High energy crystal field excitations in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

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Abstract. We have measured the high energy crystalline electric field transitions in samples of $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x \approx 0.5$ and $x \approx 1$. The fully Pr-doped sample exhibits three strong transitions with excitation energies of about 65, 85 and 105 meV, plus three more weaker ones at 113, 123 and 132 meV. Magnetic intensity is observed in the same energy range in the $x = 0.5$ sample but is largely structureless in character, with only one clear peak at about 109 meV. The large number of transitions would seem to indicate a Pr valence of $3+$, rather than $4+$, but the intrinsically broad character of the excitations is evidence for a dynamically mixed valence state.

Keywords. Neutron scattering (inelastic); crystalline electric fields; magnetic excitations; mixed valence; $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.

1. Introduction

With the exception of Ce, Pr and Tb, the superconducting properties of the rare-earth containing high temperature superconductors, $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$, are virtually insensitive to the magnetic character of R, the rare-earth ion (Hor *et al* 1987; Tarascon *et al* 1987; Soderholm *et al* 1987). Of these anomalous dopants, only Pr forms single-phase compounds with the '123' crystal structure. The superconducting transition temperature of the series $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ decreases with increasing x , and is zero at $x \approx 0.5$. A natural explanation for the suppression of superconductivity with x would be if the dopant formed Pr^{4+} ions, since the extra electron donated by the tetravalent state could go onto the Cu–O planes and neutralize the charge-carrying holes. Whilst magnetic susceptibility (Dalichaouch *et al* 1988) and Hall effect measurements (Matsuda *et al* 1988) seem to indicate a valence of greater than $3+$, X-ray absorption spectroscopy (Neukirch *et al* 1988) and structural studies (Soderholm and Goodman 1989) have yielded a value very close to $3+$ for the whole range of x values.

On the other hand, the close resemblance of the T_c vs x curve to that predicted by the theory of Abrikosov and Gor'kov suggests that a magnetic pair-breaking interaction is responsible for the suppression of superconductivity. This ties in with the suggestion of strong hybridization between the Pr $4f$ level and the Cu–O conduction band that would explain the anomalously large electronic specific heat coefficient (Jee *et al* 1989) and provide a coupling mechanism for the Pr magnetic ordering at 17 K (well above the temperature expected for simple dipole-dipole or RKKY exchange) (Kebede *et al* 1989; Li *et al* 1989). Hybridization has also been predicted by band structure calculations (Guo and Temmerman 1990).

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In an effort to gain a better understanding of the electronic properties of Pr in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ we have studied, by neutron inelastic scattering, the high-energy crystalline electric field (CEF) transitions for Pr-doped compounds with $x \approx 1$ and $x \approx 0.5$. Since the valence state of Pr determines the angular momentum J of the ion, a determination of the CEF spectrum should, amongst other things, distinguish between trivalent and tetravalent Pr. We present here a preliminary and qualitative account of the results.

2. Experimental

The samples were synthesized by solid-state reaction from the oxides in the usual way. The fully Pr-doped sample was prepared with a slightly off-stoichiometric ratio of Pr to Ba, $\text{Pr}:\text{Ba} = 1.06:1.94$, in order to prevent the formation of the impurity BaCuO_2 (Okai *et al* 1988). The powdered samples were pressed into pellets, which for the neutron measurements, were mounted in a rectangular array and separated from each other by cadmium spacers. This arrangement was employed to reduce the level of multiple scattering in the forward direction (mainly Bragg + one phonon). Approximately 100 g of material were used in these samples.

The neutron measurements were performed on the high-energy transfer spectrometer (HET) at the spallation neutron source ISIS at the Rutherford Appleton Laboratory. HET is a time-of-flight spectrometer with a high resolution detector bank which measures neutrons scattered through angles in the range 3° to 7° , and a medium resolution bank which covers the angular range 9° to 29° . To measure the high energy CEF excitations incident energies of 180 meV and 250 meV were employed. In addition to the two Pr-doped samples, an identically constructed sample of undoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was run to act as a non-magnetic blank. Because the doped and undoped compounds are very similar in structure they are expected to have nearly identical lattice vibrational modes, so the neutron spectrum of the latter may be used to determine the background of nuclear Bragg + phonon inelastic scattering on which the magnetic excitations are superimposed.

3. Results

The data presented in figures 1 and 2 are the raw, uncorrected spectra, converted from time-of-flight to energy transfer, of the three compounds measured at a temperature of 2 K. The spectra in figure 1 of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are from the high resolution detector, and it may be seen immediately that there is considerable magnetic intensity between 60 meV and 140 meV transfer. Specifically, the signal can be split up into a series of peaks at energy transfers of about 65, 85, 105, 113, 123 and 132 meV. The first three of these peaks are the strongest, and have also been observed elsewhere (Holland-Moritz *et al* 1988). The highest energy peak is not clearly developed in the displayed spectrum, but its existence was confirmed by studying the spectra measured in the medium resolution detector bank at larger scattering angles. It should be noted that since the energy resolution of the low angle detector bank is between 2 and 3 meV (FWHM) the CEF excitations must have considerable intrinsic width.

Figure 1. Excitation spectrum of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (●) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (—) measured in the angular range 3° to 7° with 180 MeV neutrons. The difference between the spectra is the magnetic scattering.

Figure 2. Excitation spectra of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (●), $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (○), $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (—) with all detectors in the angular range 3° to 29° combined.

In figure 2 we compare the magnetic response of the samples with $x \approx 0.5$ and $x \approx 1$; the spectra have been summed over all scattering angles between 3° and 29° in order to improve the statistical accuracy of the data (at the expense of poorer resolution). The magnetic intensity of the $x \approx 0.5$ samples occurs over a similar energy range as with the fully-doped sample, but the signal is largely broad and featureless and only two resolved peaks occur, at 108 meV and 132 meV. The sharpness of the latter seems to be inconsistent with the rest of the spectrum, so may originate from an impurity phase.

4. Discussion

We address first the problem of the valence state of the Pr ion in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The Hund's Rule ground states of trivalent and tetravalent Pr have $J = 4$ and $J = 5/2$ respectively, and crystal field theory determines that the CEF spectra comprise 9 singlets for the $J = 4$ state, and 3 doublets if $J = 5/2$. Neutron inelastic scattering measurements at small energy transfers (Walter *et al* 1988) indicated the presence of at least 2 energy levels below 10 meV, so taken together with those observed at high energy transfer in the present investigation the total number of observed CEF levels is strongly in favour of a $3+$ valence.

If this were the case, it ought to be possible to use the known crystal field spectra and parameters of other R^{3+} ions in $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to predict the CEF energy levels of Pr^{3+} with the assumption that the local structural environment remains approximately constant across the rare earth series. Unfortunately, due to the low symmetry D_{2h} of the rare-earth site, the complete CEF Hamiltonian requires 9 CEF parameters, and the determination of this number of parameters from experiment is difficult. So far it has only been possible to determine unambiguously the CEF parameters for one ion, Ho^{3+} (Furrer *et al* 1988). A scaling of the Ho^{3+} parameters to Pr^{3+} , taking account of the different ionic sizes, predicts a Γ_1 ground state with two excited levels below 10 meV, and six energy levels at high energy. This is qualitatively similar to the measured excitation spectrum, but it disagrees in that only three of the predicted high energy excitations have a measurable transition probability, and the overall splitting of the multiplet is much larger than that observed experimentally. A similar energy level scheme with a smaller overall splitting has been obtained by transferring the CEF parameters from the rare-earth containing garnets (Nekvasil 1988; Nekvasil *et al* 1988).

Our own attempts to fit the spectra have also yielded schemes with only three or four high energy transitions with measurable intensity, so the observation of six transitions is still a puzzle. One possibility is that variations in oxygen stoichiometry throughout the sample could result in several discrete environments around the rare earth ion, which could cause singlet levels to appear as multiple peaks. This effect has been observed in oxygen-deficient $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Allenspach *et al* 1989). Alternatively, because of the slight over-stoichiometric ratio of Pr to Ba in the sample the excess Pr may reside on the Ba site, and give rise to excitations at different energies. One final possibility is that the compound also contains Pr^{4+} ions which happen to have CEF excitations in the 60–130 meV range. Indeed, the scaling from Pr^{3+} to Pr^{4+} of our approximate fits to the neutron spectra do actually predict a strong Pr^{4+} excitation between 90 and 100 MeV.

The other interesting feature of the excitation spectra is the width of the CEF peaks. Significant lifetime broadening indicates that strong electronic interactions occur with the Pr $4f$ electrons, and is consistent with the behaviour of a mixed valence system where hybridization takes place with the electrons at the Fermi surface. Such interactions would be essential if it is the Pr ions (rather than the Cu(2) sites) which order at 17 K since the Pr^{3+} CEF ground state is non-magnetic, so the magnetic moment would have to arise out of mixing with the excited state levels.

5. Conclusion

The crystal field transitions measured in this investigation provide strong evidence that the Pr ions in $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ are of trivalent character with some valence admixing from the tetravalent state.

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