室蘭工業大学
学術資源アーカイブ

Muroran Institute of Technology Academic Resources Archive

Enhancement of critical Pr ion concentration (xcr) in (La1-xPrx)Ba2Cu3Oz

Enhancement of critical Pr ion concentration (x_{cr}) in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$

M. Murugesan,[a] T. Ishigaki, and H. Kuwano
Department of Materials Science and Engineering, Muroran Institute of Technology, 27-1 Mizumoto Cho, Muroran-050 8585, Japan

M. Chen
Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan, Republic of China

R. S. Liu and P. Nachimuthu
Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

The substitutional effect of Pr ion for La in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ bulk samples prepared under modified synthesis condition has been studied. Low field magnetization studies showed that superconductivity is retained up to the critical Pr ion concentration, $x_{cr}=0.40$. The effective magnetic moment of Pr^{3+} free ion is very low in the present series of compounds. Results of X-ray absorption near-edge structure spectra for the series of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ compounds with $0.00 < x < 0.60$ reveal that the doped Pr ion reduces hole concentration within the CuO_2 planes, leading to a destruction of superconductivity. © *1999 American Institute of Physics.* [S0021-8979(99)05924-1]

I. INTRODUCTION

It has been well established that the valence state, as well as the ionic radius of the rare earth ions, are two of the most vital factors for obtaining 90 K superconductivity in the $(RE)Ba_2Cu_3O_z$ (RE=rare earth elements) class of superconductors. Among $(RE)Ba_2Cu_3O_z$ compounds, T_c has no significant dependence on the quaternary element (88–92 K)[1,2] except for RE=La, Ce, Pr, Tb, and Lu. While the Pr compound shows neither superconductivity nor metallic conduction (although it has an orthorhombic structure isomorphic to that of $YBa_2Cu_3O_z$), the Ce and Tb analogs do not even exist in the same structure.[3] It has been argued that the nonformation of the Ce and Tb compounds and the absence of superconductivity in the case of Pr are owing to the existence of stable valence state other than +3. Ce and Tb form the stable ternary oxides, viz, $BaCeO_3$ and $BaTbO_3$, respectively.[3] On the other hand, the partial substitution of Pr for Y in $YBa_2Cu_3O_z$ results in the suppression of T_c while Tb does not alter the T_c.[4] Several mechanisms have been proposed to account for the systematic suppression of superconductivity in $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$ by Pr ion and most of them centered on the valence state of Pr, which is under controversy.[5–11]

Ionic size of the rare earth element is also crucial as it leads to steric effects, resulting in distortion of the local environment around the rare earth ion.[12] These localized effects may play a very significant role: if the perturbations extend to the adjacent layers where the superconducting electrons are confined this can cause some changes in the bond lengths of the Cu–O layers, which strongly affect the superconductivity in high-T_c cuprates. Hence, at the extreme right of the lanthanide series, the formation of single phase $LuBa_2Cu_3O_z$

in bulk form is extremely difficult.[13,14] It has also been suggested that the ionic radius of Lu^{3+} falls just short of the critical radius required for the stabilization of RE-1:2:3 phase. On the other hand, at the extreme left of the lanthanide series, the largest lanthanide ion, namely La, also does not form the superconducting 1:2:3 phase readily. Unlike the standard $(RE)Ba_2Cu_3O_z$ with $T_c \sim 90$ K, the presence of superconductivity in $LaBa_2Cu_3O_z$ is highly controversial. Having analyzed the complex phase diagram of $La_2O_3+BaCO_3+CuO$, several authors have reported that the superconducting RE-1:2:3 phase cannot be made for RE=La.[15,16] Many reports confirm a very low T_c[17] while Wada *et al.*[18] report a T_c of 90 K with a completely modified synthesis condition. There were even reports of the absence of superconductivity both in thin films and bulk samples.[19] Also, some reports say that the observation of low T_c value in $LaBa_2Cu_3O_z$ and the absence of superconductivity in $PrBa_2Cu_3O_z$ are due to the possible fractional occupation of La and Pr ions at the Ba site,[20,21] respectively.

It is a general consensus that the strong hybridization of Cu $3d$ and O $2p$ wave functions places the hole state on the oxygen sites in the hole superconductors. It is important to understand the hole distribution among the different oxygen sites and their role of superconductivity. As there are many nonequivalent oxygen sites in the cuprate superconductors, it is expected that the O K-edge x-ray absorption spectrum shows multiple pre-edge peaks due to different oxygen environments. If the substituted Pr and La occupy only the RE site, it will affect the CuO_2 plane O K-edge spectra. If, on the other hand, fraction of the Pr and La goes onto the Ba site CuO chain O K-edge spectra are affected. Therefore, it is valuable to probe this system by x-ray absorption near-edge structure (XANES) to understand the mechanism of suppression of superconductivity in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$. There

[a]Electronic mail: murugesh@oyna.cc.muroran-it.ac.jp

have been few, if any, previous reports on the suppression of superconductivity by the Pr ion in the $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ system. Hence, to get an insight into the low T_c value of $LaBa_2Cu_3O_z$ as well as the mechanism of suppression of superconductivity in the case of Pr, we have studied the synthesis and characterization of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ compounds.

II. EXPERIMENT

Samples have been prepared by the conventional solid state reaction using La_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO with 4N purity. The La_2O_3 powder was used after firing at 1000 °C for 12 h, because La_2O_3 is hygroscopic. The powders were mixed, ground, and calcined at 930 °C for 24 h. The resulting mixture was reground and calcined at 950 °C for 10 h. The recalcined powder was pressed into pellets and sintered at 980 °C for 40 h in N_2 atmosphere. As-sintered pellets were then annealed at 300 °C for 40 h in O_2 atmosphere. The crystal structure was checked by powder x-ray diffraction (XRD) using Cu K_α radiation. A superconducting quantum interference device (SQUID) magnetometer was used to get both the low field (to determine T_c) and high field (to evaluate the μ_{eff} of Pr) dc magnetic susceptibility data. The x-ray absorption measurements were performed with 6 m high-energy spherical grating monochromator (HSGM) beamline of the Synchrotron Radiation Research Center (SRRC) in Taiwan. The x-ray fluorescence yield spectra were recorded with a microchannel plate (MCP) detector.[22] This detector consists of a dual set of MCPs with an electrically isolated grid mounted in front of them. For x-ray fluorescence yield detection, the grid was set to a voltage of 100 V while the front ends of the MCPs were set to −2000 V and rear ends to −200 V. The grid bias insured that positive ions would not be detected while the MCP bias insured that no electrons were detected. The MCP detector was located 2 cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of 45° with respect to the sample normal. The incident photon flux (I_0) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. All of the absorption spectra were normalized to I_0. The photon energies were calibrated within an accuracy of 0.1 eV by using the known O K-edge and Cu $L3$-edge absorption peaks of the CuO compound. The energy resolution of the monochromator was set to 0.22 and 0.45 eV for the O K-edge and Cu L-edge absorption measurements. All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

XRD patterns for the series of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ samples with x varying from 0 to 0.6 are shown in Fig. 1. All the samples except for $x=0$ showed single phase orthorhombic $Pmmm$ structure. As the Pr concentration exceeds $x=0.4$, a small amount of an unidentified impurity phase (as marked by ''*'') was detected. It is worth noting that the pure $LaBa_2Cu_3O_z$ phase does not readily form under the normal RE-1:2:3 synthesis conditions. Even in the present modified synthesis condition, we observe strong impurity lines.
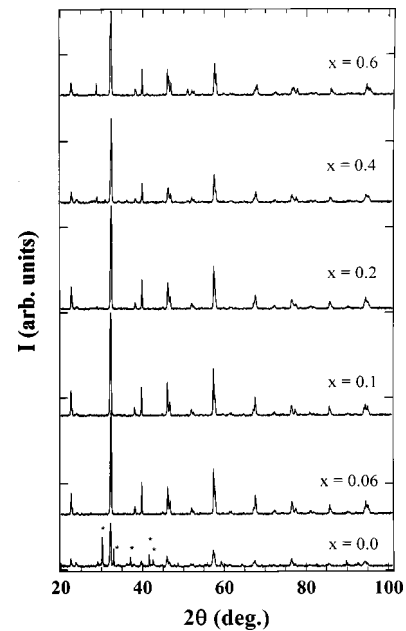

FIG. 1. XRD spectra of bulk $(La_{1-x}Pr_x)Ba_2Cu_3O_z$. Impurity peaks are marked by ''*''.

Earlier it has been suggested that the RE_2BaCuO_5 phase (found to be more stable than the corresponding RE-1:2:3 phase for temperatures in the region of 900–950 °C) could possibly prevent the formation of some of the superconducting RE-1:2:3 phase as in the case of the smallest RE=Lu.[23–25] Hence, we thought that the existence of highly stable La_2BaCuO_5 may hinder the formation of a stable $LaBa_2Cu_3O_z$ phase. To test this hypothesis, we calculated the Global Instability Index (GII),[26,27] for RE_2BaCuO_5 by using the values obtained from Refs. 25, 28, 29

$$GII= \sqrt{\left\{ \sum_{i=1}^{n} \left[\sum_{j=1}^{n} \left(\sum_{ij} = V_i \right)^2 \right] \Big/ N \right\}}, \qquad (1)$$

where V_i is the formal valence of the ith cation, which is calculated from the bond valence sum rule.[30,31]

Presented in Fig. 2 is the plot of GII for RE_2BaCuO_5 as a function of RE ionic size. It is clear from the figure that GII

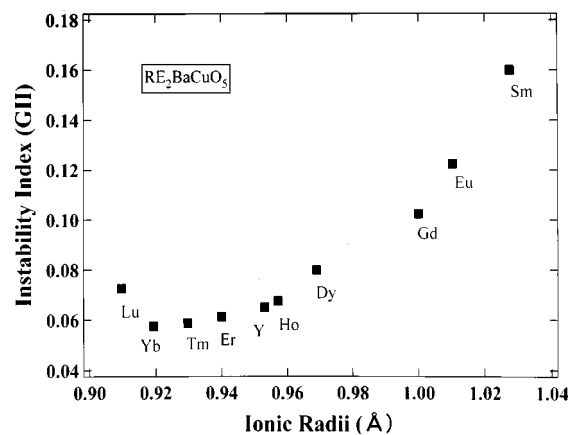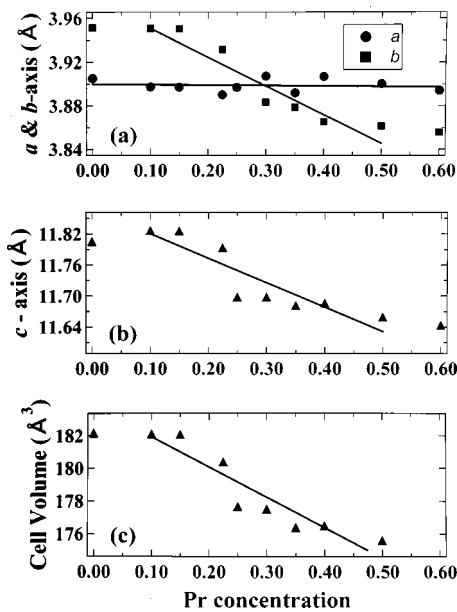FIG. 2. Variation of GII as a function of ionic radius of RE ion for RE_2BaCuO_5.

FIG. 3. Plot of lattice parameters (a) a and b, (b) c and (c) the cell volume vs Pr concentration, x for $(La_{1-x}Pr_x)Ba_2Cu_3O_z$.

FIG. 4. Temperature dependence of low field magnetization (5 Oe, field cooled) in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ samples for various x values.

values (most stable) are the minimum for RE=Yb, Tm, and Er and for RE=Y and Ho, the GII values are relatively low but still higher than the minimum. As the ionic size of the RE ion increases, the GII reaches the maximum (least stable) for Sm. This could justify the fact that for Nd_2BaCuO_5 and La_2BaCuO_5 oxides, having Nd^{3+} and La^{3+} with a larger ionic radius than Sm^{3+}, this structure does not exist. From these results it is very clear that since La_2BaCuO_5 has a very high GII and the structure does not exist, one should easily get $LaBa_2Cu_3O_z$ under normal 1:2:3 synthesis conditions. However, we fail to obtain a phase pure $LaBa_2Cu_3O_z$ with optimum T_c value of 90 K. This suggests that the stability of the 211 phase does not prevent the formation of $LaBa_2Cu_3O_z$ phase. A similar kind of contradiction has been reported in the case of $LuBa_2Cu_3O_z$,[32] where the $LuBa_2Cu_3O_z$ phase does not form in the bulk due to the smaller ionic size of the Lu^{3+} ion, and the partial substitution of larger ionic radius Pr, Tb, Ca for Lu stabilizes the superconducting phase. In the present study also, the partial substitution of even 6% Pr for La stabilizes the superconducting 1:2:3 phase to a large extent. Since the ionic radius of Pr^{3+} $(1.126 Å)$[33] is smaller than that of La^{3+}, the average effective ionic radius of the system is smaller than the critical radius, and hence, should have allowed the synthesis of phase pure superconducting $La_{1-x}Pr_xBa_2Cu_3O_z$. These studies have given sufficient evidence that it is not the stability of 211 phase that prevents the formation of the $LaBa_2Cu_3O_z$ phase. On the contrary, it is the larger ionic radius of La^{3+}, which is greater than the critical radius allowed for the existence of La_2BaCuO_5 that accounts for the nonformation of $LaBa_2Cu_3O_z$.

Lattice parameters were determined by a least-squares fit method. The calculated values (for $x=0$; $a=3.897 4(1) Å$, $b=3.950 6(4) Å$ and $c=11.804 8(2) Å$) are very close to the previously reported data.[34,35] The variation of the lattice parameters with Pr concentration is presented in Fig. 3. Although $x=0.3$ sample has close 'a' and 'b' values, in our
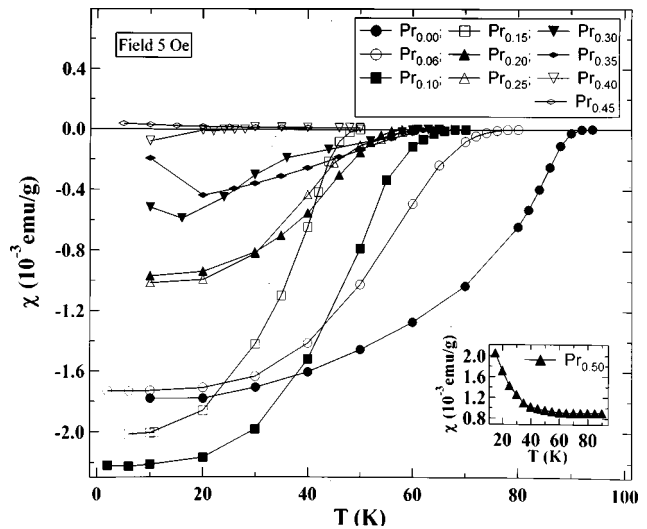
analysis we could get a better fit for *Pmmm* (orthorhombic structure) rather than *P4/mmm* (tetragonal structure). Whereas the variation of lattice parameter a with x does not exhibit any dramatic change, the lattice parameters b,c and the overall unit cell volume decreases monotonously with increase in x. Such a uniform decrease in cell parameters arises from the gradual replacement of the larger La^{3+} ions [1.160 Å for eight coordination] by smaller Pr^{3+} ions [1.126 Å for eight coordination].[33]

Depicted in Fig. 4 is the temperature dependence of low field magnetization for $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ samples. A strong diamagnetic signal around 92 K (onset) is observed for the $x=0$ sample. As the Pr ion concentration increases, the onset shifts gradually to lower temperatures and finally for $x=0.45$ the superconductivity has vanished. The superconducting volume fraction is obtained as a strength of a diamagnetic signal normalized at $x=0$ at 10 K in a 5 Oe magnetic field. T_c as well as the volume fraction decreases with increasing x as shown in Fig. 5. Reflecting a low superconducting volume fraction, the SQUID measurements show a weak, incomplete transition for $x=0.40$. The decrease in volume fraction is ascribed to the deviation from the optimum hole concentration, which is commonly observed in all high T_c superconductors.[36] In the present case, the chemical substitution of Pr for La in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ leads to a reduction in hole concentration in the CuO_2 planes, which is discussed latter. The lower volume fraction for the unsubstituted $LaBa_2Cu_3O_z$ compound, compared to the Pr substituted compound, is ascribed to the inhomogeneity of the samples which arises due to the presence of secondary phases. In order to understand the factors that lead to the absence of superconductivity in $PrBa_2Cu_3O_z$, the properties of solid solutions of the type $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$ were carefully investigated.[37–41] It has been observed that Pr systematically suppresses the superconductivity irrespective of the RE ion. However, the rate of T_c suppression in $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$ strongly depends on the ionic radius of the host rare earth ion. Further, the x_{cr} required to kill T_c completely in
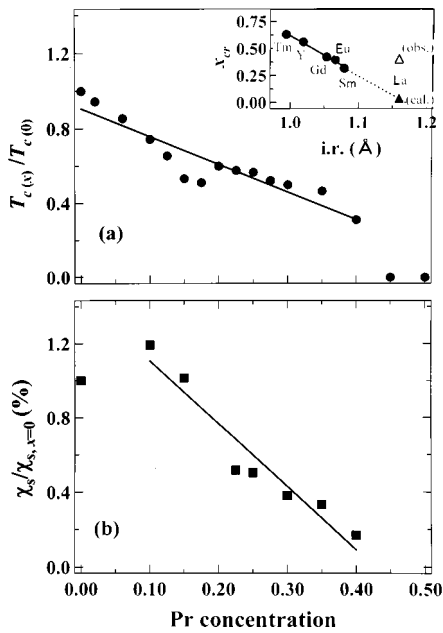
FIG. 5. (a) Plot of reduced T_c of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ compounds as a function of x. Linear line is the fit based on AG theory. Inset shows the RE ionic size (ir) dependence of x_{cr}. Solid circles correspond to the x_{cr} values for various REs (values taken from Ref. 47. Solid triangle represents the deduced value of x_{cr} for RE=La in $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$, whereas the hollow triangle corresponds to the experimentally observed one. (b) The plot of Meissner volume fraction normalized at $x=0$.

FIG. 6. Variation of (a) μ_{eff} of Pr and (b) the temperature-independent component of susceptibility, χ_0 of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ as a function of x.

$(RE_{1-x}Pr_x)Ba_2Cu_3O_z$ also varies as a function of the ionic radius of the rare earth ion. Having obtained the x_{cr} value of 0.63, 0.55, 0.42, 0.40, and 0.31, respectively in the Tm–Pr, Y–Pr, Gd–Pr, Eu–Pr, and Sm–Pr system, one would expect x_{cr} of less than 0.05 in the La–Pr system [inset of Fig. 5(a)-variation of x_{cr} with ionic size (ir) of RE]. On the other hand, we observed $x_{cr} > 0.40$. Such a high value of x_{cr} in the present system may be explained as follows. As described earlier, although pure $LaBa_2Cu_3O_z$ does not form in single phase due to the larger ionic size of La^{3+}, partial substitution of Pr for La stabilizes the superconducting phase. Therefore, a fraction of the Pr ion dopants primarily aid in the stabilization of the strained lattice by bringing down the effective ionic radius $(La_{1-x}Pr_x)$ below the critical ionic radius of La^{3+}. Subsequently, only the remaining fraction of the doped Pr ions is involved in the suppression of T_c. Thus, we propose that the interaction of Pr with the CuO_2 layer is small in the present system as compared to the other $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$.

The high temperature magnetic susceptibility, $\chi(T)$ data can be best fitted with the following equation consisting of the sum of the temperature independent component χ_0 the Curie–Weiss (CW) contribution, $\chi = \chi_0 + C/(T + \theta_P)$, where C is the Curie coefficient which is related to the effective moment, μ_{eff}, as $C = N\mu_{eff}^2/3k_B$, and θ_P is the Wiess temperature. This temperature-dependence analysis gives a straight line fit with $\theta_P = 0$ only for $T > 100$ K. The presence of the Pauli susceptibility contribution results in a nonlinear plot of $1/\chi$ vs T for $T < 100$ K. This behavior indicates the dominance of singlet ground state.[42] The plot of μ_{eff} and χ_0 as a function of Pr concentration is depicted in Fig. 6. The
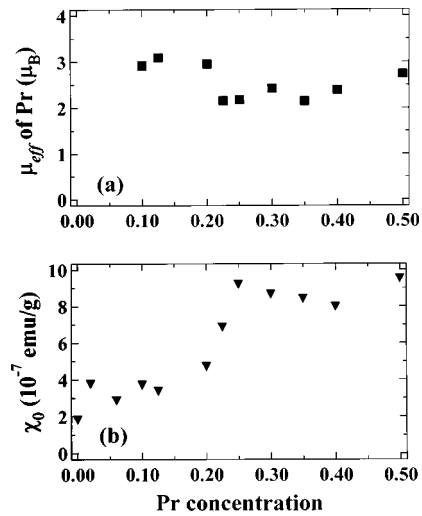
observed effective Pr magnetic moment in most of the compounds is intermediate between that expected for a Pr^{3+} free ion (3.58 μ_B) and that for a Pr^{4+} free ion (2.54 μ_B), similar to that observed for Pr ions in $PrBa_2Cu_3O_z$.[43] The observed low magnetic moment may be due to (i) a mixed valence of Pr ions (i.e., about +3.5), or (ii) the effect of crystalline electric field on the ground state $(^3H_4)$ of Pr^{3+} ions. From the structural point of view one can argue that (since Pr ion resides only in the La site, with evidences coming from XANES results that are discussed latter), had Pr been in a tetravalent $(Pr^{4+} i.r. = 0.960 \text{ Å})$ state rather than a trivalent state $(Pr^{3+} i.r. = 1.126 \text{ Å})$, it would have induced more instabilities in the system. This is because the ionic size difference between La^{3+} (i.r. $= 1.160$ Å) and Pr^{4+} is too large compared to that of La^{3+} and Pr^{3+}. It would not allow the presence of Pr^{4+} according to the simple ionic size considerations. Further, the observed low magnetic moment arises because only the low-lying energy levels of the crystal field contribute to the magnetic susceptibility, similar to that in $PrBa_2Cu_3O_z$.[43] Hence, analyzing of the magnetic susceptibility data in terms of a crystalline electric field splitting of $(^3H_4)$ of Pr^{3+}-ion ground level shows that the valence state of Pr ions is +3. The temperature-independent part of susceptibility, χ_0, increases rapidly with x, as shown in Fig. 6. Since the variation in χ_0 is not proportional to x, the major contribution to χ_0 might come from Cu electrons, whereas in an oxygen-deficient Y-1:2:3 system, the χ_0 decreases rapidly with increasing oxygen deficiency.[44] This indirectly supports that none of our samples are suffering from oxygen deficiency.

The lack of superconductivity in $PrBa_2Cu_3O_z$ has been explained on the basis of various mechanisms proposed so far, none of which is generally accepted. Of these, the direct pair breaking by Abrikosov–Gor'kov (AG) exchange scattering,[45,46] magnetic hybridization leading to pair breaking,[47] subtle magnetic interactions[48] and charge compensation[49,50] (hole filling) are well quoted. Moreover, all those mechanisms proposed to account for the systematic suppression of superconductivity in $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$

J. Appl. Phys., Vol. 86, No. 12, 15 December 1999

Murugesan *et al.*   6989

are centered on the valence state of Pr, which is under controversy. For example, magnetic[5] and chemical substitution[6,7] studies point to the tetravalent state while x-ray photoelectron spectroscopy (XPS)[8] and x-ray absorption near-edge spectroscopy[9] (XANES) investigations suggest the trivalent state. On the contrary, neutron diffraction[10] and x-ray absorption studies[11] have revealed a mixed valence state. Even though the spectroscopic (XPS) results for pure and substituted Pr-1:2:3 indicate a trivalent state, it is, however, difficult to assess the true value of Pr from the XPS core levels, i.e., the $Pr(3d_{5/2})$ overlaps directly with the $Cu(2p_{3/2})$ level and hence the dilemma. However, Blackstead *et al.* have recently reported the observation of inhomogeneous superconductivity in $PrBa_2Cu_3O_z$ and interpreted the superconductivity that on the basis of the oxygen model,[51–53] which supports that the Cu–O chain layers, are responsible for the origin of superconductivity in $(RE)Ba_2Cu_3O_z$. Also the absence of superconductivity in $PrBa_2Cu_3O_z$ is due to pair breaking by Ba-site magnetic Pr which is an inhomogeneous phenomenon. Just as is suggested in the case of $PrBa_2Cu_3O_z$, the primary reason for the observation of low T_c in $LaBa_2Cu_3O_z$ has been attributed to the larger size of La^{3+} (i.r.=1.160 Å) and consequently the possible dislocation of La^{3+} ions between the two energetically favorable lattice sites, viz., RE site and Ba site.[20,54,55] However, it has been proved that[18] the modified synthesis condition of $LaBa_2Cu_3O_z$ eliminates the disordering of La at Ba site and yields the T_c of 90 K, which is the commonly obtainable value in $(RE)Ba_2Cu_3O_z$. The observation of 90 K T_c for $x=0$ indicates the absence of La at Ba site and all our samples are highly homogeneous. Thus we rule out the possibility of the presence of La at the Ba site. If there is no Ba-site La, then there will not be any Ba-site Pr (our XANES results clearly show that Pr ion substitutes only at the La site). Additional evidence comes from the ionic size consideration. As the Ba^{2+} (i.r.=1.52 Å) site is expected to accommodate ions of comparable size, of these two ions, viz., La^{3+} and Pr^{3+}, the former would be the more probable candidate for occupying the Ba site because its ionic radius is closer to that of the Ba^{2+} ion.

As mentioned above, there are numerous experimental observations in the literature which also suggest strong hybridization of the Pr $4f$ states with the O $2p-$Cu $3d$ electronic states. The suppression of superconductivity in $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$ with Pr can be best understood on the basis of the AG theory of pair breaking, which implies appreciable interaction of magnetic Pr ions with the superconducting electrons residing presumably in the Cu–O network.[46,47] Thus, we have also been prompted to analyze the T_c suppression by Pr in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ first by the AG pair-breaking theory.[45] The modified form of the universal AG equation is given by

$$T_{c(x)}/T_{c(0)} = 1 - [(\pi^2/T_{c(0)}4k_B)x_{cr}N(E_F)R^2$$
$$\times (g-1)^2 J(J+1)]x, \qquad (2)$$

where $N(E_F)$ is the density of states at the Fermi level, g and J are the g factor and total angular momentum of the Hund's-rules ground state of the magnetic ion, and R is the

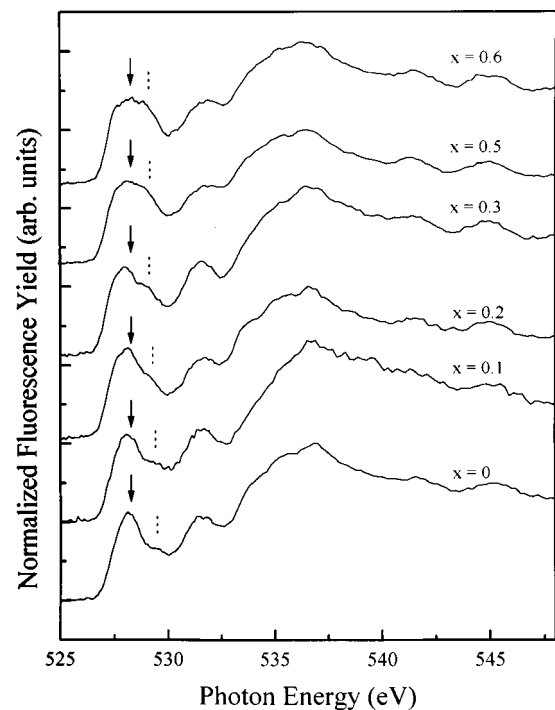FIG. 7. O K-edge x-ray absorption spectra for the series of samples obtained by a bulk-sensitive total x-ray fluorescence yield method.

exchange-interaction parameter. The de Gennes factor is given by the term $(g-1)^2 J(J+1)$. From the above relation, the plot $T_{c(x)}/T_{c(0)}$ vs x should give a straight line if the AG pair breaking mechanism is responsible here. The solid line in Fig. 5(a) shows a line fit to the T_c data. It is clear from the graph that the fit does not give a good correlation as it deviates from the observed experimental points. Having found that the T_c suppression in the present La–Pr system cannot be explained alone by the AG pair breaking theory, we tried to analyze the results with the help of XANES studies. It is expected that the O K-edge x-ray absorption spectrum shows multiple pre-edge peaks due to different oxygen environments. It is important to understand the hole distribution among different oxygen sites and their role in superconductivity.

In Fig. 7, the O K-edge x-ray absorption spectra for a series of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ samples with $x=0.00$, 0.10, 0.20, 0.30, 0.50, and 0.60 are shown in the energy range of 525–551 eV obtained using a bulk-sensitive total x-ray fluorescence yield method. The major features in the O $1s$ x-ray absorption spectrum for a sample with $x=0$ are two distinct pre-peaks at ~528.2 eV and ~529.3 eV with a shoulder at ~527.6 eV, and a broad peak at ~537 eV. The low-energy pre-peaks with energy below 532 eV are ascribed to excitation of the O $1s$ core electrons to holes with predominantly $2p$ character on the oxygen sites. Unoccupied states related to the Ba $4d$, Pr $5d$, or Pr $4f$ states hybridized with O $2p$ states could be the origin for the enhanced peaks above 532 eV in $(La_{1-x}Pr_x)Ba_{1.95}Cu_3O_z$.[56]

The observed multiple pre-edge peaks in O K-edge absorption spectra shown in Fig. 7 may be due to chemical shifts of the O $1s$ level originating from the influence of

charges on the oxygen sites and the site-specific neighborhood. Based on the polarization-dependent x-ray absorption measurements on single-crystal $YBa_2Cu_3O_{7-\delta}$,[57] the pre-peaks at $\sim$527.8 eV in O K-edge x-ray absorption spectra of $YBa_2Cu_3O_{7-\delta}$ are attributed to transitions into O $2p$ holes in the CuO_3 ribbons (apical oxygen sites and CuO chains). The high-energy pre-peak at $\sim$528.5 eV is ascribed to transitions into O $2p$ hole states within the CuO_2 planes.[57,58]

The orthorhombic $LaBa_2Cu_3O_{7-\delta}$ compound is isomorphic with $YBa_2Cu_3O_{7-\delta}$. When oxygen is removed from $PrBa_2Cu_3O_{7-\delta}$, a strong reduction of the pre-peak structure in O $1s$ x-ray absorption spectrum is observed,[56] as seen for the $YBa_2Cu_3O_{7-\delta}$ compounds.[57] As shown in Fig. 7, the O $1s$ x-ray absorption spectrum of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ for $x = 0$ exhibits similar features as observed in $YBa_2Cu_3O_{7-\delta}$ with $\delta = 0$.[57,59] We therefore adopt the same assignment scheme for the O $1s$ x-ray absorption spectra of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$. The high-energy pre-peak at $\sim$528.2 eV is attributed to the excitation of O $1s$ electrons to O $2p$ holes in the CuO_2 planes. The low-energy pre-peaks at $\sim$527.6 eV in Fig. 7 are due to the superposition of O $2p$ hole states in the apical oxygen sites and the CuO chains. The absorption peak at $\sim$529.3 eV in Fig. 7 can be ascribed to excitation to the empty upper Hubbard conduction band (UHB) with predominantly Cu $3d$ character.[60] This kind of pre-edge structure is a result of hybridization in the ground state of the Cu $3d^9$ and Cu $3d^{10}L$ states, where L is ligand hole from the O $2p$ band.[61]

As noted from Fig. 7, the pre-peak at $\sim$528.2 eV, as marked by arrows, originating from the O $2p$ hole states in the CuO_2 layers decreases in spectral weight with increasing the dopant concentration of Pr. This result clearly reveals that the chemical substitution of Pr for La in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ leads to a reduction in hole concentration in the CuO_2 planes.[62] According to the Liechtenstein and Mazin (LM) model,[63] the hole reduction upon substituting RE by Pr in $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$ originates from the hole transfer from the CuO_2 planes and CuO_3 ribbons into the LM band. As shown, the depletion in hole concentration observed in the $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ system provides an evidence in support of the LM model. It has been experimentally shown that the concentration of O $2p$ holes in the CuO_2 planes is strongly correlated with T_c in the p-type cuprates.[64] Accordingly, the T_c value in the $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ system should decrease with increasing the dopant concentration of Pr. Our experimental results clearly reveal that the quenching of superconductivity with Pr doping in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ results predominantly from the hole depletion.[62]

In addition, as shown in Fig. 7, the peak at $\sim$529.3 eV, as indicated by dash lines, originating from the UHB shows a monotonic increase in spectral weight as the Pr doping increases. This change is related to a spectral weight transfer of states from the UHB to doping-induced hole states near the Fermi level.[65]

Figure 8 presents the PrM_{45}-edge and CuL_{23}-edge x-ray-fluorescence-yield spectra for the series of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ compounds with $x = 0$, 0.1, 0.2, 0.3, 0.5, and 0.6 in the photon energy range of 920–960 eV. As

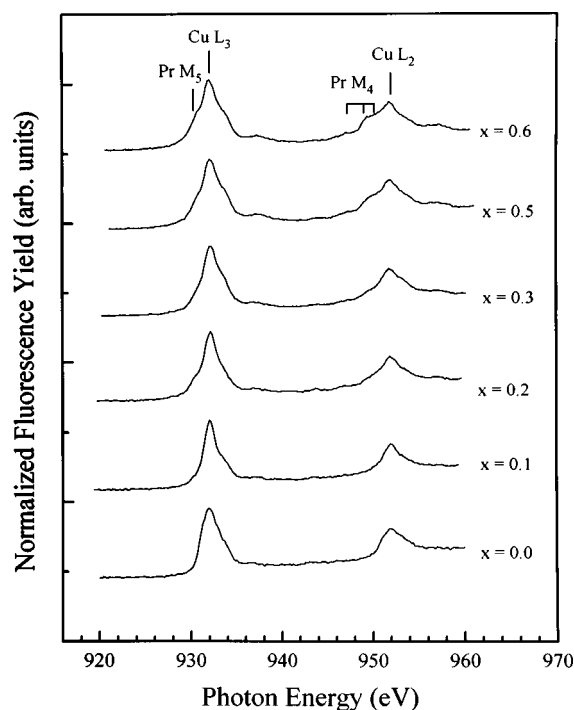FIG. 8. Pr M_{45}-edge and Cu L_{23}-edge x-ray absorption spectra of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$.

marked on the top of Fig. 8, the peak at $\sim$930.0 eV is related to the transition from Pr $3d_{5/2}$ electrons into $4f$ states. As shown, the Cu L_3-edge absorption spectra are asymmetric and a shoulder exhibits at the high-energy side of the Cu L_3 peak. The pronounced excitonic peak at 931.3 eV shown in Fig. 8 is ascribed to the excitations of the $Cu(2p_{3/2})3d^9$ ground states (formal Cu^{2+} state) to the $Cu(2p_{3/2})^{-1}3d^{10}$ excited states, where $Cu(2p_{3/2})^{-1}$ denotes a Cu $2p_{3/2}$ hole. In addition, the high-energy shoulder at $\sim$932.6 eV is attributed to the transitions from the $Cu(2p_{3/2})3d^9L$ defected states into the $Cu(2p_{3/2})^{-1}3d^{10}L$ excited states, where L denotes a ligand hole in the O $2p$ orbital.[66] The intensity of this shoulder can be regarded as the total concentration of hole states in the cuprate superconductors.

As noted from Fig. 8, the high-energy shoulder originating from the Cu $3d^9L$ defect states shows a linear decrease in spectral weight with increasing the Pr content. This indicates that the total hole concentration in the CuO_2 planes and CuO_3 ribbons $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ decreases as the dopant concentration of Pr increases. The result is consistent with the conclusion of O $1s$ x-ray absorption spectra presented above. In addition, as shown in Fig. 8, the spectral weight of Pr M_5 peak at $\sim$930.0 eV increases linearly with increasing the Pr concentration in the compounds. This supports the belief that the La ions in the $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ system are partially substituted by the Pr ions.

Figure 9 presents the La $3d$-edge x-ray absorption spectra of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ with $x = 0.00$, 0.30, and 0.60. As noted from Fig. 9, the spectra show two multiplet structures separated by the La $3d_{5/2}$-La $3d_{3/2}$ spin-orbital splitting. The intensity of La M_5 peak at $\sim$835 eV decreases linearly with increasing the Pr doping in the compounds. This confirms
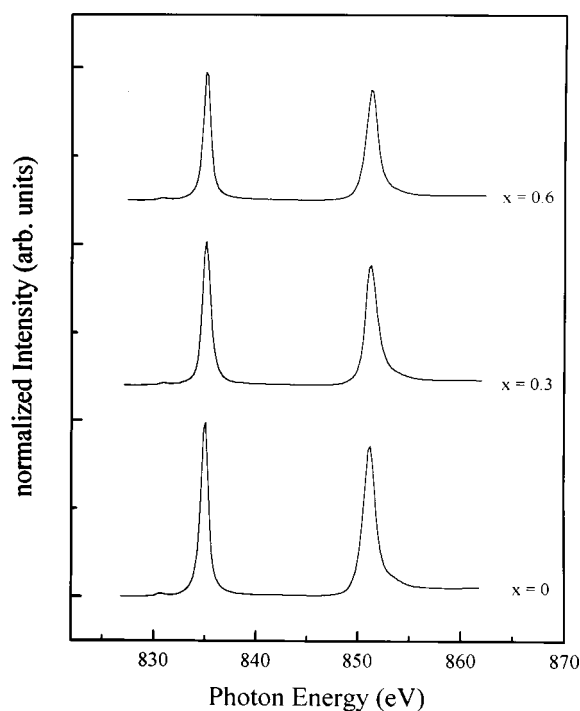
FIG. 9. La $3d$-edge x-ray absorption spectra of $(La_{1-x}Pr_x)Ba_2Cu_3O_z$.

that Pr ions in the $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ system substituted only on the La site.

IV. CONCLUSION

Suppression of superconductivity by Pr ion in $LaBa_2Cu_3O_z$ has been thoroughly investigated. Results showed that the critical concentration of Pr ion required to suppress the superconductivity is 0.40 and this magnitude is higher than the expected value as in the case of $(RE_{1-x}Pr_x)Ba_2Cu_3O_z$. The observed low value of the magnetic moment of the Pr ion in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ is explained based on the crystal field splitting of the ($^3H_4$) Pr^{3+}-ion ground levels. XANES results clearly reveal that the substituted Pr ion resides only in the La site and not in the Ba site of $LaBa_2Cu_3O_z$. Quenching of superconductivity with Pr doping in $(La_{1-x}Pr_x)Ba_2Cu_3O_z$ is predominantly due to the depletion of holes in CuO_2 planes. On this basis, the suppression of superconductivity by Pr in $LaBa_2Cu_3O_z$ is solely due to the hybridization of Pr with the CuO_2 planes resulting in hole depletion; this is unlike the absence of superconductivity in $PrBa_2Cu_3O_z$, which is due to the presence of Ba-site Pr.

ACKNOWLEDGMENT

[1] D. W. Murphy, S. Sunshine, R. B. Van Dover, R. J. Cava, B. Batlogg, S. M. Zhaurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987).

[2] P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[3] K. N. Yang, B. W. Lee, M. B. Maple, and S. S. Laderman, Appl. Phys. A: Solids Surf. **46**, 229 (1989).

[4] C. R. Fincher, Jr., and G. B. Blanchet, Phys. Rev. Lett. **67**, 2902 (1991).

[5] W. H. Li, J. W. Lynn, S. Skanthakumar, T. W. Clinton, A. Kabede, C. S. Jee, J. E. Crow, and T. Mihalisin, Phys. Rev. B **40**, 5300 (1989).

[6] J. J. Neumeier, T. Bjornholm, M. B. Maple, and I. K. Schuller, Phys. Rev. Lett. **63**, 2516 (1989).

[7] D. P. Norton, D. H. Lowndes, B. C. Sales, J. D. Budai, B. C. Chakoumakos, and H. R. Kerchner, Phys. Rev. Lett. **66**, 1537 (1991).

[8] U. Neukirch, C. J. Simons, P. Sladeczek, C. Laubschat, O. Strebi, G. Kaindl, and D. D. Arma, Europhys. Lett. **5**, 567 (1988).

[9] L. Soderholm and G. I. Goodman, J. Solid State Chem. **81**, 121 (1989).

[10] J. J. Neumeier, T. Bjornholm, M. B. Maple, J. J. Rhyne, and G. A. Cotaas, Physica C **166**, 191 (1990).

[11] F. W. Lytle, G. Von der Laan, R. B. Greegor, E. M. Larsen, C. E. Violet, and J. Wong, Phys. Rev. B **41**, 8955 (1990).

[12] M. H. Whangbo and C. C. Torardi, Science **249**, 1143 (1990).

[13] E. Hodorowicz, S. A. Hodorowicsz, and H. A. Elick, J. Alloys Compd. **181**, 442 (1992).

[14] P. Somasundaram, A. M. Ram, A. M. Umarji, and C. N. Rao, Mater. Res. Bull. **25**, 331 (1990).

[15] L. Ganapathi, A. K. Ganguli, R. A. Mohan Ram, and C. N. R. Rao, J. Solid State Chem. **73**, 593 (1988).

[16] A. Maeda, T. Noda, H. Matsumoto, T. Wada, M. Izumi, T. Yabe, K. Uchinokura, and S. Tanaka, J. Appl. Phys. **64**, 4095 (1988).

[17] M. Hikita, S. Tsurumi, K. Semta, T. Iwata, and S. Kuriha, Jpn. J. Appl. Phys., Part 2 **26**, L615 (1987).

[18] T. Wada, N. Suzuki, T. Maeda, A. Maeda, S. Uchida, K. Uchinokura, and S. Tanaka, Appl. Phys. Lett. **52**, 1989 (1988).

[19] J. M. Tarascon, L. H. Greene, B. G. Baglay, W. R. McKinnon, P. Barboux, and G. W. Hull, *Proceedings of the International Workshop on Novel Mechanisms of Superconductivity*, edited by V. Kersin and S. Wolf (Plenum, New York, 1987).

[20] E. Takayama-Muromachi, Y. Uchida, A. Fujimori, and K. Kato, Jpn. J. Appl. Phys., Part 2 **26**, L546 (1987).

[21] H. A. Blackstead, J. D. Dow, D. B. Chrisey, J. S. Horwitz, M. A. Black, P. J. McGinn, A. E. Klunzinger, and D. B. Pulling, Phys. Rev. B **54**, 6122 (1996).

[22] J. M. Chen, S. C. Chung, and R. S. Liu, Solid State Commun. **99**, 493 (1996).

[23] G. Wang, K. L. Davis, and S. R. Dennis, Adv. Ceram. Mater. **2**, 303 (1987).

[24] R. Bayers and B. T. Ahn, in *Annual Reviews in Materials Science*, edited by R. A. Hyggins, R. H. Bube, and D. A. Vermilyea (Annual Review, Palo Alto, 1991), Vol. 21, p. 335.

[25] E. Hodorowicz, S. A. Hodorowicz, and H. A. Elick, J. Alloys Compd. **181**, 442 (1992).

[26] T. Armbruster, F. Rothlisberger, and F. Seifert, Am. Mineral. **75**, 847 (1990).

[27] I. D. Brown, Z. Kristallogr. **199**, 255 (1992).

[28] A. Salinas-Sanchez, J. L. Garcia-Munong, J. Rodriquez-Carvagal, R. Saez-Puche, and J. L. Martinez, J. Solid State Chem. **100**, 201 (1992).

[29] S. Pei, A. P. Paulikas, B. W. Veal, and J. D. Jorgenson, Acta Crystallogr., Sec. C: Cryst. Struct. Commun. **46**, 1986 (1990).

[30] P. Lightfoot, S. Pei, J. D. Jorgenson, Y. C. Chang, P. Z. Jiang, and W. Veal, J. Solid State Chem. **89**, 385 (1990).

[31] I. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci. **41**, 244 (1985).

[32] K. I. Gnanasekar, M. Sharon, R. Pinto, S. P. Pai, M. S. R. Rao, P. R. Apte, A. S. Tamhane, S. C. Purandare, L. C. Gupta, and R. Vijayaraghavan, J. Appl. Phys. **79**, 1082 (1996).

[33] R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[34] A. Maeda, T. Yabe, K. Uchinokura, and S. Tanaka, Jpn. J. Appl. Phys., Part 2 **26**, L1368 (1987).

[35] R. Yoshizaki, H. Sawada, T. Iwazumi, Y. Saito, Y. Abe, H. Ikeda, K. Iami, and I. Nakai, Jpn. J. Appl. Phys., Part 2 **26**, L1703 (1987).

[36] B. Okai and K. Kato, Jpn. J. Appl. Phys., Part 2 **36**, L473 (1997).

[37] J. K. Liang, X. T. Xu, S. S. Xie, G. H. Rao, X. Y. Shao, and Z. G. Duan, Z. Phys. B **69**, 137 (1987).

[38] H. Jhans, S. K. Malik, S. K. Dhar, and R. Vijayaraghavan, Physica C **207**, 247 (1993).

[39] I. Das, E. V. Sampathkumaran, R. Vijayaraghavan, Y. Nakazawa, and M. Ishikawa, Physica C **173**, 331 (1991).

[40] H. D. Yang, P. F. Chen, C. R. Hsu, C. W. Lee, C. L. Li, and C. C. Peng, Phys. Rev. B **43**, 10568 (1991).

[41] H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).

[42] A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe, and T. Yamada, Phys. Rev. B **38**, 2910 (1988).

[43] G. Hilcher, E. Holland-Moritz, T. Holubar, H. D. Jostarndt, V. Nekvasil, G. Schaudy, U. Walter, and G. Fillion, Phys. Rev. B **49**, 535 (1994).

[44] T. Takabatake, M. Ishikawa, and T. Sugano, Jpn. J. Appl. Phys., Part 1 **26**, 1859 (1987).

[45] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960); [Sov. Phys. JETP **12**, 1243 (1961)].

[46] A. Kebede, C. S. Jee, J. Schwegler, J. E. Crow, T. Mihalisin, G. H. Myer, R. E. Salomon, P. Shlottmann, M. V. Kuric, S. H. Bloom, and R. P. Guertin, Phys. Rev. B **40**, 4453 (1989).

[47] S. K. Malik, C. V. Tomy, and P. Bhargava, Phys. Rev. B **44**, 7042 (1991).

[48] L. Soderholm, C. K. Loong, G. L. Goodman, and B. D. Dabroski, Phys. Rev. B **43**, 7923 (1991).

[49] G. Cao, J. Bolivar, J. W. O'Reilly, J. E. Crow, R. J. Kennedy, and P. Pernambuco-Wise, Physica B **186–188**, 1004 (1993).

[50] A. P. Reyes, D. E. McLaughlin, M. Takigawa, P. C. Hammel, R. H. Heffner, J. D. Thompson, J. E. Crow, A. Kebede, T. Mihalisin, and J. Schwegler, Phys. Rev. B **42**, 2688 (1990).

[51] H. A. Blackstead, J. D. Dow, W. E. Packard, and D. B. Pulling, Physica C **235–240**, 1363 (1994).

[52] H. A. Blackstead and J. D. Dow, in *Proceedings of the Second International Symposium on Quantum Confinement Physics and Applications*, edited by M. Cahay, S. Bandopadhyay, J. P. Leburton, A. W. Kleinsasser, and M. A. Osman (The Electrochemical Society, Pennington, NJ, 1994) Vol. 94–17, pp. 408–418, 419–427.

[53] H. A. Blackstead and J. D. Dow, Pis'ma Zh. Eksp. Teor. Fiz. **59**, 262 (1994). [JETP Lett. **59**, 283 (1994)].

[54] C. U. Segre, B. Debrowski, D. G. Hinks, K. Zhang, J. D. Jorgensen, M. A. Beno, and I. K. Shuller, Nature (London) **329**, 227 (1987).

[55] P. Karen, H. Fjellvag, O. Braaten, A. Kjekshus, and H. Bratsberg, Acta Chem. Scand. **44**, 994 (1990).

[56] J. Fink, N. Nücker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumeier, and J. W. Allen, Phys. Rev. B **42**, 4823 (1990).

[57] N. Nücker, E. Pellegrin, P. Schweiss, J. Fink, S. L. Molodtsov, C. T. Simmons, G. Kaindl, W. Frentrup, A. Erb, and Müller-Vogt , Phys. Rev. B **51**, 8529 (1995).

[58] J. Fink, N. Nücker, E. Pellegrin, H. Romberg, M. Alexander, and M. Knupfer, J. Electron Spectrosc. Relat. Phenom. **66**, 395 (1994).

[59] J. Zaanen, A. T. Daxton, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. **60**, 2685 (1988).

[60] H. Romberg, M. Alexander, N. Nücker, P. Adelmann, and J. Fink, Phys. Rev. B **42**, 8768 (1990).

[61] D. Vaknin, S. K. Shiha, D. E. Moneton, D. C. Johnston, J. M. Newsam, C. R. Safiva, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).

[62] J. M. Chen, R. S. Liu, J. G. Lin, C. Y. Huang, and J. C. Ho, Phys. Rev. B **55**, 14586 (1997).

[63] A. I. Liechtenstein and I. I. Mazin, Phys. Rev. Lett. **74**, 1000 (1995).

[64] A. Krol, C. S. Lin, Y. L. Soo, Z. H. Ming, Y. H. Kao, Jui H. Wang, Min Qi, and G. C. Smith, Phys. Rev. B **45**, 10051 (1992).

[65] Z. Iqbal, E. Leone, R. Chin, A. J. Signorelli, A. Bose, and H. Eckhardt, J. Mater. Res. **2**, 768 (1987).

[66] G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, Phys. Rev. B **23**, 4369 (1981).