Pr Magnetic Order and Spin Dynamics in the Cuprates

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Magnetic neutron scattering measurements are reviewed for $PrBa_2Cu_3O_{6+x}$ and compared to related materials that contain Pr. In these materials the magnetic rare earth ordering temperatures are typically an order-of-magnitude higher than for the other rare earths, indicating that exchange interactions dominate the energetics of the magnetic system. For the spin dynamics in Pr123, the strong *f*-electron hybridization produces non-Fermi liquid-like scattering, which appears to destroy any chance for superconductivity. This behavior contrasts strongly with the sharp crystal field excitations found for the heavy rare earths, as well as with the sharp levels found in other Pr systems.

I. Introduction

The magnetic ordering of the rare earth ions in superconducting systems has been a topic of active interest for many years [1]. In the conventional "magnetic superconductors" such as RMo_6S_8 (R = rare earth ion) the rare earth moments are coupled very weakly both to the metallic electrons and to each other via comparable dipolar and (weak) exchange interactions, resulting in very low ($\sim 1K$) magnetic ordering temperatures and a delicate energetic balance with superconductivity. A similar situation occurs for most of the cuprate superconductors in that the development of long range rare earth magnetic order also occurs at very low temperatures [2]. In contrast to the earlier systems, though, the superconductivity in the cuprates typically occurs at much higher temperatures, and the antiferromagnetic order that develops on the rare earth sublattice coexists with the superconducting state. These materials are of further interest because many exhibit low-dimensional magnetic behavior [3, 4], and the properties of these rare earth/superconductor systems have already been reviewed in some detail. However, from the very early days of cuprate superconductors it was known that a dramatic exception occurs for Pr, which has been the subject of extensive research. The magnetic ordering temperatures are an order-of-magnitude higher for Pr than for the other rare earth materials, and consequently the magnetic coupling is unquestionably dominated by exchange rather than dipole interactions [5]. Moreover, with the exception of

Pr_2CuO_4 where the crystal field ground state is an isolated singlet [6], the Pr materials are not superconducting at all. The origins of this suppression and the nature of the Pr magnetism are still under active investigation and debate, and here we review our neutron studies of the magnetic properties of the $PrBa_2Cu_3 O_{6+x}$ (*Pr123*) and compare the results with related systems that contain Pr.

II. Magnetic order overview

For the general case of the *R123* (*R*=rare earth) layered cuprates there are three types of magnetic sites, two associated with the Cu and one with the rare earth, as shown in Fig. 1. 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 referred to as the Cu plane layers. The second type of Cu layer contains oxygen ions only along one (*b*) axis and is then referred to as the Cu chain layer, and these oxygen ions can be removed by suitable heat treatment. With an oxygen-depleted chain layer ($x = 0$) the system is an antiferromagnetic insulator with the Cu plane layers developing long range magnetic order for temperatures as high as ~ 525 K. The spins lie within the *a-b* plane and are always coupled antiferromagnetically in this plane. With appropriate doping either directly on the chain site, or on the Ba site, the chain spins can also develop an ordered moment. Adding oxygen has the effect of doping the plane layers with holes, and this causes the Néel temperature to drop to zero at $x \sim 0.4$. Further addition of oxygen renders the system superconducting, with T_c exceeding 90 K
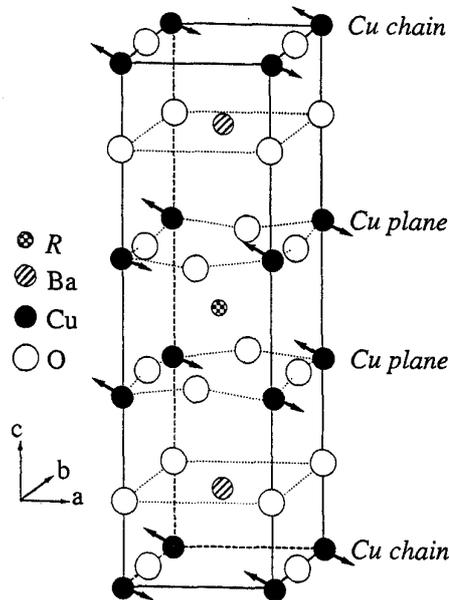

FIG. 1. Crystal structure for $RBa_2Cu_3O_{6+\delta}$. The CuO_2 plane layers order antiferromagnetically at small δ, where δ is the oxygen occupancy in the Cu chain layer. The spin direction is in the *a-b* plane, and structure is always antiferromagnetic in this plane. The rare earth ion is in the body-centered position, between the two Cu plane layers.

for $x \to 1$. The single rare earth ion in the chemical unit cell, on the other hand, sits in the bodied-centered position between the two Cu plane layers. The rare earth nearest neighbors are then a distance a away, and without direct bonding orbitals the magnetic interactions are very weak. Along the c-axis the nearest neighbor distance is three times longer so that the magnetic interactions are much weaker still, and this crystallographic anisotropy renders many of these rare earth subsystems two-dimensional in behavior.

For $PrBa_2Cu_3O_{6+x}$ a quite different behavior is found [7]. The material is a semiconductor for the full range of x, with the Cu ions retaining their high magnetic ordering temperature. This anomalous behavior originates from f-electron hybridization, which is strong enough in Pr (compared to the other rare earths) to completely disrupt the Cooper pairing of the electrons on the Cu plane layers. This hybridization has been observed directly by inelastic neutron scattering experiments, which have found that there are substantial linewidths to the crystal field excitations of the Pr [8-11]. This has the effect of dramatically increasing the exchange interactions, thereby increasing the ordering temperature by an order of magnitude and rendering the rare earth ordering three dimensional.

The first neutron diffraction experiments to investigate the Pr magnetic order were carried out on fully oxygenated polycrystalline $PrBa_2Cu_3O_7$ [12]. A simple magnetic ordering developed below $T_N = 17$ K, with antiferromagnetic coupling between nearest neighbors Pr moments in all three directions in the crystal. The observed ordering temperature was in good agreement with specific heat and susceptibility results, which have elucidated the systematics of this ordering by following it as a function of oxygen concentration and as a function of Y (and other rare earths) substitution on the Pr site [7, 13]. Bulk measurements show that as oxygen is removed T_N(Pr) monotonically decreases to 12 K for $PrBa_2Cu_3O_6$, and this has been confirmed by neutron diffraction measurements on the depleted system [14]. Replacing Pr with non-magnetic Y has the expected behavior that T_N(Pr) decreases (towards zero), while superconductivity appears above 40% replacement and monotonically increases as the pure Y composition is approached.

Studies have also been carried out to observe the effects on both the Cu and Pr order by chemical substitution on other sites in the Pr*123* system. Zn is found to substitute on the Cu planes, and this has no effect on either the Pr ordering temperature or size of the ordered moment [15], but it does change the coupling along the c-axis from antiferromagnetic to ferromagnetic. Ga, on the other hand, substitutes preferentially on the Cu chain sites. This also changes the magnetic structure along the c-axis from antiferromagnetic to ferromagnetic, but in addition T_N is reduced [16] while the ordered moment remains unchanged. Neither of these substitutions has any significant effect on the Cu Bragg peaks in the temperature regime where the Pr orders. Another type of substitution can occur for the "pure" $PrBa_2Cu_3O_{6+\delta}$, where the Pr can substitute on the Ba site forming $Pr_{1+x}Ba_{2-x}Cu_3O_{6+\delta}$. This has the effect of reducing the Pr ordering temperature [17].

Investigations on single crystals of the "pure" $PrBa_2Cu_3O_{6+x}$ (*Pr123*) have been carried out subsequently, but the results have been complicated because of contamination of the samples from the crucible, and/or Pr substitution on the Ba site. In particular, it is now known that crystals grown in alumina or MgO crucibles by the flux technique become doped by Al or Mg [18]. These (inadvertent) dopings can cause the Cu chain spins to order [19-22]. This ordering varies with oxygen content x, and is strongly coupled to the Pr sublattice because the symmetry of the two magnetic structures is the same. The chain doping can also reduce the Néel temperature for the Pr ordering, and change the nature of the Pr structure along the c-axis direction [23, 24] so that the

usual c-axis antiferromagnetic coupling is not found in these samples. During the course of these investigations there was also a suggestion from NMR measurements [25] that the Pr was actually non-magnetic in pure *Pr123*, but a reinvestigation with neutrons [26] on pure powders indicated that the Pr was indeed ordering, and Pr ordering has recently been confirmed by resonant x-ray scattering measurements [27]. It therefore appears likely that the NMR may have been detecting some Pr on the Ba site in that sample, which may well be in a nonmagnetic singlet crystal field state, while the line due to Pr on the R site is too broad to observe.

The relatively recent development of non-reactive $BaZrO_3$ crucibles has now permitted the growth and investigation of undoped single crystals. In a fully oxygenated single crystal the Cu spins order at 281 K, while the Pr moments order at 16.8 K as in Fig. 2 [28]. The initial ordering is revealed by the intensity of the $(\frac{1}{2}, \frac{1}{2}, 0)$ Bragg peak versus T shown in the center. This structure corresponds to antiferromagnetic alignment of spins in the a-b plane, while the spins along the c direction are ferromagnetically aligned. The development of the ordered Pr moment is accompanied by a modest coupling to the Cu spins as indicated by the intensity of the $(\frac{1}{2}, \frac{1}{2}, 2)$ Cu peak (top). At ~ 11 K (on cooling) a first-order "spin-flop" transition occurs to a Pr spin structure where the nearest-neighbor Pr moments along the c-axis flip, to become antiparallel rather than parallel. This corresponds to the development of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ type peak as indicated in the bottom of the figure. The data clearly indicate that there is strong hysteresis in both types of Pr magnetic peaks, and the behavior is in good agreement with the specific heat and thermal expansion data taken on warming and cooling. The results on this pure single crystal are in general agreement
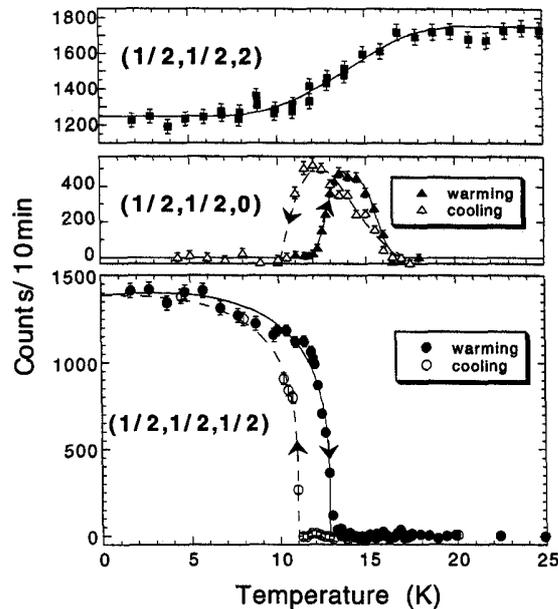

FIG. 2.   Temperature dependence of the $(\frac{1}{2}, \frac{1}{2}, 2)$ magnetic Bragg peak (top) associated with the Cu-plane spins ($T_N = 281$ K), and the $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ associated with the Pr magnetic order (from Uma, *et al.* [28]).

with the data obtained on polycrystalline samples (where crucible contamination is not a concern), but the details with regard to the crossover from ferromagnetic to antiferromagnetic nearest-neighbor alignment along the c-axis are different. These differences may be due to the very delicate balance of interactions along the c-axis, to their subtle dependence on factors such as small concentrations of defects and impurities, oxygen content, strain, etc.

There has been considerable additional work investigating the magnetic ordering of the Pr in the cuprate class of materials, and the properties for Pr systems investigated with neutrons have been reviewed recently elsewhere [5]. $PrBa_2Cu_4O_8$ also orders antiferromagnetically at $T_N \sim 17$ K like the *Pr123* material, with an analogous magnetic structure [29]. For $PrBa_2Cu_2NbO_8$ [30] the Cu chain layer is replaced with a (fully oxygenated) NbO_2 layer, which of course carries no moment. This eliminates the complication of the chain magnetism, and we still find a high ordering temperature for the Pr and no influence on the Cu plane ordering when the Pr subsystem orders. A similar situation occurs for the $TlBa_{2-y}Sr_yPrCu_2O_7$ [31, 32] where the CuO chains are replaced by TlO. There is no observable interaction between the Cu and Pr order, as would be expected since the magnetic structures have different symmetries. Similar behavior is observed for the more complicated $Pr_{1.5}Ce_{0.5}Sr_2Cu_2(Nb,Ta)O_{10}$ [33] system. Again there can be no Cu chain magnetism, and there is a high observed T_N for the Pr. The $Pb_2Sr_2PrCu_3O_8$ material [34, 35] is somewhat different in that it has no oxygen in the Cu chain layer, while the properties of the Pr are quite similar to the other systems. Finally, we note that the related $BaPrO_3$ material, which obviously has no complications of Cu ordering of any kind, exhibits a similar Pr ordering temperature and reduced moment [36] as for the cuprates. Thus in all the layered cuprates Pr carries a moment and orders magnetically at much higher temperatures than the heavy rare earths.

III. Single crystal Pr spin dynamics

Inelastic neutron scattering measurements have been carried out for polycrystalline samples to explore the Pr crystal field excitations in $PrBa_2Cu_3O_{6+x}$. In contrast to the heavy rare earth *123* systems, the crystal field levels for *Pr123* were observed to have large linewidths [8-12]. In particular, at low energies we found a distribution of quasielastic scattering with a width of ~ 5 meV [8]. The strength of this scattering followed the expected magnetic form factor for Pr, which demonstrated that this magnetic scattering originated from the Pr.

A natural interpretation for this scattering is that it is an intrinsic linewidth caused by the hybridization of the *4f* electrons. Such a hybridization would explain the disruption of the Cooper pairing and consequent lack of superconductivity, and would also explain the relatively large rare earth exchange interactions and high Néel temperature. An alternative explanation, however, is that the observed widths are due to exchange interactions, which would then appear as broadened levels due to the powder average of the inelastic scattering. In the related Pr_2CuO_4 cuprate, for example, the Pr ions are in a singlet ground state that is well separated in energy (~ 18 meV) from the first excited state. However, substantial dispersion of the excited state crystal field level at 18 meV is observed, of the order of several meV, which directly demonstrates that there is a significant exchange interaction in Pr_2CuO_4 [6]. The exchange is too small to mix much of a moment from the high-lying crystal field levels into the ground state, and thus there is only a small ordered moment on the Pr which is induced by the Cu order; the Pr moments do not order independently. For the *Pr123* system, on the other hand, there are a number of low-lying crystal field levels within a few meV of the ground state. The Pr moments of course order magnetically

at a relatively high ordering temperature, and the combination of the low energy crystal fields and the larger exchange interactions facilitates a strong mixing of these levels with the ground state to produce a substantial ordered moment.

In order to explore the question of the origin of the observed linewidths, a single crystal large enough for inelastic scattering measurements is required. The single crystals used in the present study were grown from an over stoichiometric mixture of crystal-forming oxides. A seeded growth technique with a positive temperature gradient was used, in a ZrO_2:Y crucible to avoid contamination onto the chain site. A high quality single crystal weighing 2.5 grams was employed for the initial measurements, and the oxygen content was left as-grown. However, we found that substantial Y leached out of the crucible, and was incorporated into the sample, substituting onto the Pr site. The nominal composition as determined by chemical means is $Pr_{0.85}Y_{0.15}Ba_2Cu_3O_{6+x}$. For the purposes of investigating the Pr magnetic excitations, however, the alloying of the Y is expected only to lower the magnetic ordering temperature, and not to have any qualitative effect on the spin dynamics of the system. Once it was established that there was no observable dispersion of the magnetic excitations, two additional crystals were added to increase the mass to about 5 grams. These crystals were aligned within $\pm 4^{\pm}$.

The magnetic phase transition for the Cu spins is above room temperature, and no half-integral peaks associated with the Cu ordering were observed at any temperature. Fig. 3 shows the $(\frac{1}{2}, \frac{1}{2}, 0)$ magnetic Bragg peak as a function of temperature, which is directly related to the magnetic order parameter for the Pr. A very well defined antiferromagnetic phase transition is observed at $T_N = 10.97(6)$ K. The sharpness of the transition demonstrates that the oxygen and Y distributions are quite homogeneous. No $l = half - integral$ Bragg peaks are observed for this sample, and this may indicate that the c-axis coupling depends on the Y concentration; the fully antiferromagnetic configuration is only observed in (uncontaminated) polycrystalline samples [12, 26] and high-quality (undoped) single crystals [28].
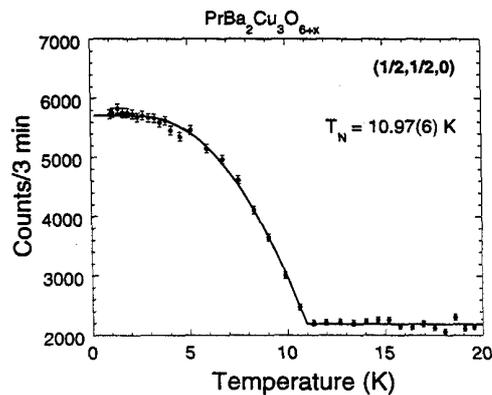

FIG. 3. Temperature dependence of the $(\frac{1}{2}, \frac{1}{2}, 0)$ magnetic Bragg for the large single crystal of $Pr_{0.85}Y_{0.15}Ba_2Cu_3O_{6+x}$. The well defined Pr ordering occurs at $\sim 10.97(6)$ K. The solid curve is a fit to a mean-field order parameter to provide a guide to the eye.
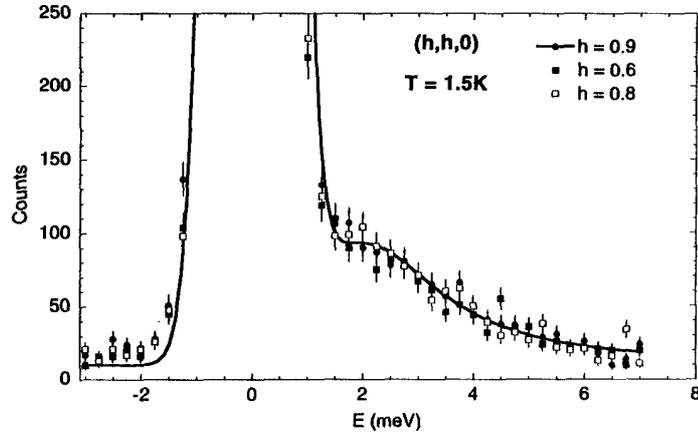
FIG. 4. Magnetic inelastic scattering of the Pr in $Pr_{0.85}Y_{0.15}Ba_2Cu_3O_{6+x}$ observed at 1.5 K. The broad distribution of scattering is independent of wave vector, demonstrating that the scattering is intrinsically broad in energy, rather than dispersive.

We now turn to measurements of the low energy inelastic scattering. In the polycrystalline sample a quasielastic spectrum was observed [8], and the results for the single crystal are shown in Fig. 4 for a series of wave vectors **q** in the *a-b* plane. The same broad distribution of **q**-independent scattering is found in the energy range 0-7 meV. This directly demonstrates that the scattering is intrinsically broad rather than dispersive. This behavior contrasts with the low energy crystal field level observed in $PrBa_2Cu_4O_8$, for example, where a relatively sharp crystal field transition is observed that exhibits a conventional temperature dependence for a crystal field level [37]. Similar behavior to that shown in Fig. 4 is also observed for the *Pr123* scattering along the *c*-axis, although this is not unexpected since the interactions are very weak in this direction. Hence for Er in the $ErBa_2Cu_3O_7$ system, there is a small but measurable dispersion in the *a-b* plane, but none along the *c*-axis [38].

Finally, we note that preliminary measurements as a function of temperature indicate that the scattering on the energy-loss (E>0) side is independent of temperature to a good approximation. The only temperature dependence is then an increase in the scattering on the energy gain side, as dictated by detailed balance. This behavior is similar to that observed in the $UCu_{5-x}Pd_x$ system, where it was attributed to non-Fermi-liquid behavior [39, 40].

IV. Discussion

The present crystals have a semiconducting behavior, as has been found in the overwhelming majority of *Pr123* samples. In particular, no superconductivity has been observed, in contrast to the recent report by Zou, *et al.* [41] However, it has been shown that the susceptibility in their sample is a factor of two smaller than they reported [42, 43], and thus it seems very likely that the floating zone technique they used produced small regions that were either Y rich, and/or Ba rich with Ba occupying the Pr site. In particular, it is known that relatively modest substitution for Ca on the Pr site provides a 90^+ K superconductor [44], and similar behavior would be expected for Ba.

The inelastic scattering we observe indicates that there is strong hybridization of the Pr *4f* levels, and that this is the correct explanation for the absence of superconductivity in *Pr123*. This is the consensus of opinion, but it is certainly not yet unanimous, and the debate will no doubt continue. For the Pr inelastic scattering, the preliminary indications of non-Fermi liquid behavior is intriguing, and it will very interesting to see if the analysis holds true in detail for the present system, including other properties such as specific heat. Further work is in progress.

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