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Evidence against hole filling by Pr in $YBa_2Cu_3O_7$

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Electron-energy-loss spectroscopy has been used to investigate the changes of the electronic structure in $Y_{1-x}Pr_xBa_2Cu_3O_7$ $(0 \leq x \leq 1)$. The O 1*s* absorption edges and the low-energy-loss function indicate that Pr does not fill holes in the CuO_2 planes. This suggests, by comparison with other experiments, that Pr localizes mobile holes thereby leading to the suppression of superconductivity and the metal-insulator transition.

After the discovery[1] of superconductivity at ~92 K in $YBa_2Cu_3O_7$ it was found[2-4] that replacement of Y by rare-earth elements with large magnetic moments does not affect its superconductive properties. There are three exceptions, namely the elements Ce, Tb, and Pr which have the common characteristics of also existing in the formally tetravalent state. Attempts to prepare $RBa_2Cu_3O_7$ (R = Y, Pr, and Gd) compounds have been found to yield multiphase materials for R = Ce or Tb (Ref. 5) and a single-phase compound that is isostructural to its superconducting $RBa_2Cu_3O_7$ counterparts, but has a slightly smaller orthorhombic distortion for R = Pr. In the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system, the superconducting transition temperature T_c decreases gradually to zero as x is increased to 0.6, and for $x \geq 0.6$, a negative temperature coefficient of electrical resistivity is observed,[6,7] which is indicative of non-metallic behavior.

Since superconductivity in these *p*-type-doped systems is dependent on the presence of holes predominantly on O sites in the CuO_2 planes,[8] it has been suggested that these holes will be filled when replacing trivalent Y by tetravalent Pr resulting in a decrease of T_c. Indeed, magnetic susceptibility,[7,9,10] Hall effect,[9] and chemical substitution studies,[11] are consistent with a valence greater than +3 for Pr and a reduction of mobile carriers. Pr valences ranging from +3 to +4 have been inferred from structural investigations.[12-14] An anomaly observed in the low-temperature specific heat can be described by a spin-$\frac{1}{2}$ Kondo anomaly,[15] suggesting that the ground state of Pr in the crystalline electric field is a doublet, which is consistent with a Pr valence of +4. Furthermore, Mössbauer spectroscopy[16] and muon-spin-relaxation measurements[17] suggest a magnetic ordering of Cu ions within the CuO_2 planes which could be explained by the filling of holes on O sites. However, high-energy-spectroscopy measurements strongly suggest trivalent Pr. X-ray-absorption spectroscopy on the L_3 edge[18] and the $M_{4,5}$ edges[19] of Pr as well as resonant photoemission[20] on the 4*f* states of Pr, all indicated a Pr valence close to +3. Finally, we note that recent spin-polarized band-structure calculations and total-energy calculations on $RBa_2Cu_3O_7$ indicate that a tetravalent Pr compound is energetically less favorable than the trivalent Pr compound.[21]

The contradictory conclusions regarding the Pr valence in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system can probably be traced to complications associated with hybridization between the Pr localized 4*f* states and the CuO_2 valence-band states as well as the layered crystal structure of these materials. Evidence for Pr 4*f*-CuO_2 valence-band hybridization in this system includes the anomalous pressure dependence of T_c (Refs. 22 and 23) and the complex line shape of the Pr 4*f* spectral weight, extracted from valence-band and resonant-photoemission measurements.[20]

In this study, we report on O 1*s* absorption edges measured in the system $Y_{1-x}Pr_xBa_2Cu_3O_7$ by electron energy-loss spectroscopy (EELS). This method measures the unoccupied density of states at the O sites having *p* symmetry, i.e., the total number of holes on oxygen sites,[8] which includes both mobile and localized holes. The data clearly show that the total number of holes on the O sites is independent of x indicating that the Pr ion does not fill but localizes mobile holes.

The samples were prepared by mixing stoichiometric amounts of oxide powders Pr_6O_{11}, Y_2O_3, $BaCO_3$, and CuO. The powder was fired the first time in air at 900 ° C for 2 d. It was then reground and fired for 2-3 d four times with intermediate grindings. Subsequently, the powder was pressed into pellets and fired in oxygen for 4 d at 980 °C. The specimens were slowly cooled at 1 °C/min to 540 °C where they remained overnight before a final slow cool at 1 °C/min to room temperature. All specimens were annealed together. Oxygen contents were determined by iodometric titration to be 6.95 ± 0.02. X-ray-diffraction shows that the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ alloys form in a single phase with an orthorhombic perovskite crystal structure as for $x=0$. Films of about 1000 Å thickness were cut from the samples by an ultramicrotome using a diamond knife. Subsequently, the films were floated on standard electron-microscope grids. The absorption edges from core levels and the low-energy-loss function were measured by high-energy EELS in transmission using a 170-keV spectrometer.[24] The full-width at half-maximum energy and momentum resolution was chosen to be 0.4 (0.15) eV and 0.2 (0.04) Å^{-1} for the absorption edges (low-energy-loss function), respectively.

In Fig. 1 we show O 1*s* absorption edges for the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for $x=0, 0.2, 0.4, 0.6, 0.8$, and 1.0. Similar EELS and x-ray-absorption spectra for the compound $x=0$ have been published previously.[8,25–28] While the spectral weight above ~530 eV is caused by O 2*p* states hybridized with Ba or Pr 5*d* and 4*f* and Y 4*d* states, in the region near threshold ($E<530$ eV) the spectral weight is caused by holes on O sites in the CuO_3 ribbons along the *b* axis and in the CuO_2 planes. The detailed form of the prepeak ($E<530$ eV) depends on the O concentration. The shape of the prepeak for $x=0$ is probably indicative of an O concentration of 6.7, i.e., $\delta=0.3$ (see Ref. 26). The small reduction of O content compared to the values derived from iodometric titration of the original pellets may be explained by an O release during the cutting process or in the ultrahigh vacuum of the EELS spectrometer. With increasing x ($x<0.5$), there is a slight increase of the prepeak intensity. Upon further increasing x there is again a slight decrease of the prepeak. The shape of the prepeak for $x=0$ and 1 is very similar, indicating that the number of holes in the two compounds is almost the same. The enhanced prepeak for $x=0.6$ is probably caused by a slightly higher O concentration compared to that of the $x=0$ and 1 compound. Furthermore, the low-energy loss function of $PrBa_2Cu_3O_{7-\delta}$ ($\delta\sim0.3$) is very similar to that measured for $YBa_2Cu_3O_{7-\delta}$ ($\delta\sim0.2$). In particular, a plasmon at ~1.5 eV is observed indicating a collective oscillation of the charge carriers, i.e., the holes on O sites.[29] Finally, our Pr 3*d* absorption edges which are contaminated by Cu 2*p* edges look very similar to those of Neukirch *et al.*[19] indicating a valence close to +3 for Pr in the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, irrespective of x. Thus, Pr does not appear to fill the holes in the CuO_2 planes.

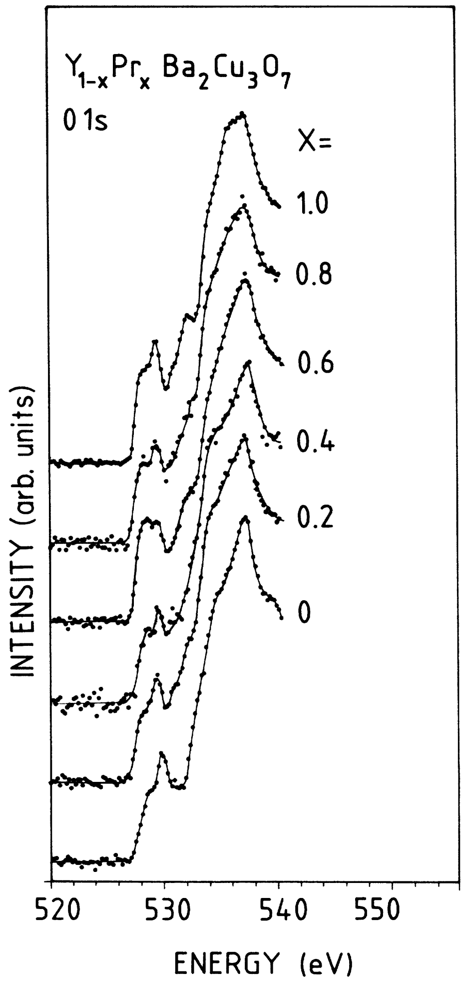

FIG. 1. O 1*s* absorption edges for the compounds $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for $x=0, 0.2, 0.4, 0.6, 0.8$, and 1.0, and $\delta\sim0.3$.

We would like to emphasize that filling of holes by increasing δ (i.e., by decreasing the oxygen concentration) is also clearly visible for the $PrBa_2Cu_3O_{7-\delta}$ compound. Release of oxygen was achieved by gently heating the film under ultrahigh vacuum conditions to 300 °C. In the case of $YBa_2Cu_3O_{7-\delta}$, this procedure results in a sample with $\delta\sim0.8$ and the same is expected to occur for the Pr compound. In Fig. 2, we compare the preedge structure of O 1*s* absorption edges for $PrBa_2Cu_3O_{7-\delta}$ samples with $\delta\sim0.2$ and 0.8. Clearly, a strong reduction of the prepeak

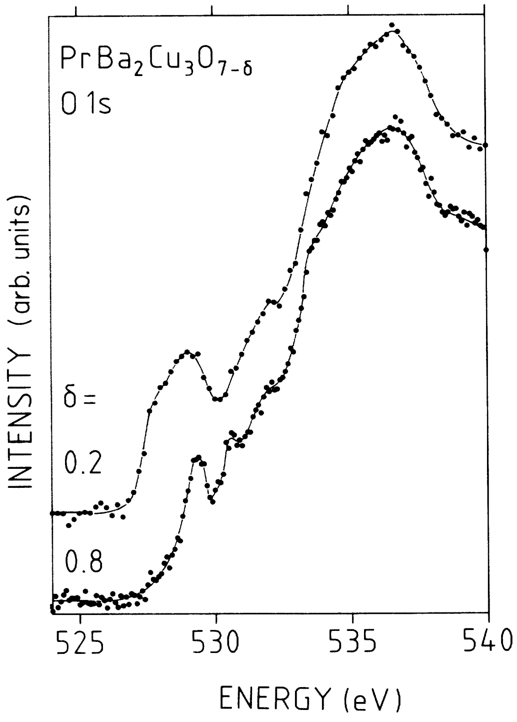

FIG. 2. O 1*s* absorption edges for the compounds $PrBa_2Cu_3O_{7-\delta}$ for $\delta\sim0.2$ and 0.8.

structure due to hole filling is realized which was also observed for the $YBa_2Cu_3O_{7-\delta}$ compound. The remaining peak at 529.5 eV in the spectrum for the compound with $\delta \sim 0.8$ is caused by transitions into the conduction band having some admixture of O $2p$ states.[26] Furthermore, in the low-energy spectrum, the plasmon has disappeared when increasing δ to about 0.8 in the $PrBa_2Cu_3O_{7-\delta}$ compound, a gap of ~ 2 eV has opened, and the sharp maximum at 4.3 eV is realized. These changes were observed[29] as well in $YBa_2Cu_3O_{7-\delta}$ compounds when changing δ.

All of the experimental results presented here strongly argue against a model where the suppression of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_7$ with increasing x is explained in terms of hole filling in CuO_2 planes and CuO_3 ribbons due to tetravalent Pr. Our results are consistent with previous high-energy spectroscopy investigations[18–20] indicating that Pr is trivalent in $Y_{1-x}Pr_xBa_2CuO_7$.

On the contrary, measurements of the Hall effect in this system[9] clearly exhibit a reduction of mobile carriers with increasing x. This suggests, by comparison with this study, that the effect of the Pr ion is not to destroy mobile holes by hole filling, but rather to localize them. We believe that an overall consistency can be realized when strong hybridization of the Pr $4f$ electrons with the conduction holes, as was suggested by the anomalous pressure dependence[22,23] of T_c and the complex line shape of the Pr $4f$ spectral weight extracted from valence-band photoemission studies,[20] is considered. This strong hybridization may lead to large crystal-field effects resulting in the reduced magnetic moment as mentioned in Ref. 20 and a large negative exchange interaction[11,30] between the Pr magnetic moments and the spins of the mobile holes in the CuO_2 planes which, in turn, could lead to the Kondo-like anomalies in the low-temperature specific heat[15] and the pair-breaking contribution to the depression of T_c which is linear in Pr concentration x for low values of x.[11] This hybridization may also be responsible for the observations here, that is, while the mobile hole concentration becomes smaller,[9] the total hole concentration remains essentially unchanged implying that the effect of Pr substitution for Y is the localization of mobile holes. This localization of mobile holes could account for the metal-insulator transition at $x \simeq 0.6$, the reduction of mobile carriers observed in Hall-effect studies,[9] the occurrence of Cu antiferromagnetism,[16,17] and the quadratic contribution to $T_c(x)$ in Ref. 11 that was previously attributed to the filling of mobile holes by Pr ions with a valence greater than +3. The analysis of Ref. 11, which was based upon measurements of $T_c(x,y)$ in the $(Y_{1-x-y}Ca_y)Pr_xBa_2Cu_3O_7$ system, would still be tenable, except that the parameters α and β would be interpreted as the optimal concentration of mobile holes and the fraction of a hole in the CuO_2 planes localized per Pr ion, respectively. It is remarkable that upon replacement of Cu by Zn in $YBa_2Cu_3O_7$, a similar quenching of superconductivity and a transition to a semiconductor is realized. As in this system, in the semiconducting state, holes on O sites were detected in the O $1s$ spectra and explained in terms of a localization of these holes.[31] Further investigations into the mechanism which leads to the localization of mobile holes in the CuO_2 planes in the Zn and Pr substituted $YBa_2Cu_3O_7$ systems may provide important information concerning superconductivity in the copper oxide high-T_c superconductors.

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