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TITLE

Electronic Structure of the Quenched Superconductivity Materials $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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Electronic Structure of the Quenched Superconductivity Materials $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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ABSTRACT

The superconductivity of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is quenched as x increases. It has been speculated that Pr has valence 4+, resulting in extra charge in the Cu-O planes, and causing T_c-quenching. To study the Pr electronic state, we have measured valence band resonant photoemission of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system for x=0, 0.2, 0.4, 0.6, 0.8 and 1.0. We find that the Pr valence is close to 3+ for all x and that the extracted Pr 4f spectral weight has a complex lineshape, implying extensive Pr 4f/ O 2p hybridization which probably causes the T_c-quenching by disrupting the electronic or magnetic structure of the x=0 material, perhaps via a Pr-Cu superexchange interaction.

I. INTRODUCTION

A clue to the origin of the high temperature superconductivity of $YBa_2Cu_3O_{7-\delta}$ may lie in the interesting finding that the superconductivity of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is quenched with increasing x[1-3]. Except for La, with transition temperature T_c - 70K to 80K, and Tb and Ce, for which the compounds do not form[4], superconductivity with T_c near 90K has been found in $RBa_2Cu_3O_{7-\delta}$ [5-9]. From the magnetic susceptibility measurements an effective magnetic moment of $2.7\mu_B$/ Pr-ion was extracted, independent of x[1], suggesting that the Pr valence has a fixed value of about 3.8. It can be speculated that if Pr has valence 4+, there will be extra charge in the Cu-O planes, causing T_c-quenching, by filling the holes in the Cu-O planes. In contrast, the lattice constants[9] of the $RBa_2Cu_3O_{7-\delta}$ series strongly suggest that Pr is trivalent. In fact, the Pr valence was concluded to be close to 3+ from x-ray absorption (XAS) measurements[10,11], although it was proposed that the T_c-quenching is due to charge transfer, arising from a modest deviation of valence from 3+ toward 4+.

It is thus important to know whether the Pr ion in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ alloy system is mixed valent or not. The discrepancy in the Pr valence obtained from different experiments stimulated us to investigate whether there are systematic changes in the Pr 4f electronic states as well as in the O 2p and Cu 3d states, as a function of x, using electron spectroscopy, which is one of the most powerful and direct measurements of the electronic structure of the materials.

In this paper we focus on the Pr electronic state, which we have studied by measuring valence band resonant photoemission (RESPES) of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, near the Pr 4d absorption edge (for x=0, 0.2, 0.4, 0.6, 0.8, and 1.0), including photoelectron energy distribution curves and two yield spectra, the constant-initial-state (CIS) spectrum and the constant-final-state (CFS) spectrum, described below. In agreement with XAS, we find that the Pr valence is close to 3+ for all x, and we also find the new information that the extracted Pr 4f spectral weight is very broad and asymmetric, implying extensive hybridization between Pr 4f and other valence band states. We speculate that the hybridization probably causes the T_c-quenching by disrupting the electronic or magnetic structure of $YBa_2Cu_3O_{7-\delta}$. This mechanism would apply particularly to the rare earths Pr, Ce and Tb, which have small 3+ ionization energies degenerate with the other valence band states.

The RESPES technique is used for this material to enhance the 4f emission[12] relative to that from filled Cu and O states, which otherwise dominate the valence band spectrum because of cross-section differences[13] and because many more electrons contribute. The resonance in the total 4f cross-section arises from the transition of a 4d electron into the 4f shell, producing intermediate excited states, followed by an Auger decay, such as

$4d^{10}4f^{n}$+ photon $\rightarrow$ $[4d^{9}4f^{n+1}]$ $\rightarrow$ $4d^{10}4f^{n-1}$+ photoelectron

The quantum interference between this and the direct photoionization channels gives rise to a Fano-type lineshape[14] in the total 4f cross-section with a minimum near the 4d absorption edge followed by a subsequent maximum. These resonance lineshapes can be observed in CIS and CFS yield spectra. CIS spectra are taken by sweeping the photon energy ($h\nu$) and the kinetic energy (E_k) of the electron analyzer simultaneously, so as to maintain $E_i=E_k+\phi-h\nu$ fixed, where ϕ is the work function of the analyzer. This technique therefore measures the $h\nu$-dependence of the cross-section of a fixed binding-energy photoelectron peak. CFS spectra are obtained by fixing E_k at a small value (which we set to be E_k=5 eV) and varying the photon energy $h\nu$. The CFS collects primarily inelastically scattered electrons coming from deep within the bulk ($E_k=h\nu+E_i-E_{loss}-\phi$), where E_{loss} is the energy lost due to inelastic scattering, and hence is generally thought to be proportional to the bulk photoabsorption spectrum.

Considering interconfiguration fluctuations (ICF), the scenario for the valence band spectrum in an insulating rare earth oxide is different from that in a metallic material.[15] In the metallic case, with ICF between Pr^{3+} and Pr^{4+}, the traditional ICF view is that the peak corresponding to $4f^2\rightarrow 4f^1$ is located at E_F, and a new peak corresponding to $4f^1\rightarrow 4f^0$ appears at approximately U below E_F, where U is the onsite Coulomb interaction between two f electrons. In this view, some electrons from the 4f shell fill conduction band states at E_F. For ICF in an insulating Pr-oxide, with stoichiometry such that Pr^{3+} corresponds to a filled oxygen band, Pr^{4+} can occur only by hybridization to conduction band states across the insulating gap, a process reduced by the gap and by the weak hybridization, which usually involves coupling of a Pr 4f wavefunction on one site with a Pr 5d wavefunction on another site. Instead hybridization between Pr 4f and oxygen 2p states mixes $4f^3L$ states into the otherwise ionic $4f^2$ ground state, where L means a ligand hole in the valence band. The valence band spectrum then shows an 'ionization' peak from $4f^1$ final states, and a 'relaxation' peak from $4f^2L$ final states pinned to the top of the valence band, so that the energy separation between the former peak and the latter peak is not related to U[15]. In either case, RESPES can provide a method to separate emissions from different valence states[16,17] because the intermediate state of the resonance is different for the different valence states and so their photon-energy dependences, i.e., the CIS spectra, are not the same. CFS spectra for the ICF material typically show absorption features due to two different valence states.

In the rest of this paper, we present in section II the experimental details and in section III, the RESPES results for Pr 4f emission. In section IV, we give a summary and discuss the implications for T_c-quenching.

II. EXPERIMENTAL DETAILS

The samples were prepared as described in Ref. 1, by mixing stoichiometric amounts of the oxide powders of Pr_6O_{11}, Y_2O_3, $BaCO_3$ and CuO. The powders were sintered three times at 900° C for several hours in air. The samples were then annealed at 950° C in flowing oxygen for about 40 hours and then slowly cooled to room temperature in about 30 hours. X-ray diffraction shows that the alloys $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ form in a single phase with the same orthorhombic perovskite crystal structure as for x=0, but that the degree of the orthorhombic distortion relative to the corresponding tetragonal structure is noticeably diminished[1] upon substitution of Pr. With increasing x from x=0, the normal state electrical resistivity shows a transition from metallic to semiconducting behavior, and a monotonic suppression of T_c which reaches zero at x~ 0.6. $BaCuO_2$ in amounts less than 8 mol% is observed in the x-ray data for x=0, 0.2, and 0.4. Since it does not involve Pr, this impurity will not affect the results reported here.

Room temperature resonant photoemission measurements were performed at the Stanford Synchrotron Radiation Laboratory using photons obtained from the grasshopper monochromator on beam line III-1 and using a commercial double-pass cylindrical mirror analyzer (CMA) to analyze the kinetic energies of the emitted electrons. The measured surfaces were obtained by cleaving the samples *in situ* in a vacuum chamber having a base pressure of 7×10^{-11} Torr. The experimental resolution, determined mostly by the CMA, is 0.5 eV unless otherwise indicated. The Fermi level of the system was determined from the valence band spectrum of a gold sample evaporated onto a stainless steel subtrate *in situ*. The photon flux was monitored by the yield from a stainless-steel target and the spectra reported below have all been normalized to this yield.

III. Results

Fig. 1 shows normalized valence band spectra for x=1.0 at several photon energies near the Pr 4d→4f absorption edge. Inelastic backgrounds were removed from the spectra by a standard method[12]. Although the overall shape for x=1.0 is very similar to those for x=0 in the literature[18-23], there are new features due to the resonating behavior of the Pr 4f states. The Pr 4f emission between E_F and –6 eV shows a Fano minium at $h\nu$=115 eV and a Fano maximum at $h\nu$=124 eV. The resonating Pr 5p emission can also be seen at around -20 eV, under which lies a rather broad bump with the character of Y 4p and O 2s states. The main band with a peak at about -5 eV is emission from Cu 3d/ O 2p states and the -9 eV feature present in all the spectra is not well understood yet. The -2.5 eV shoulder, which is also not understood in detail, but certainly involves oxygen states, can be seen clearly in the off-resonance spectrum with $h\nu$=115 eV. We have observed that this shoulder increases with x relative to the main peak. The -12 eV Cu d^8 satellite peak[22] is hard to distinguish for these photon energies because of the large emissions from the Ba 5p states at -13 eV and -16 eV. The emissions from the Ba 5p states decrease as the photon energy increases from 115 eV because the cross-section has a Fano resonance at $h\nu$=108 eV due to Ba 4d→4f absorption. Similarly, the emission at around –29 eV from the Ba 5s state is also decreasing.

Fig. 2 compares the Pr 4f spectra extracted from RESPES for x=0.2, 0.4, 0.6, 0.8, and 1.0. The spectra are scaled to have the same magnitude at the main peak. Each is obtained by subtracting the spectrum at the Fano minimum ($h\nu$=115 eV) from that at the Fano maximum ($h\nu$=124 eV), both taken with resolution of 0.35 eV. Before subtraction, the 115 eV spectra were scaled by α =0.9 to account for the $h\nu$-depedence of the non-4f emission where α was determined from the CIS spectrum of the Cu 3d/ O 2p main band for x=0. The shapes of the off-resonance spectra ($h\nu$=115 eV) are almost identical for all x. The areas under the Pr 4f spectral weights, calibrated by scaling the off-resonant spectra to be identical, are roughly proportional to the Pr-concentration as expected, with the relative ratios of *A(x=0.2): A(0.4): A(0.6); A(0.8); A(1.0)* = 0.34 : 0.44 : 0.58 : 0.80 : 1.18.

The main feature of Fig. 2 is that the shapes of the extracted Pr 4f spectra are essentially the same for all x, with the Pr 4f spectral weight essentially zero at E_F, rising to a large peak just below E_F, and then spreading out asymmetrically through the Cu 3d/ O 2p states, extending to −8 eV. The absence of weight at E_F is contrary to what is usually expected for strong mixed valence, while the spectral shape for the 4f state reflects extensive hybridization between Pr 4f and other valence band states. Broad and asymmetric 4f lineshapes also were observed in several Pr intermetallic compounds[24,25] having valence close to 3+, and could be analyzed using the impurity Anderson Hamiltonian[26]. In this treatment, hybridization effects and the large 4f Coulomb interaction play an important role[12,26]. Even in Pr metal, a weak 4f feature[27] near −1eV was described[26] as due to hybridization effects using the impurity Anderson Hamiltonian.

The top part of Fig. 3a shows the CIS spectra taken at the binding energy E_i= −0.8 eV for x=0.2, 0.4, 0.6, and 0.8, scaled to one another to compare their lineshapes. They are essentially identical for all x, suggesting no valence change as a function of x, which is consistent with the magnetic moment results[1]. The Pr 4f CIS spectrum of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ is very similar to the 4f CIS of Pr-metal[28], for which the Pr valence is close to 3+, in having a Fano lineshape with a maximum at $h\nu$=124 eV, which suggests that the valence of the Pr states at E_i= −0.8 eV is also close to 3+. The Pr metal CIS is shown at the bottom of Fig. 3a. The only difference is that the

Pr 4f CIS of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ has a more pronounced shoulder near 131eV than does the Pr 4f CIS of Pr metal. Such an extra shoulder occurs in the CIS for states near E_F in Pr metal[28]. In Fig. 3b, three CIS spectra taken at E_i values of -0.8 eV, -3.1 eV, and -6 eV, are compared on the same intensity scale for x=0.8. For other values of x (not shown here), the spectra are very similar to those of Fig. 3b. The bigger intensity at E_i= -0.8 eV reflects the peak in the Pr 4f spectral weight at this E_i. This figure shows that the lineshape of the CIS is invariant for different values of E_i over the range of the Pr 4f spectral weight distribution, which indicates that the emission does not have separate, non-overlapping contributions from two valence states. Thus the CIS spectra of the Pr 4f states give evidence that the valence of Pr is close to 3+ for all x.

Fig. 4a shows CFS spectra for hν near the Pr 4d absorption edge for x=0.2, 0.4, 0.6, and 0.8, scaled to one another as is done in Fig 3a. The spectra have two absorption features at 124 eV and 131 eV which are similar to those for Pr metal[28], and an extra feature at 119 eV. Since the CFS spectrum for x=0 (not shown here) shows the same feature at about 119 eV but no features at 124 eV or 131 eV, this extra feature is identified as coming from Ba 4d→4f absorption. To account for the non-Pr absorption for x>0, the CFS spectrum for x=0 is subtracted from each CFS spectrum for x>0, after matching the flat region between hν=105 eV and hν=117 eV.

The upper part of Fig. 4b displays the CFS spectra corrected by removing the non-Pr 4d absorption features as described above. The spectra are scaled to have the same magnitude at 131eV. They are essentially identical for all x, giving evidence of no valence change as a function of x. The overall lineshapes of these CFS spectra are very similar to that for Pr metal[28], shown at the bottom of the figure. Because of insufficient statistics, the weak fine-structure features[29-31] which are usually observed between 105 eV and 120 eV just before the giant absorption edge for Pr 3+, can not be seen clearly in the CFS of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. Due to the dynamical effects of hybridization, XAS spectral weights typically are not in direct proportion to the valence and require detailed theoretical analysis to extract a valence[26]. At present our conclusions are limited to the observation that there is no indication of a separate 4d→4f absorption process corresponding to a different valence state in any of the CFS spectra, which shows, at least, that strong mixed valence does not occur, and certainly not a pure Pr^{4+} state.

We have also measured the RESPES valence band spectra near the Cu 3p→3d absorption edge and near the O 2s→2p absorption edge, the conduction band bremsstrahlung isochromat spectrum and the core-level x-ray photoemission spectra of Cu 2p/ O 1s/ Ba 3d states for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system. All of these results will be reported in detail in another paper. Among other things, we find that the Cu valence is essentially unchanged with x.

IV. SUMMARY AND DISCUSSION

We now discuss the implications of our results for the magnitude of the Pr magnetic moment and the mechanism of T_c-quenching. We have found that the Pr valence is close to 3+ for all x, consistent with XAS results and with lattice parameter measurements[9]. In addition, the extracted Pr 4f spectrum has almost no weight at E_F, while the Pr 4f spectral lineshape indicates much hybridization to other valence band states. As discussed in the introduction, the measured Pr magnetic moment is smaller than one would expect for Pr^{3+}. A reduced moment could arise from quenching of the orbital angular momentum due to the low-symmetry crystal field. Although such effects are usually expected to be larger for transition metal ions than rare earths because the 4f shells of the latter lie deep inside the filled 5s and 5p shells, the observed strong hybridization, which is one microscopic origin of the crystal field, suggests that the crystal field effects could be large in this case. Indeed, crystal field splittings were observed in specific heat data[32] for $RBa_2Cu_3O_{7-\delta}$ materials, although not specifically for R=Pr. In Ce intermetallic compounds[33] there is strong evidence that hybridization between the 4f and conduction band electrons leads to magnetic moment suppression due to the Kondo effect. But for the Pr alloys considered here the density of states at the Fermi level seems too small for this mechanism, and for x=1, the materials are insulators. At present, then, it seems that the the magnetic moment reduction must be attributed to the large hybridization but the exact mechanism has not been identified.

Our findings in this study strongly suggest an alternative to the previous suggestions that superconductivity is quenched by the charge transfer mechanism, i.e., that the Pr valence departs from 3+ so that extra electrons from the Pr ion are transferred to the Cu-O planes. The fact that Pr is close to 3+ makes this mechanism implausible. Our result suggests the alternative that extensive hybridization between Pr 4f and other valence band states may have disrupted some feature of the electronic or magnetic structure of the x=0 material which is essential for superconductivity. This mechanism would apply particularly to the rare earths Pr, Ce and Tb for which the 4f states have small 3+ ionization energies degenerate with the other valence band states, a situation favoring strong hybridization.

The Y/Pr layer is located between two Cu-O planes in the crystal structure[34] and the nearest neighbors of an Y/Pr-site are oxygens in the Cu-O planes, and so it is expected that hybridization between Pr 4f states and 2p states of the O atoms in the Cu-O planes is the largest. A likely result is a superexchange interaction between the moments of Pr atoms and those of the planar Cu atoms. Rare earth-transition metal exchange interactions are known to occur for the perovskite rare earth orthoferrities and orthochromites.[35] Neutron scattering experiments now being performed[36] for $PrBa_2Cu_3O_{7-\delta}$ may provide direct evidence concerning such exchange interactions in the near future. We might speculate that such interactions could quench superconductivity by altering magnetic correlations in the Cu-O planes, if indeed these correlations play an important role in the pairing interaction, as many believe. Alternatively the superconductivity may be affected through changes in the electronic structure of the oxygen states, since it appears likely that holes in these states provide carriers for pairing. Moreover, orbitals perpendicular to the Cu-O planes are expected to have larger hybridization with the Pr 4f states rather than those parallel to the Cu-O planes because the Y/Pr layer is located between two Cu-O planes. This may provide a way to understand the fact that the orthorhombic distortion is greatly diminished with increasing x in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$[1]. The orthorhombic distortion is determined by the distribution of oxygen atoms along the Cu-O chains[34] and it is possible that these oxygen atoms feel the effect of Pr substitution via the coupling between the oxygen orbitals perpendicular to the Cu-O planes and the oxygen orbitals in the bridging sites.

To summarize, our major finding in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is that the Pr valence is close to 3+ for all x and that the extracted Pr 4f spectral weight has a broad and asymmetric lineshape which implies a large hybridization with other valence band states. From this finding, we infer that Pr 4f/O 2p hybridization must have altered the electronic or magnetic structure of the x=0 material in some essential way to cause the T_c-suppression, possibly involving superexchange with planar Cu.

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FIGURE CAPTIONS

Fig.1.The normalized valence band spectrum for x=1.0 near the Pr 4d to 4f absorption edge. The Pr 4f emission shows a resonant behavior between E_F and –6 eV.

Fig.2.The extracted Pr 4f spectra for x=0.2, 0.4, 0.6, 0.8, and 1.0. Note the broad and asymmetric lineshape.

Fig.3.(a) Top: the CIS spectra at E_i= –0.8 eV for x=0.2, 0.4, 0.6, and 0.8. Note that the spectra are essentially identical.

Bottom: Pr 4f CIS of Pr-metal (Gerken, ref. 24).

(b) The CIS spectra for $Y_{0.2}Pr_{0.8}Ba_2Cu_3O_{7-\delta}$ at different E_i's in the Pr 4f spectrum, (a) E_i= –0.8 eV, (b) E_i= –3.1 eV, and (c) E_i= –6 eV.

Fig.4.(a) The raw CFS spectra near Pr 4d absorption for x=0.2, 0.4, 0.6, and 0.8.

(b) Shown at the top are CFS spectra, corrected from those in Fig. 4a as described in the text. The linehsapes are same for all x and very similar to that for Pr-metal (Gerken, ref. 24), shown at the bottom.

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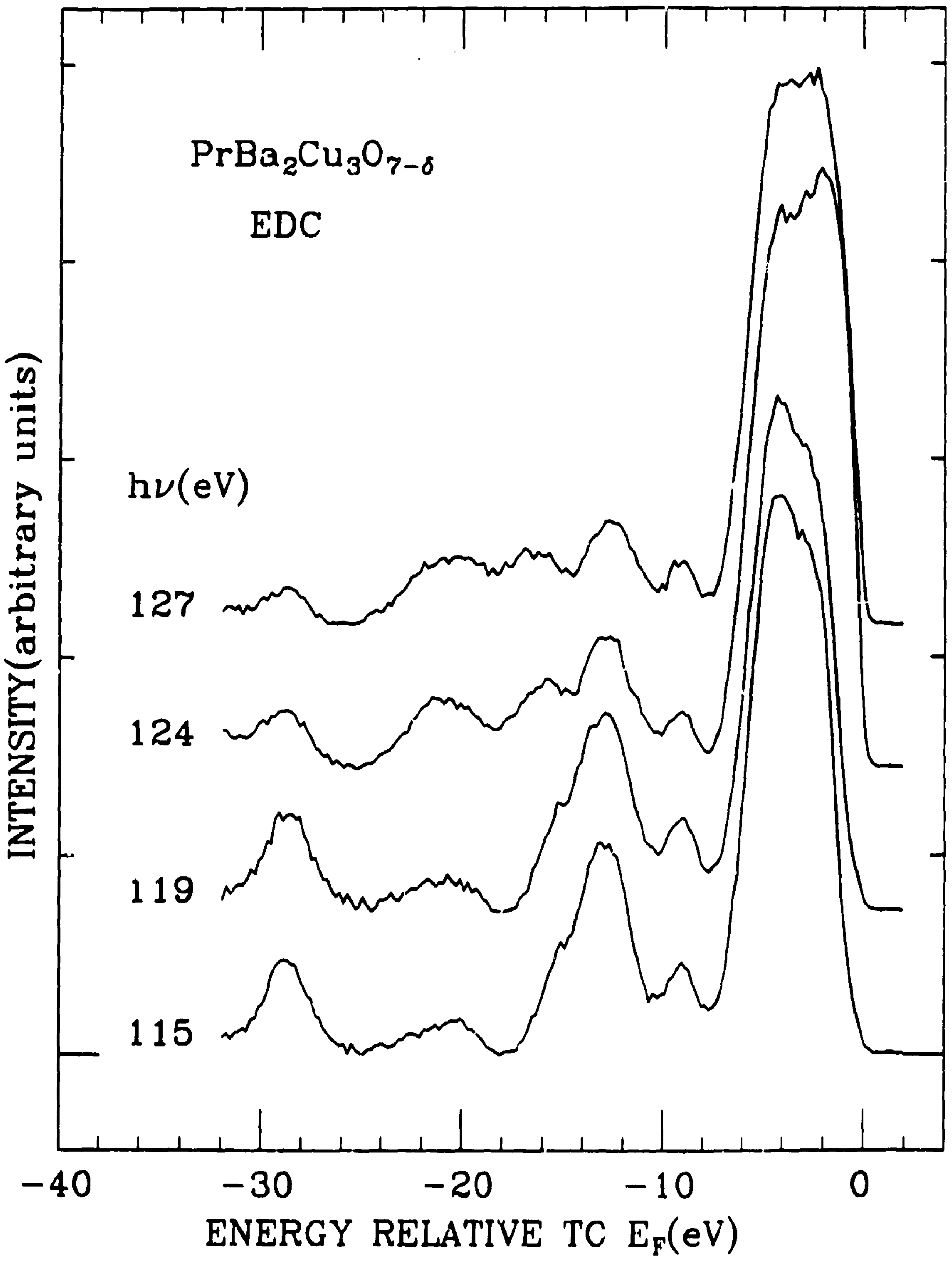
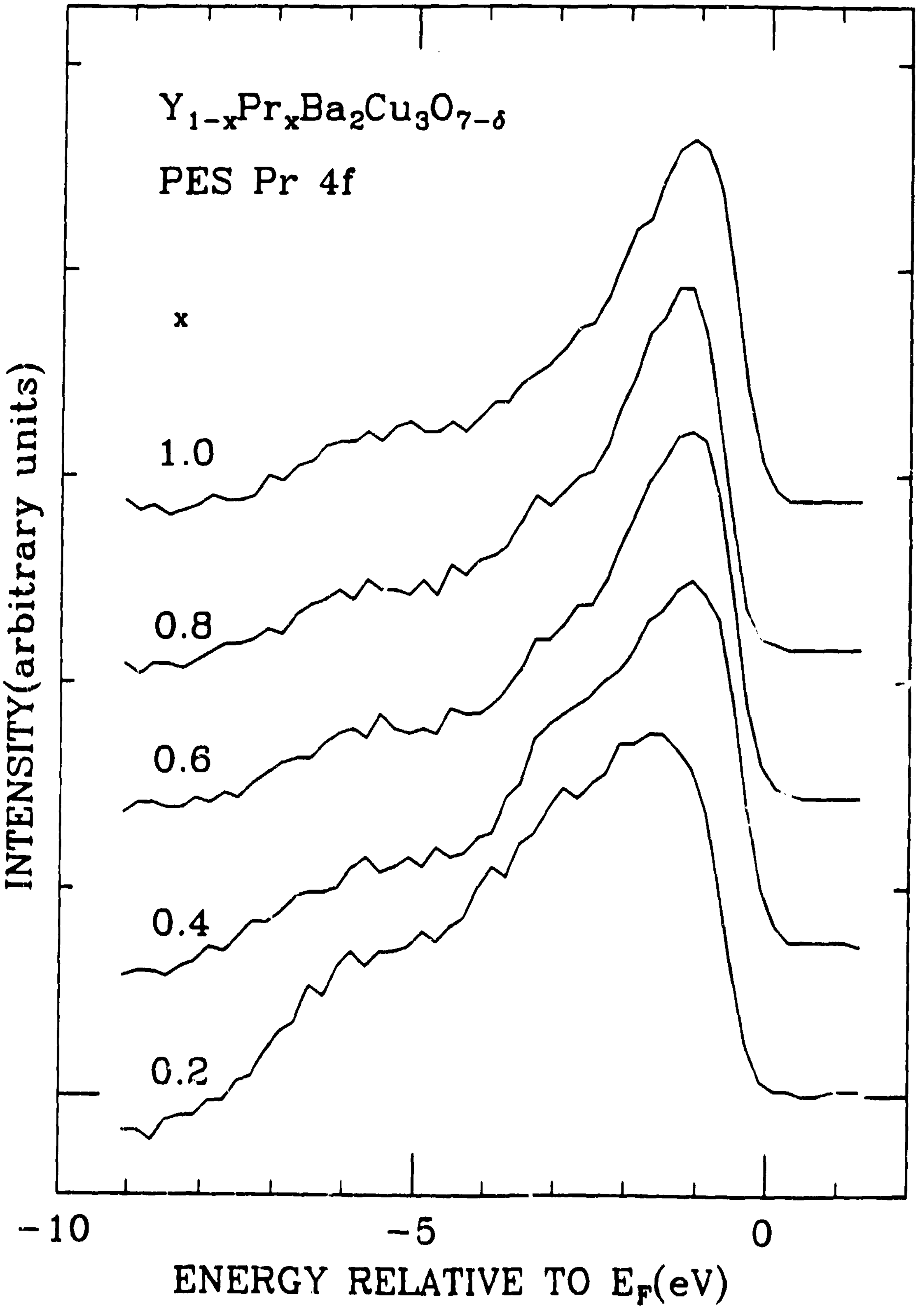
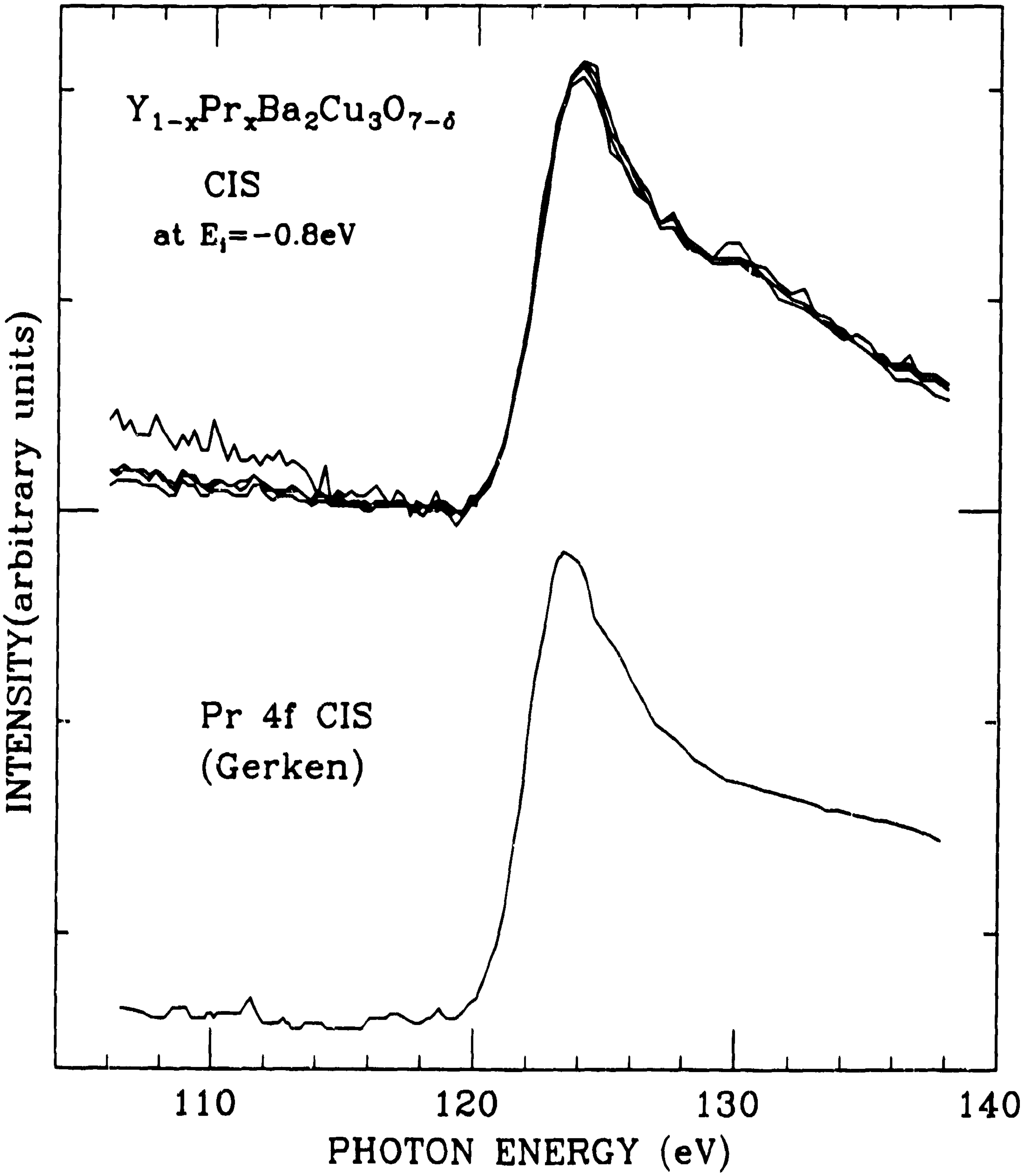

$PrBa_2Cu_3O_{7-\delta}$
EDC
hν(eV)
127
124
119
115
INTENSITY(arbitrary units)
−40
−30
−20
−10
0
ENERGY RELATIVE TC E_F(eV)

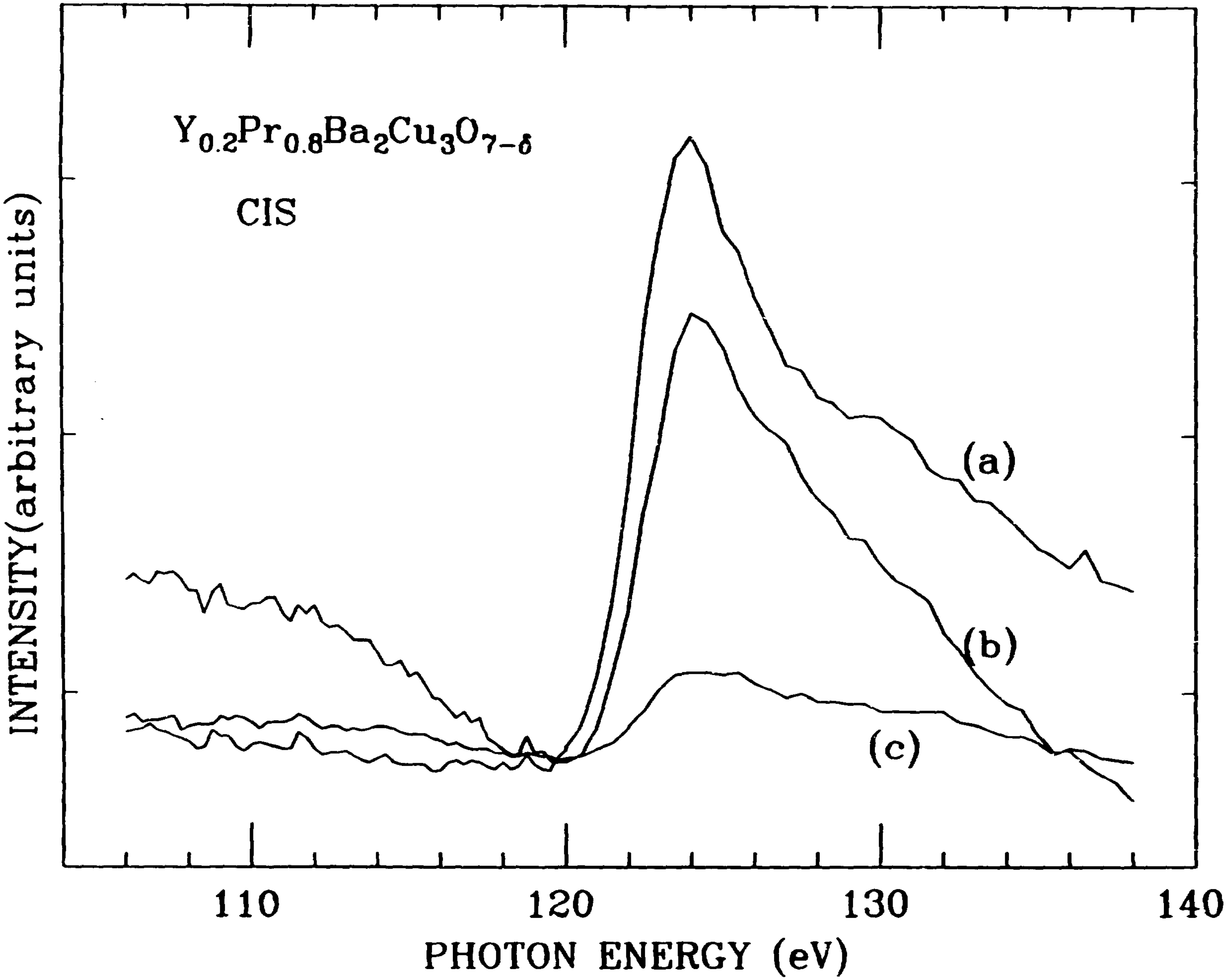
(Fig. 1)


$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$
PES Pr 4f
x
1.0
0.8
0.6
0.4
0.2
INTENSITY(arbitrary units)
−10
−5
0
ENERGY RELATIVE TO E_F(eV)

(fig 3a)

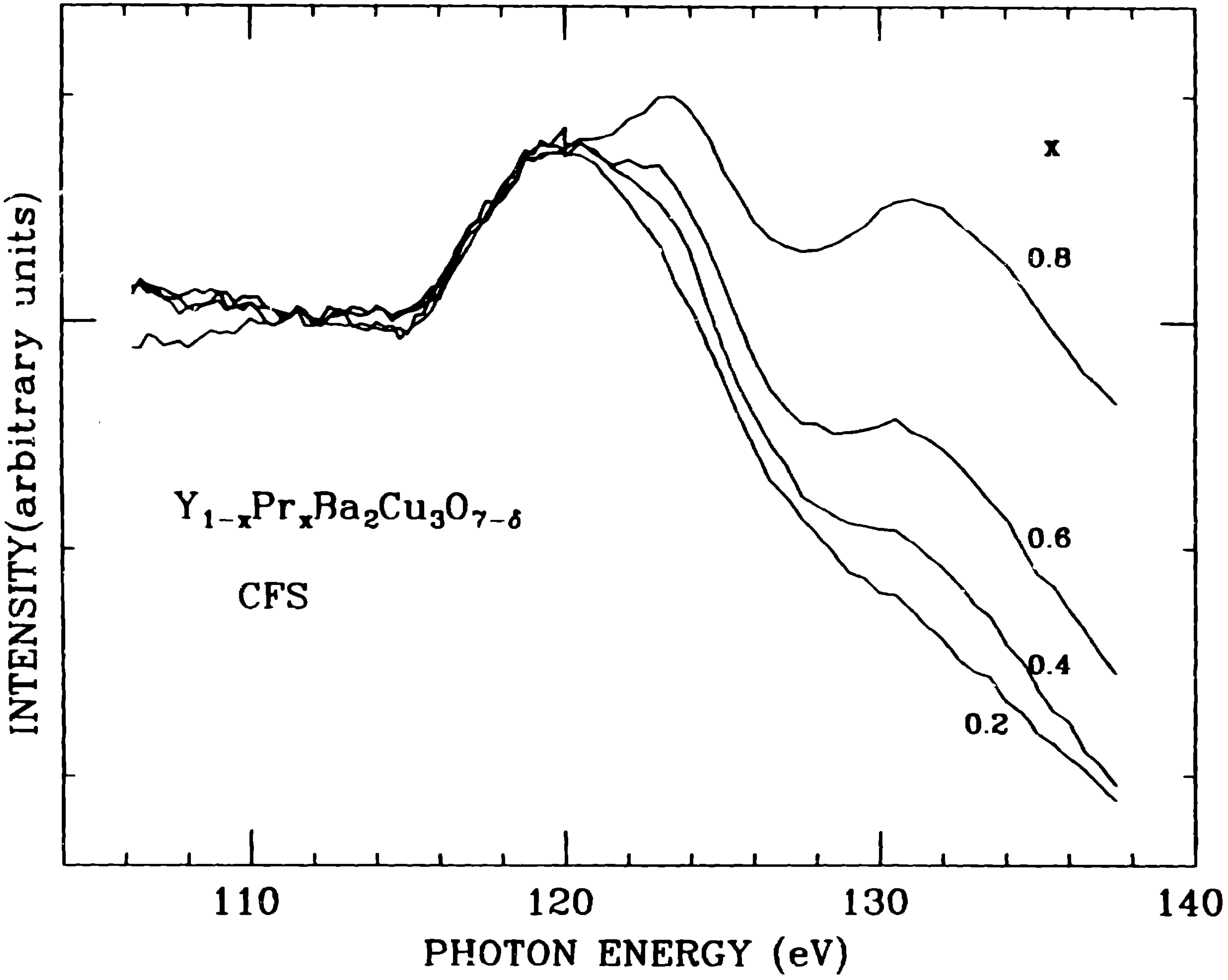

$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$
CIS
at E_i=−0.8eV
Pr 4f CIS
(Gerken)
INTENSITY(arbitrary units)
110
120
130
140
PHOTON ENERGY (eV)

(Fig 3b)

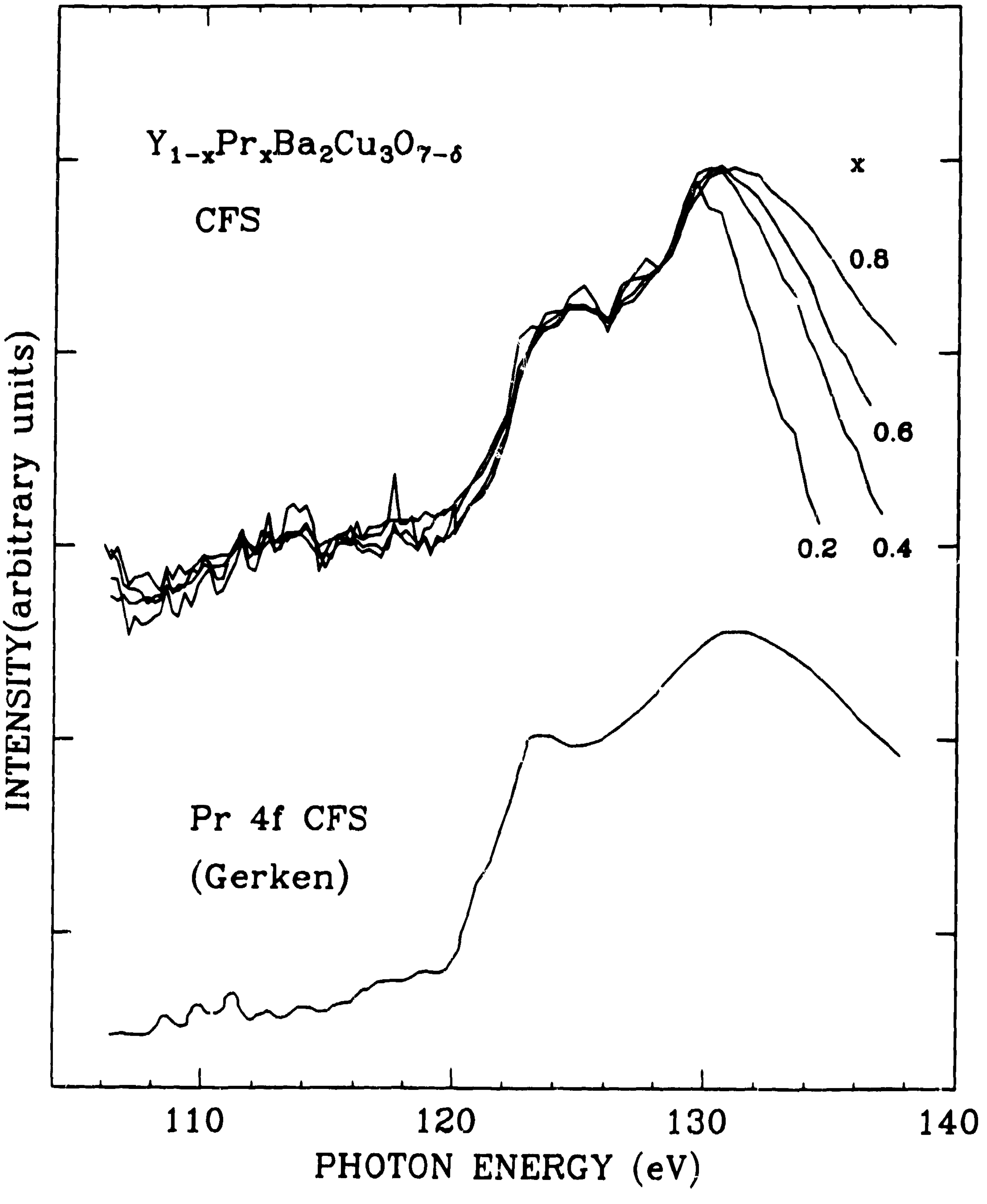


$Y_{0.2}Pr_{0.8}Ba_2Cu_3O_{7-\delta}$
CIS
(a)
(b)
(c)
INTENSITY(arbitrary units)
110
120
130
140
PHOTON ENERGY (eV)

(fig 4a)


x
0.8
0.6
0.4
0.2
$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$
CFS
INTENSITY(arbitrary units)
110
120
130
140
PHOTON ENERGY (eV)

(Fig 4b)



$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$
CFS
x
0.8
0.6
0.2
0.4
Pr 4f CFS
(Gerken)
INTENSITY(arbitrary units)
110
120
130
140
PHOTON ENERGY (eV)