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LETTER TO THE EDITOR

Superconductivity suppression in $(Er_{1-x}Pr_x)Ba_2Cu_4O_8$: an x-ray absorption spectroscopic study

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Abstract. In this letter we report our measurements of Er and Pr L_3 edges in $Er_{1-x}Pr_xBa_2Cu_4O_8$, $0 \leqslant x \leqslant 0.6$. The normalized L_3-edge intensity is seen to closely follow the behaviour of T_c with the Pr concentration in these compounds. This can be related to the fact that there is a reduction in the number of mobile carriers with increasing Pr-doping level. This picture lends support to a recent model proposed by Liechtenstein and Mazin (Liechtenstein A I and Mazin I I 1995 *Phys. Rev. Lett.* **70** 1000) according to which the holes are localized in a band which crosses the Fermi level along with a hybridized state of $4f^2L$ and $4f^1$ at the Pr site, where L is a ligand hole.

The suppression of superconductivity in the rare-earth cuprates possessing the 123- and the 124-type structure(s) due to Pr doping has attracted a lot of interest in recent years. It is well known that both $PrBa_2Cu_3O_7$ (Pr-123) and $PrBa_2Cu_4O_8$ (Pr-124) are structurally similar to the other rare-earth counterparts (with exception of the Ce and Tb ones); however, they are non-superconducting [1, 2].

The superconducting transition temperature T_c of the system $R_{1-x}Pr_xBa_2Cu_3O_7$ has been seen to decrease with Pr content x, and eventually the superconductivity disappears at a critical concentration varying from 0.32 to 0.60 depending on the rare-earth ionic radius [3, 4]. Various studies [5–7] of the Hall effect, magnetic susceptibility, etc suggest that Pr in these compounds has a valency greater than three, and it is this extra electron which compensates the hole in the Cu–O network and thereby decreases T_c. Several spectroscopic measurements [8, 9] are in disagreement with this possible 'tetravalency mechanism' for the depression of T_c, and instead it is suggested that T_c is suppressed through changes in the band structure when Pr is substituted for Y in Y-123. A lot of theoretical models have been proposed to explain the depression of superconductivity in Pr-123 compounds. These include hole filling [10], magnetic pair breaking [10, 11], hole localization [7], percolation [12], and hybridization [13–15]. However, no model gives a consistent interpretation of all experimental data. Recent experimental studies [16, 17] on Pr-doped 123 compounds indicate that the T_c-suppression predominantly results from the hole depletion effect.

While considerable efforts have been made to understand the effects of Pr incorporation in R-123, there are only a few reports [18–20] concerning the superconducting behaviour of the Pr-substituted R-124 system possessing double-Cu–O-chain networks. With this in mind, a systematic study on the Pr-doped R-124 compounds was undertaken in our laboratory to examine various possibilities for the T_c-depression mechanism.

In this letter we report measurements of the L_3 edges of Er and Pr in the $Er_{1-x}Pr_xBa_2Cu_4O_8$ system. An attempt has been made to understand the decrease in the normalized intensity of the L_3 edges of Er with increasing Pr doping in the framework of hole depletion.

The samples of pure and Pr-substituted $ErBa_2Cu_4O_8$ were prepared by the solid-state reaction method with Er_2O_3, $Ba(NO_3)_2$, CuO, and Pr_6O_{11}, each of 4N purity, as starting materials. These were mixed in the correct stoichiometric ratios required for each sample along with a 0.2 mole fraction of sodium oxalate ($Na_2C_2O_4$). The homogeneously mixed constituents were prereacted in powder form for 30 minutes at 900 °C and then cold pressed into pellets which were again heated for 24 h at 900 °C in a continuous flow of oxygen. The temperature was then reduced to 815 °C for another 48 h. The x-ray diffraction patterns were recorded to confirm the phase purity of all of the samples.

Measurements of the temperature-dependent resistivity of the pure and substituted Er-124 samples were carried out by the standard four-probe technique using a closed-cycle refrigerator. Air-drying silver paste was used to make electrical contacts. The L_3 edges of Er and Pr were recorded using a single-crystal x-ray absorption spectrometer. The data were recorded in the ± 200 eV region either side of the edge.

In figure 1 some of the Er L_3-edge x-ray absorption spectra for a series of $Er_{1-x}Pr_xBa_2Cu_4O_8$ samples are displayed. In the case of rare-earth L_3-edge spectra, the main absorption jump, often called the white line, indicates a transition from $2p_{3/2}$ to the
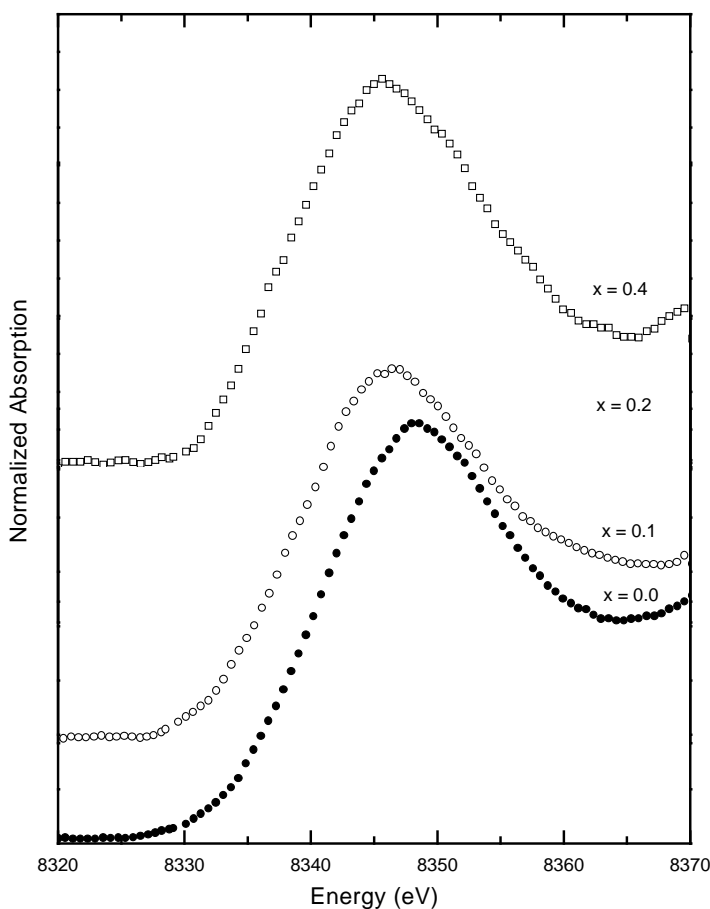

Figure 1. Er L_3 edges in $Er_{1-x}Pr_xBa_2Cu_4O_8$ for $x = 0$, 0.1, 0.2 and 0.4 compounds.

narrow conduction band having 5d symmetry above the Fermi level. An interesting feature to be noted here is the monotonic decrease in the intensity of the 'white line' with increasing Pr concentration x. In fact, the dependence of T_c on x is remarkably similar to that of the L_3-edge intensity (figure 2). The decrease of the Er L_3-edge intensity clearly indicates that Pr substitution results in a decrease of the hole concentration near the Fermi level.
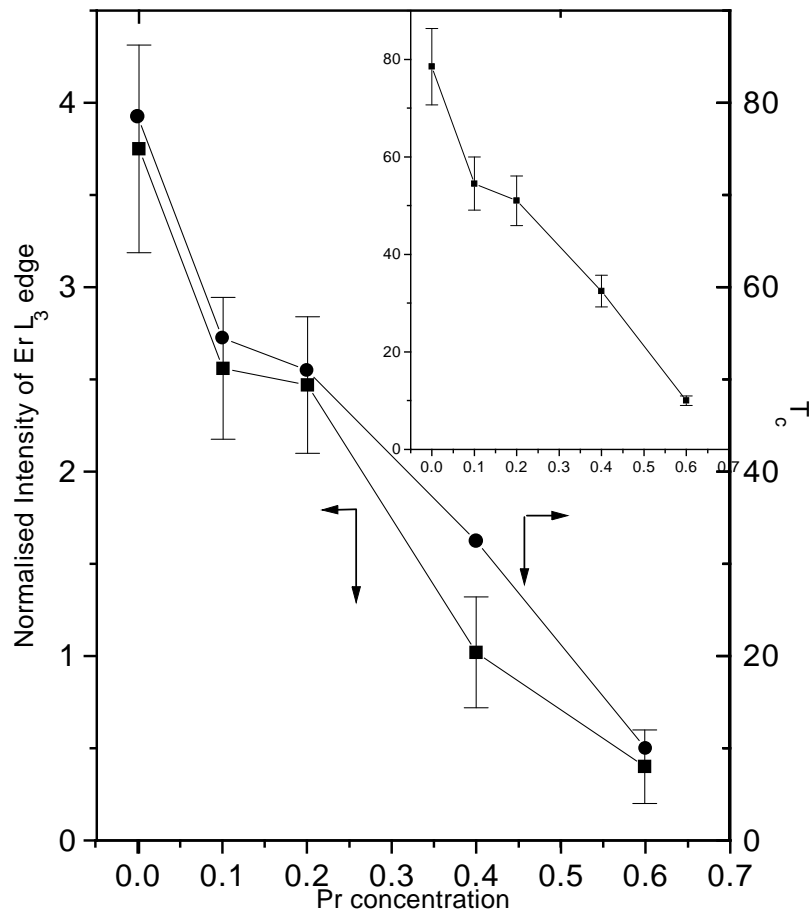

Figure 2. A plot of the variation of the Er L_3-edge intensity and T_c as a function of the Pr concentration. Error bars are shown for L_3-edge intensity data. The inset shows a plot of T_c versus Pr concentration with error bars.

Fehrenbacher and Rice (FR) have proposed that in the Pr-123 compound the holes are localized in a hybridized state at the Pr sites with a mixture of $4f^2L$ (+3) and $4f^1$ (+4) configurations [21]. Here, L is a ligand hole in the O 2p orbital around the Pr site, which is distributed over the eight nearest oxygen sites. They also proposed that the extra valence in addition to +3 of the Pr ion may not be detectable in some optical measurements, as the total probability of the $4f^1$ (Pr^{4+}) configuration is only about 15–20%. Hybridization of the Pr 4f electrons with those of copper and oxygen has also been proposed by Torrance and Metzger [13].

Recently, Liechtenstein and Mazin (LM) have modified the work of FR and proposed that, in $PrBa_2Cu_3O_7$, an additional hole-depleting band forms which crosses the Fermi level

and consequently takes holes from the CuO_2 band [22]. On doping $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ with different rare-earth elements, the position of this hole-depleting band shifts with the atomic number of the rare earth, through the energy level of the 4f orbitals, resulting in the R-dependent destruction of T_c. Hence, on substitution of Pr for R in R-123 or R-124, the hole depletion is due to charge transfer from holes in the CuO_2 planes and CuO_3 ribbons into the LM band. This model has been successfully used to explain the superconductivity suppression in $Dy_{1-x}Pr_xBa_2Cu_3O_7$ [16]. The indication of hole reduction in $Er_{1-x}Pr_xBa_2Cu_4O_8$ as obtained from Er L_3 edges gives support to the hole-depletion model proposed by LM.

The L_3 absorption edges of Pr in the 40 at.% and 60 at.% Pr substituted Er-124 system are shown in figure 3. The spectra are very similar to the Pr L_3-edge spectra for $Y_{1-x}Pr_xBa_2Cu_3O_7$ reported by Alleno *et al* [23]. The valency of Pr calculated from these edges demonstrates that Pr in the Er-124 system is close to trivalent, with an upper limit to the valence of 3.14 ± 0.05 for the 40 at.% sample and 3.16 ± 0.06 for the 60 at.% sample. Considering the accuracy of the experimental data, an admixture of about 10% Pr^{4+} cannot be excluded. This is in agreement with the FR and LM models.
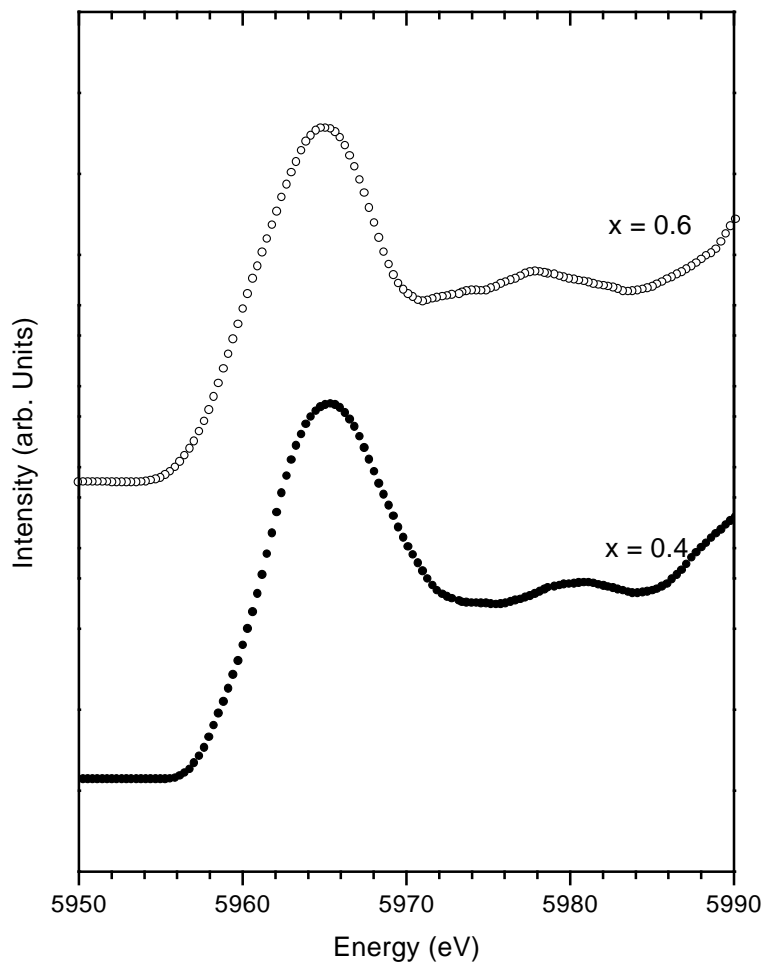

Figure 3. Pr L_3 edges in $Er_{1-x}Pr_xBa_2Cu_4O_8$ for $x = 0.4$ and 0.6 compounds.

In this letter we have studied the L_3 edges of Er and Pr in the Pr-doped Er-124 compounds. The monotonic decrease of the L_3-edge intensity with increasing Pr concentration suggests that the suppression of superconductivity with Pr doping is caused predominantly by hole depletion. The valence of Pr in these compounds shows that Pr ions are mostly trivalent and that they localize rather than fill the mobile holes in the CuO_2 planes. It is inferred that the mechanism for localizing the mobile holes would presumably be associated with Pr 4f and CuO_2 valence band hybridization.

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