Carrier doping in Pr$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ studied by NMR

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We investigated the type of the carriers doped in the CuO$_2$-planes of non-superconducting Pr$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ single crystals by nuclear magnetic resonance of Pr and chain-site Cu. The different spectra in the solid solution system show that the holes in Pr-rich crystals are localized in states similar to the ones in stoichiometric samples, that is in the 4$f^2$ – 2$p\pi$-hybridization band proposed by Fehrenbacher and Rice. In contrast, the spectra of crystals prepared under conditions favoring Ba-rich phases indicate the presence of holes in Zhang-Rice singlets in the CuO$_2$-plane. Our results strongly support the model that superconductivity reported recently for Pr123-crystals is due to Ba-rich regions in the inhomogeneous samples.

PrBa$_2$Cu$_3$O$_7$ has been investigated for more than a decade because it is the only antiferromagnetic insulator in the isostructural (R123)-family of superconducting cuprates ($T_c = 92 \pm 2$ K for RBag$_{2,0}$Cu$_{3-x}$, R=Y, La, rare earths). The most common model for this exceptional property of Pr123 assumes a carrier localization in antibonding oxygen orbitals hybridized with the 4$f^2$ shell of Pr, the so-called Fehrenbacher-Rice (FR) states. As a consequence the concentration of Zhang-Rice (ZR) singlet hole carriers in the CuO$_2$-plane is reduced below the threshold of superconductivity. Numerous experimental investigations since 1987 indicated that superconductivity may be restored in Pr123 only by dilution of the Pr-sublattice. Isovalent substitution, e.g. by Y, leads to an (AF) insulator- (SC) metal transition above app. 40% Y. As expected, this dilution effect is enhanced by additional hole doping if one substitutes Pr$^{3+}$ by Ca$^{2+}$.

This situation seemed to change when Zou et al. prepared pure superconducting Pr123-crystals with $T_c$-values above 80K (> 100 K under pressure). They considered two reasons for the occurrence of superconductivity in their crystals, both due to the special preparation procedure. First, the hybridization could be suppressed in a stoichiometric modification of Pr123, as indicated by the longer Pr-O(2)-bond length. This is, however, very difficult to verify in the inhomogeneous crystals. The second possibility is a Ba-substitution of Pr, favoring superconductivity in a similar way like Ca does. The occurrence of nonstoichiometric phases R$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ especially in the case of light rare earths is known since 1987, when Takekawa et al. reported the substitution of Ba by the rare earths with large radii. Before the result of Zou et al. it has been assumed generally that $x$ is always positive. If superconductivity in Pr123 is in fact due to $x < 0$ one expects to observe holes in the FR states in Pr-rich samples, and in ZR singlets in Ba-rich crystals. In order to verify this expectation we studied the nuclear magnetic resonance (NMR) of Cu(1)- and Pr-nuclei in Pr$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$. The magnetic field ($B_{hf}$) and the electric field gradient (EFG) tensor ($V_{ij}, i, j = x, y, z$) of these sites allow not only to distinguish between a doping of the chain- or plane-layers, but also between a doping of the planes by ZR singlets, which may lead to superconductivity, or by FR states, which stay localized. The dependence of the spectra on the preparation conditions should give, therefore, insight into the origin of superconductivity in Pr123.

The so-called solid solution (R123ss) or homogeneity range in principle is a four-dimensional volume in the plane diagram spanned by temperature $T$, partial oxygen pressure $p(O_2)$, and the (2D-) triangle of cation concentrations sketched for fixed $T$ and $p(O_2)$ in fig.1. The allowed, stable compositions form the surface of this volume with the ellipses in fig.1 indicating cross sections. In the absence of other metals which may substitute for Cu (e.g. Al from the crucibles) one may assume a constant Cu content. In this case the ellipses in fig.1 degenerate to horizontal lines at the concentrations R$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$, and the homogeneity range has only the three degrees of freedom $T$, $p(O_2)$, and $x$.

The accessible range of $x$ depends on temperature, oxygen partial pressure, and on the rare earth radius. In general, $x$ increases with increasing oxygen partial pressure and rare earth radius, and with decreasing temperature, at least in the vicinity below the peritectic temperature of the R123ss. Accordingly, the largest $x$ in air atmosphere was observed in the Ln123ss system ($x = 0.7$), whereas $x$ is below 0.01 for rare earth ions smaller than Gd.

We grew Pr123ss single crystals with different Pr/Ba ratios from CuO/BaO fluxes in MgO crucibles by the slow cooling method. The Pr/Ba ratio of the growing crystals was set by the Cu/Ba ratio of the flux via the conodal line to the solidus surface. Temperature and oxygen pressure were chosen to obtain non-superconducting crystals with $x > 0$, $x = 0$, and, if possible, $x < 0$ (see tab.1), denoted below Pr$^+123$, Pr$^0123$, and Pr$^-123$, respectively.
respectively. We note that we expect $x \approx 0.05$ from neutron work on crystals from the batch of Pr$^{0}$123.$^{[2]}$ After growth the remaining flux has been removed with a porous piece of ZrO$_2$ ceramic. The crystals were cooled to room temperature and, finally, oxidized in 1 bar flowing oxygen in the temperature range 600–300°C. Neither susceptibility measurements down to 6 K nor the NMR experiments to 1.3 K described below gave any indications for superconductivity in our crystals.

The symmetry and the morphology of the oxidized crystals depend in a characteristic way on $x$ that we also find in the La123ss and Nd123ss. Pr$^{-}123$ and Pr$^{0}123$ exhibited an orthorhombic structure with twins, whereas Pr$^{+}123$ kept its tetragonal structure even after additional oxidation treatments under high oxygen pressures. This result was expected because Pr ions on the Ba site force extra oxygen ions on the O(5) sites between the Cu(1)O-chains,$^{[3]}$ which reduces the orthorhombicity. The morphology of the crystals changes with increasing $R$/Ba-ratio from isometric blocks, sometimes with additional (101)-faces, formed by stoichiometric samples, to the formation of (100)/(001) growth twins and, finally, even to (001)/(111) growth twins at large $x$ (see below and fig. 2). The same twin structures have also been observed in 123 thin films. From the degree of their structural perfection and from the number of crystal nuclei of a growth experiment we infer that the $R$/Ba-ratio of the growing crystal is closely related to the supersaturation during growth.

The local Pr/Ba-ratio of a given sample with fixed overall $x$ can be influenced by an additional heat treatment, but the composition of the resulting crystal is inhomogeneous. For small deviations from the equilibrium surface a crystal may decompose either into a member of the R123ss with a different cation ratio, and other stable phases like BaCuO$_2$, or into two R123ss phases with different $R$/Ba ratios. Larger deviations from equilibrium may lead to a spinodal decomposition where, for example, the Pr/Ba-ratio varies lateraly and changes with time. The final state of these decomposition reactions depends on the initial $R$/Ba-ratio and whether or not this cation ratio is located inside the four-dimensional volume of the R123ss. In the case of a spinodal decomposition the regions of different Pr/B ratios within a sample are very close to each other (10 - 100 nm), and any integral chemical analysis will reproduce the composition of the untreated sample. The regions with a lower Pr/B ratio may, however, be large enough to be superconducting.

Fig. 2 shows the field-sweep spin echo Cu(1)-spectra of three crystals. The external field is applied along the $a$- and $b$-axes of the twinned samples. In the present case of a large Zeeman splitting the position of the central line is very close to each other (10 - 100 nm), and any integral chemical analysis will reproduce the composition of the untreated sample. The regions with a lower Pr/B ratio may, however, be large enough to be superconducting.

|      | Pr$^{-}123$ | Pr$^{0}123$ | Pr$^{+}123$ |
|------|-------------|-------------|-------------|
| at%Pr | 2           | 2           | 2           |
| at%Ba | 37          | 30          | 28          |
| at%Cu | 61          | 68          | 70          |
| 300 mbar air | 1 bar air | 1 bar O$_2$ |
| $[^{\circ}C]$ | 970$\rightarrow$906 | 1000$\rightarrow$939 | 1000$\rightarrow$948 |
| $[^{\circ}C}$/h | -0.4      | -0.5        | -0.35       |
| Quench | slow cool  | quench      | quench      |
| (100)/ (010) | orthor.   | orthor.     | tetr.       |

**TABLE I.** Preparation parameters and characterisation of the crystals. The flux composition is given in the first block, followed by the preparation atmosphere and the temperature program, with a slow decrease at the indicated rate in the given interval, and a quench or slow cooling to RT. The morphology and possible growth twins are indicated in the last block.
The widths of the central lines show, on the other hand, that the magnetic structure of the Cu(2)-sublattice is unchanged, indicating that no ZR singlet hole states are doped in the CuO$_2$-planes.

The spectrum of the nonstoichiometric crystal Pr$^{-123}$ is, in contrast, best described by two subspectra. One with app. 30% relative intensity is the same as for the stoichiometric crystal, accordingly the environment of 1/3 of the Cu(1)-sites is unchanged. A significant broadening of the central transitions together with a severe broadening of the satellites shows the presence of inhomogeneous magnetic fields together with charge disorder for the majority of the Cu(1)-sites. The inhomogeneous width of the central transition corresponds to internal magnetic fields of $\approx 0.2$ T, in full agreement with the transferred hyperfine fields from the Cu(2)-moments at the Cu(1)-site ($\approx 0.1$ T) that are known from studies of the so-called AF-II structure in Al-doped Y123. The defect structure in this crystal affects, therefore, the magnetic structure of the Cu(2)-sublattice, as is expected if ZR singlets are doped in the CuO$_2$-planes. If we assume that only the eight nearest Cu(1)-neighbors of a hole contribute to this subspectrum we arrive at a concentration of $\approx 0.2$/unit cell. It is tempting to assign the signal in this way to Cu(1)-neighbors of localised Zhang-Rice singlets, but it should be noted that disorder in the stacking sequence of perfect antiferromagnetic CuO$_2$-planes may lead to the same inhomogeneous transferred hyperfine fields.

The above interpretation of the Cu(1)-spectra is supported by the properties of the Pr-resonance, which provides a very sensitive probe of the van Vleck susceptibility of the 4$f^2$-shell and, therefore, of the crystalline electric field (CEF) from the neighboring ions (not of the EFG at the Pr-nucleus, the quadrupole splitting is too small to be resolved). Let us assume that the Pr-signal is due to Pr on regular rare earth sites, as discussed in refs. Comparison of the Pr-spectra in the three crystals shows immediately that the shape of the line is independent of $x$ for Pr/Ba-ratios larger than the stoichiometric value. In contrast, we have scarcely been able to detect any Pr-resonance in the sample Pr$^{-123}$. The first observation shows clearly that the electronic state of the CuO$_2$-Pr-CuO$_2$-trilayer is the same in both crystals, so the holes are localised in the same states. The second result shows that the electronic configuration is different in crystals prepared under conditions favouring Ba-rich phases, even if they are not superconducting. Taking into account the magnetic broadening at the Cu(1)-sites this is strong evidence for the presence of Zhang-Rice singlets. Such a defect will change the CEF of neighboring Pr-ions, and most probably it will extinguish the contribution of its neighborhood to the Pr-signal by inhomogeneous broadening or fast relaxation. The singlets might be induced by a structural modification like the larger Pr-O(2)-bond length considered by Zou et al. We think, however, that the correlation with the preparation conditions supports the second possibility that Ba$^{2+}$ substitutes Pr on the

![FIG. 2. Cu(1)-field-sweep spectra in Pr$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ at 81 MHz, 4.2 K with $B_0$[a, b]. See tab.1 for the preparation conditions. At the high-field satellites of Pr$^0$123 the assignment of the $^{63}$Cu-lines to the orientation of the twins in the field is indicated, showing that $|V_{zz}| \approx |V_{yy}|$. At the low field satellites the difference in the splitting between Pr$^+$ 123 and Pr$^0$123 is marked. The two shoulders assigned to (111)-twins appear at the positions expected if the field is along the space diagonal of the EFG-tensor, supporting the existence of these twins in the crystal.](image)

four oxygen nearest neighbors is known from the other R123-compounds. The fourfold coordination is characterized by $|V_{zz}| \approx |V_{yy}|$ or $\eta = 0.9$ (see fig.2). It is the only one which we could identify in our crystals, as is expected for filled chains.

The spectrum of sample Pr$^+123$ shows a larger splitting than for Pr$^0$123 as well as an inhomogeneous broadening of the satellite lines, but no significant broadening of the central line. The high field shoulder of the central transitions at 7.4 T can be assigned to the (111) growth twins mentioned above. The satellite line broadening shows immediately the presence of disorder in the charge coordination of chain site Cu, and the unchanged central line proves the absence of internal magnetic fields at the Cu(1)-site. The substitution of divalent Ba by Pr induces the inhomogeneity in the charge distribution of the chain layer detected in the Cu(1)-EFG. The result confirms, therefore, the previous observations that Pr-rich crystals with $x > 0$ form in oxygen rich atmosphere.
FIG. 3. Pr-field-sweep spectra at 102 MHz, 1.3 K, in a field $B_0 \parallel c$. The amplitudes are scaled to allow comparison of the line shapes. The signal in Pr$^{-}123$ is smaller by more than one order of magnitude.

We investigated single crystals of the solid solution system Pr$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ grown under preparation conditions chosen to obtain non-superconducting stoichiometric, Pr-rich, and Ba-rich specimen. The low temperature NMR-spectra of the Cu(1)- as well as of the Pr-sites show that the hole states in the CuO$_2$-layers of the stoichiometric and the Pr-rich crystal are very similar, and we assign them to the $4f^2 - 2p\pi$-hybridization band. The spectra of the crystal prepared under conditions favoring Ba-rich phases show in contrast a significant magnetic inhomogeneous broadening at the Cu(1)-site and a vanishingly small Pr-signal, both indications for the presence of Zhang-Rice singlets. We argue that the occurrence of these singlets at the preparation conditions favoring the Ba-rich phases is a strong indication that in Pr$_{1+x}$Ba$_{2-x}$Cu$_3$O$_7$ Ba can substitute Pr under certain conditions. This gives a natural explanation for the recent observations of intrinsic superconductivity in Pr123 crystals.

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