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MAGNETIC PROPERTIES OF Pr IN NON-SUPERCONDUCTING $PrBa_2Cu_3O_7$

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The magnetic order and spin fluctuations of Pr in non-superconducting $PrBa_2Cu_3O_7$ have been studied by specific heat, susceptibility and neutron scattering measurements. The neutron data show that the basic ordering consists of a simple antiferromagnetic arrangement, with an ordering temperature of ~17 K, while the specific heat data reveal a large value of the electronic specific heat coefficient γ, comparable to heavy fermion like materials. The observed magnetic inelastic scattering shows a broad quasi-elastic response as a function of energy, similar to mixed valent-like systems. These results suggest that there is substantial f-electron character at the Fermi level in this material.

The superconducting properties of the $Y_{1-x}\mathcal{R}_xBa_2Cu_3O_7$ ($\mathcal{R}$ = rare earth) system are not affected significantly by the concentration x of heavy rare earth elements [1]. The existence of these rare earth superconductors suggests that the 4f electrons are well localized, and the rare earth and copper sublattices are electronically decoupled for all practical purposes in these systems, similar to conventional "magnetic-superconductor" systems. Exceptions to this basic behavior are provided by Ce, Pr and Tb. In particular, Pr forms the same orthorhombic structure as for the heavy rare earths [2], but the superconducting state is found to be strongly suppressed as a function of Pr concentration [3–6], and superconductivity is lost for Pr concentrations $x \gtrsim 0.6$. Moreover, the observed suppression is consistent with the classical Abrikosov–Gorkov depairing theory [7]. In the present paper we report both elastic and inelastic neutron scattering measurements of the magnetic properties of Pr in $PrBa_2Cu_3O_7$. A simple antiferromagnetic order, with a moment of $0.74\mu_B$, is observed below a Néel temperature $T_N \simeq 17$ K [8]. This Néel temperature is two orders of magnitude higher than would be expected if one scales the T_N for the heavy rare earth materials, assuming either purely dipolar interactions, or Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange. The small ordered moment, the large value of electronic specific heat coefficient which we have observed [8], and the broad spectrum of inelastic magnetic scattering indicate that the Pr f-electrons are strongly hybridized in this material.

The polycrystalline samples were prepared by the usual solid state reaction technique, starting from high purity powders of Pr_6O_{11}, $BaCO_3$ and CuO. Details of the sample preparation technique can be found elsewhere [6, 8]. Both X-ray diffraction and high resolution neutron profile refinement measurements were used to characterize the samples prepared for these measurements. From the neutron measurements, the nominal oxygen concentration was determined to be 7.00 ± 0.08.

The neutron experiments were conducted at the National Institute of Standards and Technology Research Reactor. The inelastic neutron scattering measurements were taken on the time-of-flight (TOF) spectrometer. An incident energy of 14.8 meV was employed for most of the measurements, which provides an energy resolution of 0.76 meV at the elastic position. Measurments with a higher incident energy (28 meV) were also taken to explore a larger range of energy transfers, and this experimental configuration provided an energy resolution of 1.2 meV. The 64 detectors of the TOF spectrometer were arranged to cover scattering angles over a range from 6.35° to 116.4°. The data collected from many detectors may be summed to obtain data of high statistical accuracy, while the momentum dependence of intensities may also be readily extracted from the experimental data. Additional experimental details of the diffraction experiments and the magnetic structure, as well as the specific heat and susceptibility measurements, can be found elsewhere [8].

Two magnetic Bragg peaks, which may be indexed on the basis of the chemical unit cell as $\{\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\}$ and $\{\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2}\}$, were obtained from neutron diffraction

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measurements. Hence the underlying magnetic structure consists of nearest neighbor spins in all three directions which are aligned antiparallel, which is the same structure observed for most of the rare earth systems [1]. However, because of the small moment and the polycrystalline sample, only two peaks were observed, and the question has been raised whether the ordering is due to Pr or to the ordering of the copper chain layer, which also gives $\{\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\}$ and $\{\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2}\}$ peaks [9]. To resolve this question, we note that the observed intensities in the present case are the same as for the other rare earth compounds. In the case of the Nd compound, for example, the ratio between the $\{\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\}$ and $\{\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2}\}$ peaks is about 1:0.3 [10]. In the case of the Cu chain ordering, on the other hand, the ratio of the intensities is 1:30 [9]. Since in the present case our data gave the ratio of 1:0.3, we do not believe that the ordering originates from the Cu chains. We should point out, however, that it is likely that the Cu planes in this system are in fact ordered, and at quite high temperatures. The Cu ordering in this material will be the subject of a separate study.

The low-temperature ordered moment and the Néel temperature we obtain from our data [8] are $\langle \mu_Z \rangle = (0.74 \pm 0.08)\mu_B$ and $T_N \simeq 17$ K respectively. The tentative spin direction is along the tetragonal *c*-axis. The observed Néel temperature is two orders of magnitude higher than expected from either dipolar or RKKY interactions alone [8]. The small value for the ordered moment ($0.74\mu_B$), along with the large electronic contribution to the specific heat we have observed [8], suggests that there is a significant hybridization of the 4f electrons due to the mixed valent nature of Pr in this system.

To explore the nature of the magnetic excitations of the Pr system, we performed inelastic neutron scattering experiments with the TOF spectrometer. The data from each detector were examined separately, and detectors which contained Bragg peaks were discarded. The data summed from the rest of the detectors are shown in fig. 1, for a temperature of 30 K. The full spectrum, showing the strength of the elastic scattering, is given in the inset for comparison. Positive energy transfer indicates that we are creating excitations in the sample (neutron energy loss). The data reveal a broad distribution of scattering, which is centered around zero energy transfer, and with a half width of ~5 meV. Spectra have been taken at a series of temperatures from 30 to 160 K, and reveal that there is little change in the intrinsic shape of the scattering other than the thermal detailed balance factor. A similar spectrum has recently been observed by Walter et al. [11] and also by Loong et al. [12].

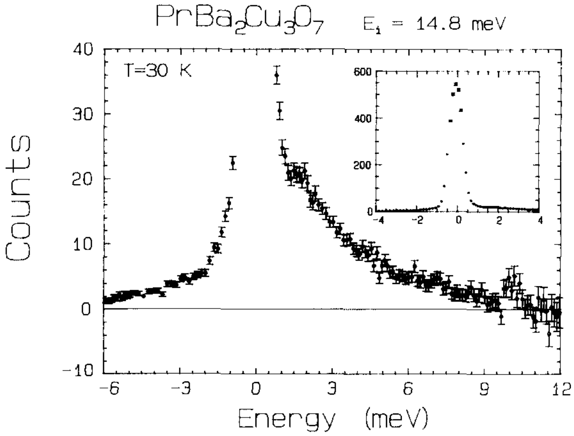

Fig. 1. Inelastic scattering observed on a powder sample of $PrBa_2Cu_3O_7$ via the time-of-flight technique. The inset shows the full spectrum including the elastic component of the scattering.

To establish that this inelastic scattering is magnetic in origin, in fig. 2 we plot the normalized intensity obtained by integrating the data between 2 and 4 meV, as a function of the magnitude of the wave vector $\boldsymbol{Q}$. The intensity is seen to decrease with increasing $\boldsymbol{Q}$ as expected for magnetic scattering. The solid curve is the theoretical result for the square of the magnetic form factor for Pr^{3+}, and the good agreement confirms that the inelastic scattering is magnetic in origin [13].

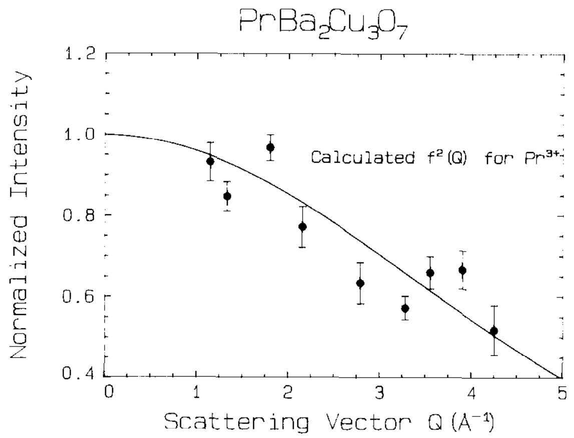

Fig. 2. $\boldsymbol{Q}$ dependence of the normalized intensity integrated between 2 and 4 meV. The solid curve is the spherically symmetric theoretical calculation for the square of the magnetic form factor of Pr^{3+}.

We remark that the intensity of the small "bump" in the scattering observed at ~1.6 meV increases with Q, and hence originates from a small phonon contribution to the scattering at this energy.

It is important to compare these data with the results obtained for the heavy rare earth systems, where sharp crystal field excitations are clearly observed [14]. Generally the crystal field levels fall in two widely separated groups, one in the low energy range, below ~15 meV, and the other above ~55 meV. In the present system we find no crystal field excitations up to an energy transfer of ~22 meV, but only a broad distribution of magnetic quasi-elastic scattering, which is more typical of the scattering expected from a mixed valent material.

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