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Magnetic ground state of Pr in $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$

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Abstract. Inelastic neutron scattering experiments were performed on $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ to determine the magnetic ground state of the Pr ions. In this compound, superconductivity is suppressed by the presence of Pr ions. The magnetic ground state is found to be very similar to that in $PrBa_2Cu_3O_x$ and $Pb_2Sr_2PrCu_3O_8$. However, the high energy spectrum has a stronger resemblance to that of $Pr_{2-x}Ce_xCuO_4$, where the Pr ions see a very similar local structure. Therefore, a similar set of higher order crystalline-electric-field parameters and an inversion of B_0^2 can explain qualitatively the neutron spectra. The suppression of superconductivity and the quasi-triplet magnetic ground state support models which correlate the unusual magnetic properties with T_c suppression by Pr.

1. Introduction

Since the discovery of high-T_c superconductivity, isostructural compounds which suppress superconductivity have attracted great interest. In particular, the exceptional properties of cuprate superconductors and related materials containing the rare earth ions Ce, Pr and Tb have been studied in great detail [1, 2]. Partial replacement of Y by these rare earth ions leads to different, magnetic, electronic and structural properties. Whereas the Pr analogue of $RBa_2Cu_3O_x$ (R = rare earth or Y) exists, only partial substitution of Y by either Ce or Tb is possible (20% for powders and 50% for films [2]). A partial replacement of Y by Pr or Ce strongly suppresses the superconducting transition temperature T_c, whereas for Tb replacement, no effect on T_c has been observed [2]. High antiferromagnetic ordering temperatures of the Pr and Tb sublattices are found for $PrBa_2Cu_3O_x$ and $Pb_2Sr_2TbCu_3O_8$, 17 K and 5.3 K [3, 4], respectively. It has been shown that the incorporated Ce is in the tetravalent oxidation state, and therefore non-magnetic [5]. This explains both the inability to form the $RBa_2Cu_3O_x$ structure (charge equilibrium) as well as the suppression of T_c (annihilation of holes due to charge transfer). Terbium which partially substitutes Y is trivalent, and it has been argued that the stable $Tb^{4+}BaO_3$ precursor, which forms in the solid-state sintering procedure, prevents the formation of $TbBa_2Cu_3O_x$ [6]. Praseodymium substituting for other R ions suppresses T_c in the $RBa_2Cu_3O_x$ series; however it has no influence on T_c in the electron-doped $R_{2-x}Ce_xCuO_4$ series. In the $Bi_2Sr_2CaCu_2O_8$ [7] and the $Pb_2Sr_2R_{1-x}Ca_xCu_3O_8$ [8] series, superconductivity is only weakly suppressed by Pr.

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Recently, a non-magnetic ground state of Pr ions in $PrBa_2Cu_3O_x$ was reported in a Pr NMR study [9]. However, several investigations [10–12] could convincingly show that the Pr ions are magnetic and that they order at approximately 17 K. Even more recently, bulk superconductivity was reported [13] in a single crystal of $PrBa_2Cu_3O_7$ prepared by the travelling-solvent floating-zone method.

A variety of mechanisms have been proposed to account for the suppression of superconductivity by Pr in the $RBa_2Cu_3O_x$ series including charge transfer (tetravalent Pr ions), magnetic pair breaking and hybridization with the CuO_2 bands [14–17]. The experimental results from electron-energy-loss spectroscopy, inelastic neutron spectroscopy and x-ray absorption studies could be satisfactorily explained assuming predominantly trivalent Pr. In the Ca-doped superconductor $Pb_2Sr_2R_{1-x}Ca_xCu_3O_8$ an enhancement of ground-state splitting of Pr compared to the undoped case has been reported. This observation has been interpreted in terms of a 'weaker' magnetic ground state, which leads to a less effective suppression of the superconducting transition temperature T_c compared to the $RBa_2Cu_3O_x$ series [18]. Despite considerable experiment and theory effort, no consensus exists on why Pr suppresses superconductivity. More experimental information, in particular on other systems than $PrBa_2Cu_3O_x$, appear to be necessary for a more complete understanding.

The isostructural $(R_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ family becomes superconducting [19] at approximately 28 K, for R = Nd, Sm and Eu. Here as well the Pr analogue does not superconduct [19]. This is particularly interesting, because this material contains only single CuO_2 layers, and is hence very similar to $Pr_{2-x}Ce_xCuO_4$ (see figure 1), in which Pr does not affect superconductivity. An electron-energy-loss spectroscopic study has shown that the Pr ions are nearly trivalent in this material [20]. In addition, an antiferromagnetic ordering of the Pr sublattice is found [21] near 10 K. This value of T_N is similar to that in $PrBa_2Cu_3O_x$, indicating a general correlation between the anomalous Pr magnetism and the absence of superconductivity.

Inelastic neutron scattering (INS) is a sensitive method of investigating the ground state of Pr. In particular one can test whether a correlation exists between the degeneracy of the ground state and T_c suppression. Here we present INS results on the magnetic excitations of Pr in $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$. We find that the magnetic scattering at low energy transfer (ΔE) is similar to that in $PrBa_2Cu_3O_x$ [22] and $Pb_2Sr_2Pr_{1-x}Ca_xCu_3O_8$ [23]: no well defined crystalline-electric-field (CEF) transitions are observed at low energy transfers and a broad, weak magnetic feature is seen at high energy transfers. These results are interpreted and compared with the observations on $PrBa_2Cu_3O_x$, $Pb_2Sr_2PrCu_3O_8$ and $Pr_{2-x}Ce_xCuO_4$. Our findings support models which correlate the suppression of superconductivity with the anomalous magnetic properties of the Pr ions.

2. Experiment

The sample was prepared by the standard solid state reaction method (mixing, pressing, sintering) [24]. X-ray powder diffraction (XRD) confirmed the single phase character of the sample. Details of the XRD structural refinement can be found in [24]. The INS experiments were performed on the low-resolution medium-energy chopper spectrometer of the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory. Experiments with incident neutron energies of 20, 40 and 120 meV were performed. The sample (50 g) was filled in a flat alumina container and attached to the cold finger of a closed-cycle refrigerator providing temperatures down to 8 K.

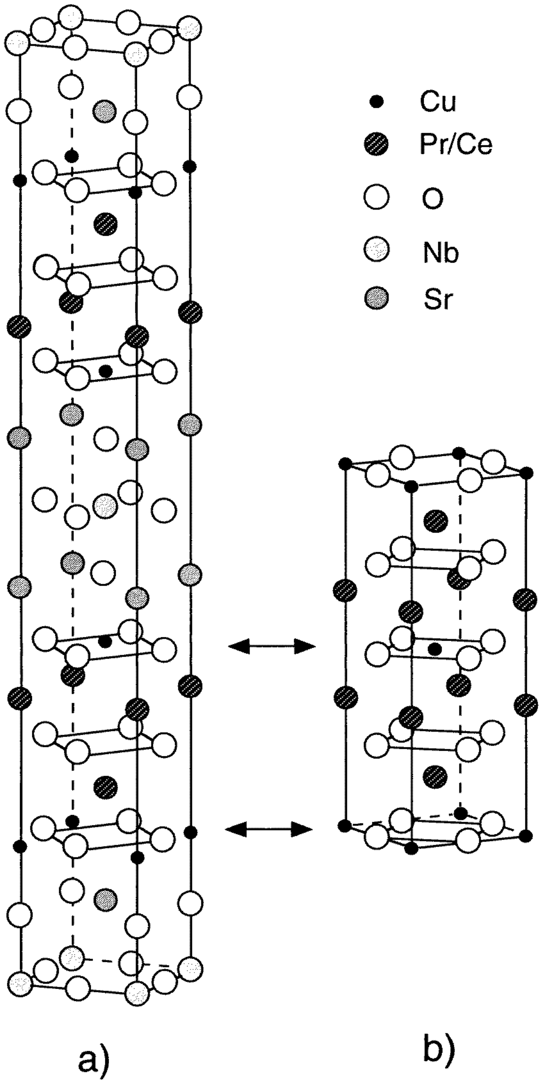

Figure 1. Structural comparison of $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ and $Pr_{2-x}Ce_xCuO_4$, (a) and (b), respectively. ((a) $a = b = 3.887$ Å, $c = 28.752$ Å.)

3. Results

$(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ crystallizes in the T′-type crystal structure ($I4/mmm$ symmetry, see figure 1). The ground state of the trivalent Pr is a $^3H_4$ multiplet, which is split under the tetragonal CEF into five singlets and two doublets. However, the local symmetry of the CEF potential is expected to be monoclinic due to the solid solution of trivalent Pr and tetravalent Ce ions on the same site. Figure 2 shows the low-energy INS spectra of $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ taken at 12 K, just above the antiferromagnetic ordering temperature of the Pr sublattice ($T_N \approx 10$ K [21]). A very broad peak is observed at low energy transfer, with a maximum between 3 and 4 meV. In order to distinguish between magnetic excitations and lattice vibration, the dependence of the spectra on both temperature

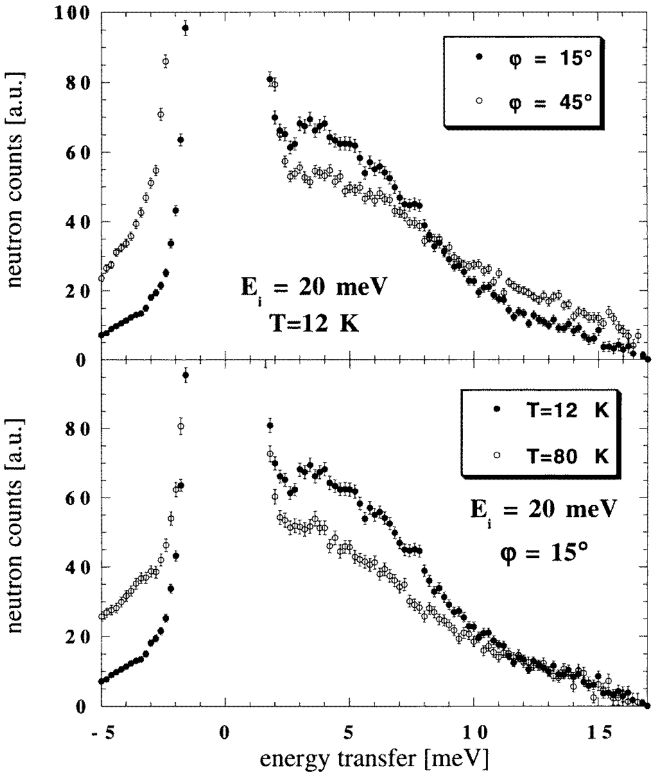

Figure 2. Low-energy inelastic neutron scattering spectra in $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$. The dependence is shown on the momentum transfer (scattering angle φ) (upper part) and on the temperature (lower part).

and momentum transfer (Q) was investigated (see figure 2). In contrast to the Q-dependence of phonon scattering, the Q-dependence of the magnetic excitations is described by a form factor which decreases with increasing Q. At energy losses smaller than 8 meV, the low-Q intensity exceeds the high-Q intensity; above 8 meV, the situation is reversed. In the limit of weakly interacting R ions, this can be interpreted in terms of magnetic excitations at low ΔE. In the higher energy region, the phonon contribution dominates. We note that due to the relatively strong R–R interaction, the magnetic excitations are expected to be strongly dispersive, and data taken at different Q-values average these excitations differently in reciprocal space, possibly leading to a redistribution of intensities. However, the temperature-dependent spectra (figure 2) show a high temperature reduction of intensity at energies up to 10 meV, indicating that the scattering is predominantly magnetic.

Figure 3 shows high energy spectra of $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ taken at 12 K. Two peaks are observed, centred at 72 and 82 meV. The intensity below 70 meV distinctly increases with increasing Q, whereas the intensity in the energy range 82 to 94 meV is constant or slightly decreases. The phonon density of states shows significant contributions up to 90 meV in such cuprates [25], which allows us to interpret our data as follows. The intensity below 70 meV is dominated by phonons. Between 70 and 90 meV, some weak magnetic excitations compete with the phonon density of states. The maximum of this weak feature is at approximately 84 meV. Above 90 meV, no significant intensity is observed.

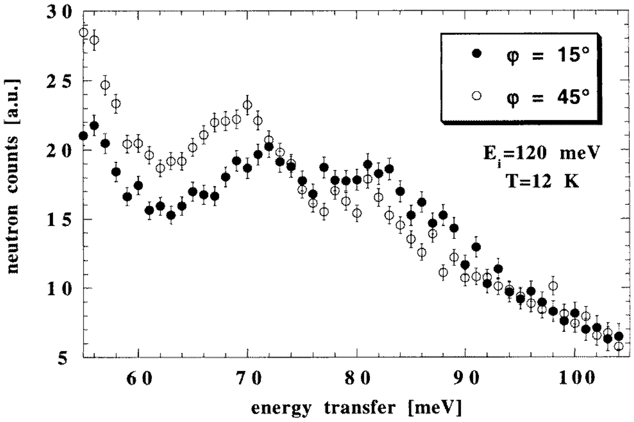

Figure 3. Q-dependence (scattering angle φ) of the energy spectra of neutrons scattered from $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ at 12 K.

The spectroscopic information obtained is clearly insufficient for a determination of the details of the CEF energy level scheme and the corresponding CEF parameters. However, it allows a comparison with results obtained on other Pr cuprates. We find that the observed magnetic scattering in the low energy window is similar to that obtained in $PrBa_2Cu_3O_x$ [22, 26] and $Pb_2Sr_2PrCu_3O_8$ [23], whereas it is distinctly different in the high-energy regime. In contrast, a comparison of the present spectra from $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ with those from $Pr_{2-x}Ce_xCuO_4$ [27] shows similarities at high energy transfer, but the low energy spectra are completely different. We note that Pr in $Pr_{2-x}Ce_xCuO_4$ has a non-magnetic singlet ground state well separated from the next doublet state by 18 meV [27], whereas $PrBa_2Cu_3O_x$ and $Pb_2Sr_2PrCu_3O_8$ have a magnetic quasi-triplet ground-state [22, 23, 27]. In the high-energy region, $Pr_{1.85}Ce_{0.15}CuO_4$ exhibits a broad magnetic peak near 86 meV [27], whereas for $PrBa_2Cu_3O_x$ and $Pb_2Sr_2PrCu_3O_8$, three magnetic excitations between 60 and 100 meV are observed [23, 26, 28].

The CEF potential can be expressed as

$$H_{CEF} = \sum_{n,m,i} B^n_m (C^n_m(i) + C^n_{-m}(i)) \tag{1}$$

where B^n_m are the CEF parameters and $C^n_m(i)$ correspond to the mth component of a spherical tensor operator of rank n for the ith electron. The use of tensor operators allows us to include information on higher-lying J-multiplets, whose wave functions are mixed with the ground-state multiplet by the large CEF potential [29]. Due to the average tetragonal symmetry, five independent CEF parameters contribute to the potential, namely B^2_0, B^4_0, B^4_4, B^6_0 and B^6_4. Because the local structure around the Pr ions is almost identical to that in $R_{2-x}Ce_xCuO_4$ (see figure 1), a similar CEF potential is expected. Although the high energy spectra of $Pr_{1.85}Ce_{0.15}CuO_4$ [27] and $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ are very similar (both show a weak magnetic excitation near 85 meV), the low energy spectra are completely different. This indicates that the CEF parameters dominated by the short range part of the CEF potential, the higher order (fourth and sixth order) parameters, are close to those in $Pr_{1.85}Ce_{0.15}CuO_4$, whereas the second order B^2_0 term, which is dominated by the long range part of the CEF potential, is strongly different. By using the higher order CEF parameters from Pr_2CuO_4 and inverting the sign of B^2_0, a quasi-triplet ground state is obtained. This fact leads to the following interpretation of the energy-level scheme of Pr in $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$.

The magnetic intensities observed at low energy transfer correspond to transitions within the quasi-triplet ground state, and the weak magnetic scattering observed near 84 meV corresponds to several transitions from the ground state into a series of higher lying states. Therefore leading CEF parameters, B_0^4, B_4^4, B_0^6 and B_4^6, are expected to be similar to those found in Pr_2CuO_4. B_0^2 is expected to have the same sign and magnitude as in $PrBa_2Cu_3O_x$ [22, 26] and $Pb_2Sr_2PrCu_3O_8$ [23]. It is well known that hybridization effects between the 4f electrons and other orbitals can give a significant contribution to the B_0^2 parameter. Therefore, the opposite sign, compared to B_0^2 in $Pr_{2-x}Ce_xCuO_4$, may reflect the strong hybridization between the 4f electrons and the CuO_2 bands, resulting in a magnetic ground state which effectively suppresses superconductivity. However, the found for the other rare earth ions in these two series ($RBa_2Cu_3O_x$ [30, 31], $Pb_2Sr_2(R/Ca)Cu_3O_8$ [32]) have the same sign, indicating that the long range part of the CEF potential is the cause for the quasi-triplet ground state.

4. Conclusions

Inelastic neutron scattering experiments were performed on non-superconducting $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$. This is an example of exceptional compounds for which superconductivity is suppressed by Pr ions. The magnetic ground state is found to be very similar to those in $PrBa_2Cu_3O_x$ and $Pb_2Sr_2PrCu_3O_8$, and is interpreted as a quasi-triplet. However, the high energy spectra resemble more closely of $Pr_{2-x}Ce_xCuO_4$, in which the Pr ions occupy a very similar local structure. Therefore, a similar set of higher order CEF parameters and a change of sign of B_0^2 can qualitatively explain the observed magnetic intensities. Even though the local structure is very similar compared to $Pr_{2-x}Ce_xCuO_4$, where Pr has a non-magnetic singlet ground state (with no influence of Pr on the superconductivity), Pr in $(Pr_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$ exhibits a quasi-triplet magnetic ground state and suppresses superconductivity. This is an indication that a magnetic ground state is required for T_c suppression.

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