will be presented.

## 2. Magnetic ordering in $PrBa_2Cu_3O_{6+x}$

### *2.1. Background*

One of the first unusual features of the magnetism in $PrBa_2Cu_3O_{6+x}$ is the occurence of antiferromagnetic (AF) order of the Cu spins that sets in at temperatures in the vicinity of room temperature. This AF order exists throughout the entire range of oxygen composition between $x=0$ and 1 [13,14] with only a small reduction in the ordering temperature $T_N$ with oxygen doping, ranging from 325–350 K ($x\approx0.1$) to 265–285 K ($x\approx0.95$). This behaviour contrasts strongly with that of $YBa_2Cu_3O_{6+x}$ in which the value of $T_N$ drops from 410 K at $x\approx0.1$ to zero at $x\approx0.4$, and for $x>0.4$ a superconducting phase appears with a maximum superconducting transition temperature of approximately 92 K at $x\approx0.95$.

The antiferromagnetic phase below $T_N$ in both $PrBa_2Cu_3O_{6+x}$ and $YBa_2Cu_3O_{6+x}$ is the well-known AFI phase, in which the spins on the Cu(2) sites within the $CuO_2$ layers (see Fig. 1) align antiparallel to their nearest neighbours along all three crystallographic axes, as illustrated in Fig. 2. The magnitude of the saturated ordered moment on the Cu(2) sites is $\mu_{Cu}\approx0.6\ \mu_B$; and no ordered moment is present on the Cu(1) site in the basal plane or on the Pr site. The AFI phase can be identified in X-ray and neutron diffraction experiments by the occurence of peaks with indices ($h+1/2$, $k+1/2$, $l+1/2$), where $h$, $k$ and $l$ are integers. The intensities of these peaks show a sinusoidal modulation with $l$ because there are two $CuO_2$ layers per unit cell.

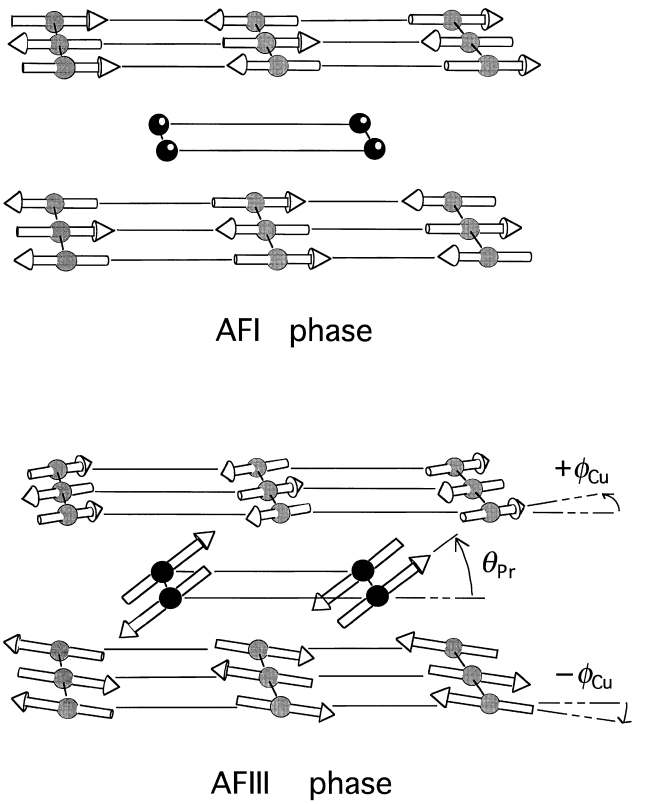


Fig. 2. The upper drawing shows the collinear AFI antiferromagnetic arrangement of Cu spins. The lower drawing depicts the AFIII non-collinear magnetic structure of $PrBa2Cu_3O_{6+x}$ observed below $T_{Pr}$ [22]. Part of one magnetic unit cell is shown, including the two $CuO_2$ planes either side of the Pr layer. In the AFIII phase axes of the Cu spins in each plane are rotated by $\pm\phi_{Cu}$ relative to their direction in the collinear antiferromagnetic phase above $T_{Pr}$. $\theta_{Pr}$ is the angle of the Pr moments away from the $CuO_2$ plane.

A reorientation of the AFI Cu spin ordering is sometimes observed which produces a different structure, known as AFII, characterised by diffraction peaks at ($h+1/2$, $k+1/2$, $l+1/2$) positions. The AFII phase can in principle involve ordering of both the Cu(1) and Cu(2) sites, but in practice there have been no decisive reports of a large Cu(1) moment. There is strong evidence that the AFII phase is triggered by the presence of certain cation impurities in the basal plane or on the Ba site [15], and for this reason the AFII phase is not believed to be an intrinsic property of the $RBa_2Cu_3O_{6+x}$ family (R=Y, rare earth).

In $PrBa_2Cu_3O_{6+x}$ the AFI phase spans from $T_N$ down to a temperature between 10 and 20 K depending on $x$, at which point a second magnetic transition is observed. This low temperature transition was first detected as a rather

broad peak in the specific heat capacity [16,17] and as an anomaly in the magnetic susceptibility and other properties [13,14,18]. These features were identified with magnetic ordering of the Pr sublattice, but it was noted that the ordering temperature $T_{Pr}$ was at least an order of magnitude larger than the ordering temperature of the rare earth sublattice in other isostructural $RBa_2Cu_3O_{6+x}$ compounds.

### 2.2. Neutron diffraction studies

Shortly after the discovery of the low temperature magnetic transition, Li et al. [19] performed neutron diffraction measurements on a polycrystalline sample of $PrBa_2Cu_3O_7$, and found extra scattering intensity below $T_{Pr}\approx 17$ K in the form of two peaks. These peaks were indexed as (1/2, 1/2, 1/2) and (1/2, 1/2, 3/2) and ascribed to antiferromagnetic ordering of the Pr sublattice [20]. The authors proposed the simplest model for the magnetic structure consistent with the relative intensities of the two peaks. In their model the ordered Pr moments lie parallel or antiparallel to the *c*-direction and neighboring moments are oppositely aligned along each crystallographic axis. Assuming this model, the authors calculated the magnitude of the ordered Pr moment to be $\mu_{Pr}=(0.74\pm0.08)\ \mu_B$.

Further progress in refining the low temperature magnetic structure by neutron diffraction was made when single crystals became available. In single crystal diffraction the Bragg peaks are more clearly separated from one another than when polycrystalline samples are used, and an additional advantage is that the signal to background ratio is far superior, even with crystals as small as a few milligram in mass.

To date, three single crystal neutron studies of the Pr ordering phase have been reported [21–23], and I will summarise the salient points from each. Longmore et al. [21] employed single crystals grown in $Al_2O_3$ crucibles, and in consequence found a small amount of Al (approximately 5% of the amount of Cu) incorporated into their crystals. This is thought to be responsible for the presence of the AFII magnetic phase in the crystals used by Longmore et al. and also for the ~5 K reduction of $T_{Pr}$ compared with polycrystalline samples. The AFII phase Bragg peaks first appeared at temperatures of 11 K for an oxidised crystal and 100 K for a reduced crystal. Despite the complications created by the AFII phase, Longmore et al. obtained enough data to enable them to propose a magnetic structure for the Pr ordered phase. Their model differed from that given by Li et al. [19] in the following ways: (i) the ordering wavevector was (1/2, 1/2, 0), i.e. the same as the Cu AFI phase; (ii) the ordered Pr moment was tilted at an angle of (59±3°) to the *c*-axis; (iii) the magnitude of the ordered moment was $\mu_{Pr}=(0.50\pm0.04)\ \mu_B$.

Boothroyd et al. [22] used crystals of higher chemical purity grown in MgO crucibles. Their crystals contained a small amount of Mg and Sr impurities (0.5% and 3% of Cu, respectively), but did not exhibit the AFII phase[1]. $T_{Pr}$ was found to be 19.5 K in oxidised crystals ($x=0.92$), slightly enhanced above the value reported in powder samples most likely due to the Sr impurity which is known to increase $T_{Pr}$ [24]. The ordering wavevector of the magnetic structure for $T<T_{Pr}$ was found to be (1/2, 1/2, 0) in agreement with Longmore et al., but when the diffraction intensities were analysed it became apparent that a change in the Cu spin structure took place in addition to the ordering of the Pr spins. The simplest model that described the data is that shown in Fig. 2 labelled AFIII phase. Accompanying the antiferromagnetic ordering of the Pr sublattice there is an in-plane counter-rotation of the axes of the Cu spins on the antiferromagnetically ordered $CuO_2$ planes either side of the Pr site. This twist leads to a non-collinear Cu spin structure. The ordered Pr moment was found to be $\mu_{Pr}=(0.56\pm0.07)\ \mu_B$ oriented at an angle of 35±20° to the *c*-axis, and the Cu spins were found to have rotated by 30±5°.

The observation that magnetic ordering of the Pr sublattice leads to a change in the magnetic structure of the Cu spins is strong evidence for an unconventional Pr–Cu magnetic coupling. The largest coupling is expected to be the isotropic Heisenberg exchange term $\mathbf{S}_{Pr}\cdot\mathbf{S}_{Cu}$, but this type of coupling is completely frustrated because the Pr site is at a centre of inversion symmetry with respect to the AFI magnetic structure. A symmetry analysis of the possible couplings [25] showed that the AFIII structure is consistent with a coupling of dipolar symmetry, corresponding to off-diagonal terms in the Pr–Cu exchange tensor. As dipole forces are too weak to produce such effects the origin of this coupling must reside in the details of the overlap between the Pr 4*f* and O 2*p* orbitals, and we refer to it as a *pseudodipolar* interaction. Sachidanandam et al. [26] proposed a similar type of coupling to explain the magnetic structure of $Nd_2CuO_4$, and Maleev [27] has

[1]The occurence of the AFII phase in Al-doped crystals but not in Mg/Sr-doped crystals is interesting. The AFI–AFII transition is believed to be caused by the presence of free spins in the chain layer of the $RBa_2Cu_3O_{6+x}$ structure [15] (see Fig. 1). These free spins become polarised by the exchange field from the AF ordered $CuO_2$ planes on either side of the chain layer, causing an effective ferromagnetic coupling which favours the AFII spin configuration. When Al impurities are incorporated onto the Cu(1) sites extra oxygen is attracted around the $Al^{3+}$ ions because its oxidation state is higher than that of the Cu in the chains. This oxygen redistribution breaks up the chains and produces isolated magnetic $Cu^{2+}$ ions ($S=1/2$) which act as the free spins. Divalent non-magnetic impurities, on the other hand, should be able to substitute for Cu(1) without disrupting the chains, and so would not produce free spins. This, together with their relatively low concentration, probably explains why $Mg^{2+}$ impurities do not result in AFII phase formation. In the case of $Sr^{2+}$, the chemical similarity to $Ba^{2+}$ most probably means that Sr substitutes on the Ba site and has little effect on the local environment. Hence, there is no obvious way for Sr to modify the *c*-axis magnetic coupling so as to favour the AFII magnetic arrangement.

confirmed that the non-collinear AFIII structure is energetically consistent with a pseudodipolar interaction.

The third single crystal neutron diffraction study of $PrBa_2Cu_3O_{6+x}$, by Uma et al. [23], employed crystals grown in unreactive $BaZrO_3$ crucibles. Such crystals should be as chemically pure as polycrystalline sintered material. Below $T_{Pr}=17$ K the authors observed, firstly, a transition to a magnetic phase with ordering wavevector (1/2, 1/2, 0), and then between $T_2=11$ and 13 K (the variation being due to hysteresis) a second transition to a structure with ordering vector (1/2, 1/2, 1/2). Evidence for Pr–Cu coupling was again found, but the precision of the data was insufficient to allow a quantitative analysis.

### *2.3. Resonant X-ray magnetic scattering studies*

Neutron diffraction is the technique of choice for finding magnetic ordering wavevectors, for measuring Bragg peak intensities from which the magnetic structures can be deduced, and for determining the absolute size of ordered moments. One problem with neutron diffraction, however, is that the magnetic scattering amplitude depends primarily on the size of the total moment on the ion, and not on which type of atom carries the moment. This makes magnetic structure determination in samples with more than one magnetic ion, such as $PrBa_2Cu_3O_{6+x}$, more difficult. In some cases the magnetic form factor can be used to identify the source of the scattering, but the variations in form factor from ion to ion can be subtle.

One way round this problem is to use resonant X-ray magnetic scattering. X-ray beams from today's powerful synchrotron sources are sufficiently intense that one can now measure routinely the weak magnetic Bragg peaks from magnetically ordered crystals (with the exception of ferromagnets, where the magnetic and charge scattering coincide). More importantly, enhancements in the X-ray scattering are observed when the X-ray energy is tuned close to an atomic absorption edge, and this resonant enhancement enables one to study the magnetic structure of each element in the system independently.

Several X-ray studies have now been performed on $PrBa_2Cu_3O_{6+x}$ [28–30], all of which employed the same crystals as used in Ref. [22]. The resonant enhancement of the X-ray scattering is large for energies tuned to the Pr $L_{II}$ and $L_{III}$ edges, and these resonances have been utilised to study in detail the Pr magnetic ordering behaviour[2]. A much weaker resonance at the Cu K edge has recently been observed and used to explore how the AFI Cu spin structure changes below $T_{Pr}$ due to Pr–Cu coupling [30].

The main results of the X-ray measurements at the Pr L edges on a crystal with $x=0.92$ are as follows: (i) the transition at $T_{Pr}$ was confirmed as a magnetic ordering transition involving the Pr ions; (ii) the second transition at $T_2$ involves a reorientation of the Pr magnetic structure[3]; (iii) for $T_2<T<T_{Pr}$ the magnetic structure is *incommensurate* with an ordering vector $(1/2+\delta, 1/2, 0)$ or $(1/2, 1/2+\delta, 0)$[4] with $\delta\approx0.007$, corresponding to a very long range modulation with a period ~600 Å, whereas when $T<T_2$ the Pr spins form a *commensurate* antiferromagnetic structure with an ordering vector (1/2, 1/2, 1/2), as observed by Li et al. [19] and Uma et al. [23].

To illustrate the scattering from the incommensurate magnetic order Fig. 3(a) shows a contour plot of the intensity measured at $T=12$ K in the ($h$, $k$, 9) plane in reciprocal space centred on the (1/2, 1/2, 9) antiferromagnetic position. Fig. 3(b) shows a linear scan parallel to $h$ through the centre of two of the satellites. From the width of the peaks we calculate that the correlation length for the incommensurate order is at least 1000 Å. The satellites were subsequently resolved in high resolution neutron diffraction measurements, both in fully-doped [28] and oxygen-deficient crystals, showing that the incommensurate ordering is a property of the bulk of the crystal.

The observation of incommensurate Pr magnetic ordering was unexpected, and it raises the question as to whether there is incommensurability in the Cu magnetism. This is important because incommensurate magnetic ordering of the Cu spins has been found in other layered cuprates, such as Nd-doped $La_{2-x}Sr_xCuO_4$ [31], where it is caused by the pinning of spin-charge stripe correlations and is associated with the anomalous absence of superconductivity.

To answer this question the resonant X-ray magnetic scattering technique was used once again [30], this time with the X-ray energy tuned in the vicinity of the Cu K edge in order to utilise the resonant enhancement of the magnetic scattering from the Cu sublattice. The low spin of $Cu^{2+}$ ($S=1/2$) and the small K edge enhancement (a factor 2–3 over the non-resonant scattering) makes the scattering from the Cu ordering much more difficult to observe than that from the Pr sublattice. In fact, the data reported in Ref. [30] represent the first observation of X-ray magnetic scattering from magnetically ordered Cu spins.

Measurements made at $T>T_{Pr}$ confirmed the AFI

[2] Indeed, the observation of resonant magnetic X-ray scattering at the Pr L edges at temperatures below $T_{Pr}$ proved conclusively that there was a substantial ordered moment on the Pr ion, a premise that had been challenged by K. Nehrke, M.W. Pieper, Phys. Rev. Lett. 76 (1996) 1936.

[3] Rather surprisingly, the reorientation transition at $T_2$ was observed in the X-ray experiments but not in neutron measurements on the same crystal! This means that the reorientation occurs only in the near surface layer of the crystal (depth ~1 μm), presumably due to variations in the chemical composition with depth. The reorientation behaviour observed with X-rays is very similar to that observed by Uma et al. [23] using neutron scattering from crystals of high purity, and this suggests that the features measured in the X-ray experiments, including the incommensurate phase, are intrinsic properties of $PrBa_2Cu_3O_{6+x}$.

[4] It is not possible to say along which direction ($a$ or $b$) the modulation runs because of structural and/or magnetic twinning.

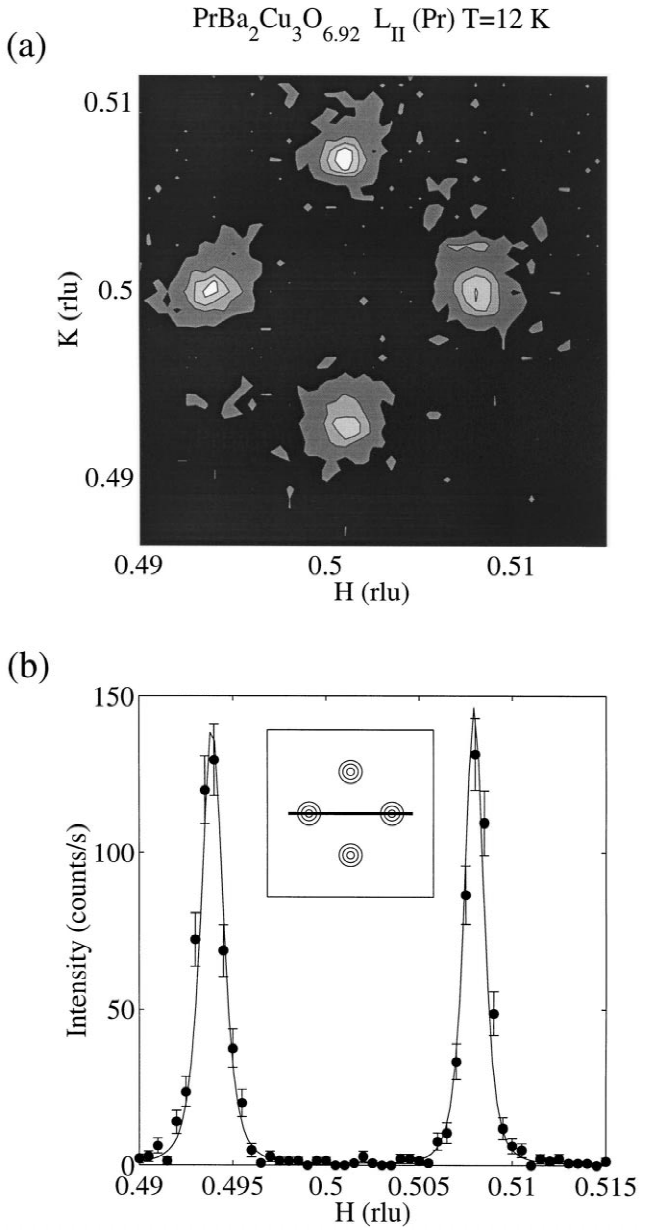


Fig. 3. Resonant X-ray magnetic scattering from $PrBa_2Cu_3O_{6.92}$ measured with the X-ray energy tuned to the Pr $L_{II}$ dipole resonance. (a) Contour plot of the intensities measured in the ($h$, $k$, 9) plane in the neighbourhood of the (0.5, 0.5, 9) antiferromagnetic point in reciprocal space showing the incommensurate satellites in the AFIII(i) phase. (b) Cut through the satellites at ($0.5\pm\delta$, 0.5, 9), $\delta=0.007$. The scan direction is shown in the inset. The data were collected on the ID20 instrument at the European Synchrotron Radiation Facility (ESRF).

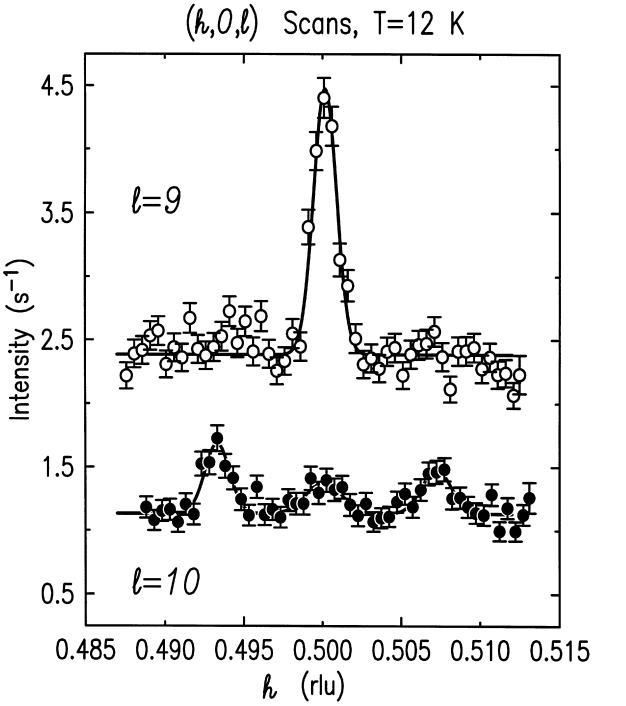


Fig. 4. X-ray magnetic scattering from $PrBa_2Cu_3O_{6.92}$ with the X-ray energy tuned to the Cu K resonance (8.979 keV). The upper and lower data were obtained from $h$ scans through the (1/2, 1/2, 9) and (1/2, 1/2, 10) positions, respectively, at $T=12$ K. The two scans have been displaced for clarity. The $l=9$ and 10 positions are close to the maximum and minimum, respectively, of the antiferromagnetically coupled bilayer structure factor shown in Fig. 5. The data were collected on the ID20 instrument at the ESRF.

magnetic structure of the Cu spins and established that this ordering is commensurate in $PrBa_2Cu_3O_{6.92}$. On lowering the temperature below $T_{Pr}$, however, a decrease in the intensities of the Cu magnetic Bragg peaks at the commensurate positions was observed (by a factor ~2), and incommensurate peaks appeared near to certain antiferromagnetic positions. Fig. 4 shows $h$ scans through the (1/2, 1/2, 9) and (1/2, 1/2, 10) positions at $T=12$ K. The $l=9$ scan shows only a commensurate peak, whereas at $l=10$ there is a small commensurate peak flanked by incommensurate satellites displaced from (1/2, 1/2, 10) by ($\pm\delta$, 0, 0) with $\delta=0.007$, the same modulation vector as observed in the Pr ordering.

The significance of the $l$ dependence is as follows. As mentioned in Section 2.1, the existence of two antiferromagnetically coupled $CuO_2$ planes in the unit cell causes the intensities of the Bragg peaks from the Cu spin ordering in the AFI phase to vary with a factor $\sin^2(\pi lz)$, where $z$ is the intra-bilayer separation as a fraction of the unit cell ($z=0.30$ for $PrBa_2Cu_3O_{6+x}$). Measurements at temperatures above $T_{Pr}$ exhibit this modulation, as shown in Fig. 5. For a ferromagnetically coupled bilayer the variation would be $\cos^2(\pi lz)$, as indicated by the broken line on Fig. 5. Thus, a reduction in intensity of the (1/2, 1/2, 9) peak and corresponding increase at (1/2, 1/2, 10), as observed for $T<T_{Pr}$, implies a reduction in the Cu spin component stacked antiferromagnetically along the $c$-axis, and the development of a ferromagnetically coupled component. This change in stacking is consistent with the twisting of the Cu spin axes that takes place when the AFI structure transforms into the AFIII structure, as may be seen from Fig. 2.

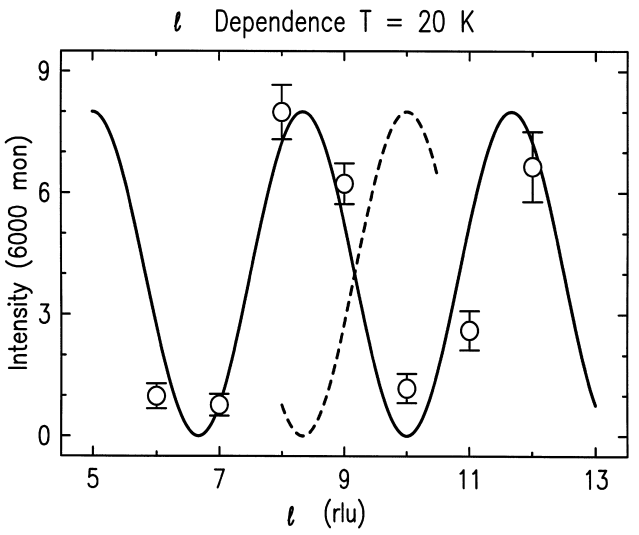


Fig. 5. Integrated intensities of several (1/2, 1/2, $l$) peaks measured from $PrBa_2Cu_3O_{6.92}$ by X-ray magnetic scattering at the Cu K resonance. The peaks were measured at a temperature of 20 K corresponding to AFI ordering of the Cu spins. The full line shows the $\sin^2(\pi lz)$ variation in the structure factor for an antiferromagnetically coupled bilayer ($z=0.30$ for $PrBa_2Cu_3O_{6.92}$). The broken line is part of the corresponding $\cos^2(\pi lz)$ variation for a ferromagnetically coupled bilayer. The data were collected on the ID20 instrument at the ESRF.

### *2.4. A model for the magnetic structures of $PrBa_2Cu_3O_{6+x}$ for $T<T_{Pr}$*

The most important feature revealed by these studies is the existence of Pr–Cu magnetic coupling of pseudo-dipolar symmetry that is strong enough to cause a substantial change in the Cu spin structure below $T_{Pr}$. An ability to account for this coupling would be an important property of any model of the electronic structure of $PrBa_2Cu_3O_{6+x}$. It is interesting to note that the twisting movement performed by the Cu spins in the AFI–AFIII transition is the same as the motion of the Cu spins in the bilayer optic spin wave [32], both of which depend upon the exchange energy $J_\perp$ between Cu spins along the $c$-axis. It is possible, therefore, that the optic spin wave will be found at a different energy in $PrBa_2Cu_3O_{6+x}$ than in $YBa_2Cu_3O_{6+x}$, and if so this could reflect important differences in the electronic structure of these compounds.

Although the AFIII arrangement shown in Fig. 2 describes the local magnetic structure at $T<T_{Pr}$ it does not represent the incommensurate nature of the magnetic order found in the range $T_2<T<T_{Pr}$. Defining the $x$-axis as the direction of the Cu spins when $T>T_{Pr}$, the simplest model for this phase is one in which the Pr moments rotate in the $x-z$ plane with wavevector $0.5+\delta$ either along $x$ (to form a cycloid) or $y$ (to form a spiral). At the same time, the Cu spins oscillate harmonically in the $x-y$ plane about the $x$-direction with the same wavevector as the spiral.

Finally, the reorientation at $T_2$ to a new antiferromagnetic structure with a doubling of the unit magnetic unit cell in the $c$-direction can be understood to originate from the non-collinearity of the AFIII local arrangement. I will call the two observed Pr magnetic structures AFIII(i) and AFIII(ii), corresponding to $T_2<T<T_{Pr}$ and $T<T_2$, respectively. These structures are represented in Fig. 6. Both have the same non-collinear arrangement of Pr and Cu spins within a bilayer, but differ in the orientation of spins in adjacent bilayers. In AFIII(i) the sense of the in-plane rotation angle $\phi_{Cu}$ of the Cu spins follows the sequence (−, +) (−, +) (−, +) etc. in the $c$-direction. This means that adjacent Cu spins in neighbouring bilayers are at an angle of $2\phi_{Cu}$ to one another and adjacent Pr spins in the $c$-direction are parallel to one another. One would expect, however, the superexchange interaction along the $c$-axis to favour a collinear, antiparallel alignment of adjacent spins along the $c$-axis, and this is precisely what is found in the AFIII(ii) magnetic structure. The transition to AFIII(ii) involves a doubling of the magnetic unit cell along $c$ such that adjacent Pr spins become antiparallel. $\phi_{Cu}$ now follows the sequence (−, +) (+, −) (−, +) etc., and so the Cu spins in adjacent bilayers are also antiparallel (the non-collinearity *within* the bilayer remains due to the Pr–Cu coupling). The absence of any incommensurate modulation in AFIII(ii)

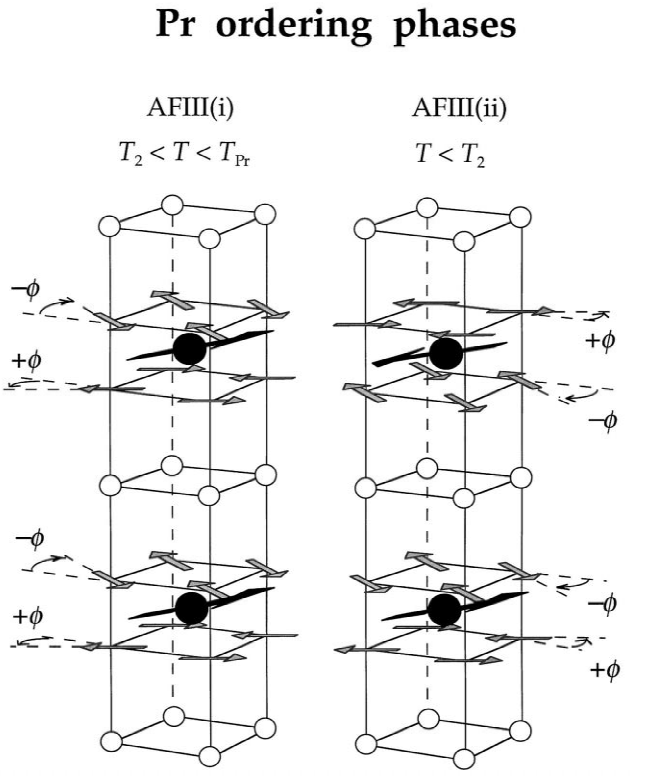


Fig. 6. Illustration of the two magnetic structures observed in $PrBa_2Cu_3O_{6+x}$ at temperatures below $T_{Pr}$. The principal difference is in the propagation of the ordering along the $c$-axis, the AFIII(ii) structure having twice the periodicity of the AFIII(i) structure. In addition, the AFIII(i) structure has an incommensurate modulation (not shown) along $x$ or $y$.

Table 1
Summary of the magnetically ordered phases of $PrBa_2Cu_3O_{6+x}$ based on neutron and magnetic X-ray scattering experiments. Most data have been obtained with oxygen-doped crystals ($x\approx1$) for which $T_N=265$–$285$ K, $T_{Pr}=17$–$19$ K and $T_2=9$–$13$ K (when present). The ordering wavevector is given for each ordered spin component. The letters *F* and *A* against a particular component of the Cu spins indicates ferro- or antiferromagnetic alignment on adjacent planes of the bilayer. The direction of the Cu spins in the AFI phase is arbitrarily chosen to be *x*

| | Magnetic phase | | |
|---|---|---|---|
| | AFI | AFIII(i) | AFIII(ii) |
| Temperature range | $T_{Pr}<T<T_N$ | $T_2<T<T_{Pr}$ | $T<T_2$ |
| Modulation wavevector | Cu($x$) (1/2, 1/2, 0) *A* | Cu($x$) (1/2, 1/2, 0)[a] *A*<br>Cu($y$) (1/2+$\delta$, 1/2, 0)[b] *F*<br>Pr($x$, $z$) (1/2+$\delta$, 1/2, 0)[b] | Cu($x$) (1/2, 1/2, 0) *A*<br>Cu($y$) (1/2,1/2,1/2) *F*<br>Pr($x$, $z$) (1/2, 1/2, 1/2) |
| Ordered moment ($\mu_B$)[c] | $\mu_{Cu}\approx0.58$ | $\mu_{Cu}\approx0.58$<br>$\mu_{Pr}\approx0.56$ | No data available |

[a] The Cu spins oscillate back and forth about their equilibrium direction (the *x*-axis) in the direction of the modulation wavevector, with the spins constrained to the *xy* plane. In effect, the *x* components of the Cu spins are longitudinally modulated, and so in addition to peaks at the commensurate antiferromagnetic position (1/2, 1/2, 0) there should also be very weak sidebands displaced from the main peak by ($\pm\delta$, 0, 0). The X-ray data is not of sufficient quality to check for the existence of these sidebands (see Fig. 4 $l=9$ scan).

[b] $\delta\approx0.007$ and is weakly temperature dependent [29]. Because of twinning it is not known whether the modulation wavevector is (1/2+$\delta$, 1/2, 0) or (1/2, 1/2+$\delta$, 0).

[c] From Ref. [22] for a crystal with oxygen content $x=0.92$.

suggests that the incommensurability in AFIII(i) is associated with frustration inherent in the non-collinearity of the magnetic structure.

A summary of the principal features of the magnetically ordered phases of $PrBa_2Cu_3O_{6+x}$ is given in Table 1.

## 3. Magnetic excitations in $PrBa_2Cu_3O_{6+x}$

Now that a detailed picture of the static magnetic ordering properties of $PrBa_2Cu_3O_{6+x}$ has been obtained it is natural to proceed to a study of the excitations. Experimental measurements of the dispersion of the various excitation modes are essential for a quantitative understanding of all the magnetic couplings. Data with the required energy and wavevector sensitivity can only be obtained by inelastic scattering of neutrons.

Naively, the magnetic excitations can be divided into two categories, (1) local excitations of the Pr 4*f* electrons under the influence of the crystal electric field, and (2) highly dispersive, propagating antiferromagnetic spin excitations of the Cu sublattice. An additional complication, however, is the effect of the Pr–Cu coupling discussed above which very likely modifies this simple picture, especially at low energies.

Until recently, the only data available on the excitations in $PrBa_2Cu_3O_{6+x}$ was from polycrystalline samples [33–36]. These studies revealed a series of broadened crystal field transitions of the Pr ions which have been analysed in terms of models for the crystal field acting on $Pr^{3+}$ ions. In the absence of exchange (molecular) fields these models predict a quasitriplet ground state for the Pr ion. Measurements on single crystals are now needed to examine the dispersion and broadening of the Pr magnetic excitations, and to see whether the highly dispersive Cu spin excitations differ in $PrBa_2Cu_3O_{6+x}$ relative to $YBa_2Cu_3O_{6+x}$.

Experiments on single crystals have recently begun, and data are now available on the low energy excitations in oxygen deficient $PrBa_2Cu_3O_{6+x}$ [37]. Fig. 7(a) and (b) show representative energy scans measured at two different positions in reciprocal space at a temperature of 2 K. Peaks are observed centred at energies of 1.7 and 3.8 meV. These two peaks are also present in the energy spectrum measured on polycrystalline samples [33–36], and so can readily be identified with magnetic excitations within the quasitriplet ground state of the Pr ions.

The intensities of the two peaks are found to vary considerably with direction in reciprocal space. In Fig. 7(a), for example, the neutron scattering vector **Q** is in the *ab* plane and the 1.7 meV peak is much stronger than the 3.8 meV peak, whereas in Fig. 7(b) **Q** is parallel to the *c*-axis, the 1.7 meV peak is considerably reduced in intensity and the 3.8 meV peak is larger. This wavevector variation is found to be consistent with the symmetry of the transition matrix elements calculated from the crystal field wavefunctions.

In tetragonal symmetry the crystal field splits the quasitriplet into a doublet ground state and a singlet excited state. The observation of two transitions at low temperatures suggests that Cu–Pr and Pr–Pr exchange interactions split the doublet. The Pr–Pr coupling should give rise to dispersion of the excitations at temperatures below $T_{Pr}$, and measurements of the low energy peak confirm this expectation. Fig. 8(a) and (b) show how the peak energy varies along the (1, 0, 0) and (1, 1, 0) directions in reciprocal space, respectively. The difference between the maximum and minimum energies is approximately 0.5 meV for directions in the *ab* plane, but the dispersion in the *c*-direction was too small to measure.

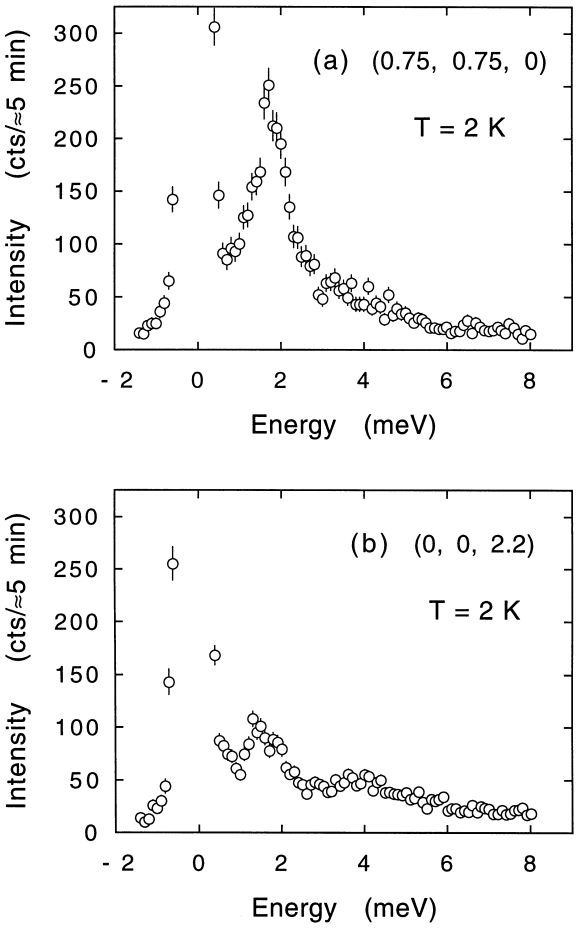


Fig. 7. Neutron energy scans measured on a single crystal of $PrBa_2Cu_3O_{6+x}$ ($x \approx 0.2$) at scattering vectors of (a) (0.75, 0.75, 0), and (b) (0, 0, 2.2). Both data sets were collected at a temperature of 2 K. The peaks centred at 1.7 and 3.8 meV are essentially single-ion magnetic excitations of the Pr ions influenced by Pr–Pr and Pr–Cu magnetic coupling. The measurements were made on the RITA spectrometer at Risø.

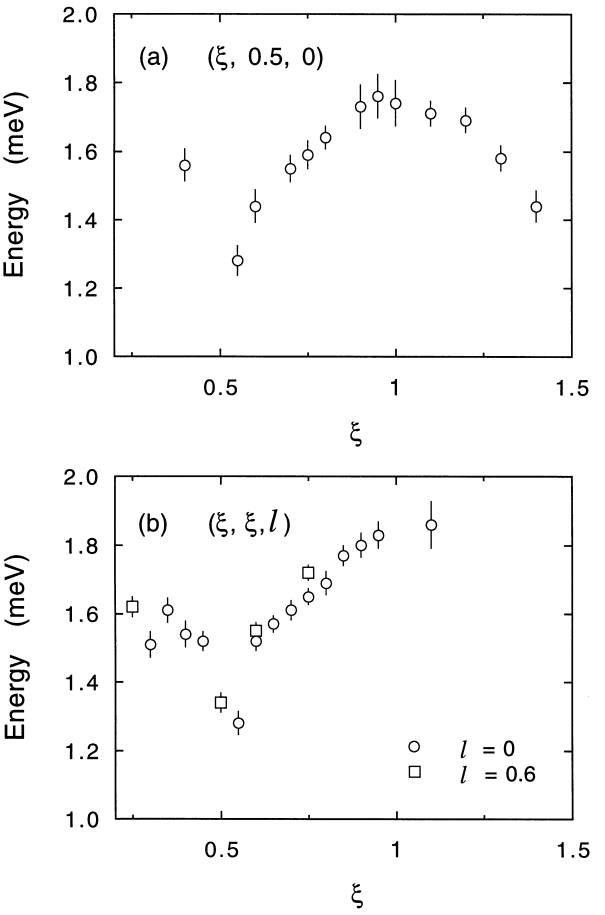


Fig. 8. Dispersion of the low energy peak shown in Fig. 7 along the (a) (1, 0, 0), and (b) (1, 1, 0) directions in the *ab* plane. In (b), data from two different scattering planes ($l=0$ and $l=0.6$) are shown The measurements were made on the RITA spectrometer at Risø.

It is notable that the minimum in the dispersion curve at the antiferromagnetic zone centre (1/2, 1/2, 0) is particularly sharp. At this wavevector there is a crossing between highly dispersive (in the *ab* plane) Cu spin wave excitations and the rather flat Pr excitation branch. Because of the Pr–Cu coupling the magnetic excitations are expected to be of mixed Pr/Cu character in the vicinity of (1/2, 1/2, 0), and this is most likely why the energy drops abruptly here. A spin wave model for the coupled Pr and Cu magnetic sublattices is currently under development [38].

## 4. Outlook

A great deal is now known about the magnetic ordering in $PrBa_2Cu_3O_{6+x}$, but a number of questions remain unanswered: (1) What is the specific interaction that causes the AFIII(i) phase to be incommensurate? (2) Several measurements have obtained the signature for a magnetic transition at $T \approx 5$ K [18,20]. What is the nature of this transition? (3) There is evidence for a field-induced transition in the Pr ordering phase [39]. What is the nature of this transition ? (4) Under applied pressures up to 18 kbar it is found that both $T_{Pr}$ and $T_N$ increase [37]. Why is this, and what happens at higher pressures? In addition to these questions the effects on the Pr magnetic order of chemical impurities in the samples needs to be clarified, and a related issue is the role, if any, played by the occurence of a small amount of Pr on the Ba site.

Studies of the magnetic excitations are less advanced than the magnetic ordering, and I would anticipate that there will soon be considerably more data characterising the excitations in single crystals over the full range of oxygen content. This data will enable us to determine the exchange interactions both within and between the Cu and Pr sublattices. It will be interesting to compare the results with what is observed in $YBa_2Cu_3O_{6+x}$, to see if the introduction of Pr has any effect on the Cu–Cu coupling, and if so, whether it can be traced to changes in the electronic structure on the $CuO_2$ planes. It is also im-

portant to study the changes that take place with hole doping. These should tell us about the dynamics of the holes, and perhaps lead us to the ultimate goal, an explanation for why these doped holes do not superconduct.

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