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Raman study of $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ (R = Y, rare earth)

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The polarized Raman scattering of the $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ series (R = La, Pr, Nd, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm, Yb, Lu; $\delta \sim 0$) which undergoes a superconductor-to-nonsuperconductor transition between R = Gd and Dy was studied. It was found that the appearance of superconductivity correlates with observation of a two-mode behavior of the R-ion-size-sensitive B_{1g}-like mode of O(2),O(3) out-of-phase vibrations. It was also established that the Ba (xx, A_g) phonon line is of asymmetrical (Fano) shape for all R. The origin of the Fano effect usually attributed to interference with an electronic continuum is discussed.

I. INTRODUCTION

The substitution of most rare-earth elements (R) for Y in the $YBa_2Cu_3O_{7-\delta}$ (Y-1:2:3:7) system does not change the crystallographic structure and hardly affects the critical temperature $T_c \sim 90$ K.[1] The *praseodymium* is an exception: It forms a Pr-1:2:3:7 compound which is an antiferromagnetic semiconductor. In the intermediate compounds $R_{1-x}Pr_x$1:2:3:7, T_c falls rapidly with increasing Pr content (for a review see Ref. 2). It has been established that the x value corresponding to the loss of superconductivity varies with R: It increases with the difference Δr of the ionic radii of Pr and R.[3,4] It has also been found that there exists a critical average $R_{1-x}Pr_x$ ionic radius $r_{\rm av} = 1.090$ Å (calculated according to the Shannon's data[5]) above which the superconductivity in $R_{1-x}Pr_x$-1:2:3:7 systems does not persist.[6]

Several different mechanisms have been proposed to account for the effect of Pr on the superconductivity of R-1:2:3:7 materials. Among them are hole filling,[7] pair breaking,[2,7] hybridization and hole localization.[6,8] The experimental results, however, are controversial.[2] While the hole-filling picture, based on the assumption that the valency of Pr is 4+ or between 3+ and 4+, is supported by a number of experimental results, other experiments provide evidence that the valency is precisely 3+.[2] Magnetic pair breaking and hybridization mechanisms have often been connected with a 4+ or mixed valent state. Ce doping,[9] however, has the same effect as Pr doping although Ce^{4+} is a nonmagnetic ion. The Pr doping x and oxygen deficiency δ have the same effect on the resistivity $\rho(T)$ dependence of $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. This suggests, in support for the "hole-filling" hypothesis, that the only relevant parameter is $x + \delta$.[10]

Raman scattering has often been used to characterize the $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, in particular for the cases R = Y ($0 \le x \le 1$), $\delta \sim 0$,[11–13] and R = rare earth, $x \sim 0$, $\delta \sim 0$.[14–16] It has been found that the frequencies of the O(2),O(3) out-of-phase (B_{1g}-like) and the O(4) apex-oxygen-stretching (A_g) modes depend linearly on the rare-earth [or the average ($R_{1-x}Pr_x$)] ionic radius and shift significantly towards lower and higher wave numbers, respectively. However, while Yang *et al.*[12] reported a two-mode behavior of the B_{1g} line shape for x = 0.6 and 0.8 in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0$), Iliev *et al.*[13] and McCarty *et al.*[17] came to a conclusion for the one-mode behavior of the same line for $0.1 \le x \le 0.9$ and $x \sim 0.44$, respectively, although they did find a much larger linewidth if compared to the end compounds with $x = 0$ and $x = 1$. A multimode behavior of the B_{1g} mode has been reported recently for the superconducting $[M]Ba_2Cu_3O_{7-\delta}$ "cocktails," where $[M_1] = Y_{0.2}Sm_{0.2}Eu_{0.2}Nd_{0.2}Yb_{0.2}$ and $[M_2] = Y_{0.013}La_{0.4}Sm_{0.087}Nd_{0.5}$.[18]

Unlike the case of $\rho(T)$, x and δ have different effects on the Raman spectra of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, in particular on the Raman line intensities in the xx-polarized spectra.[13,19] Such a difference could in principle be explained with the assumption that the increase of x and/or δ results in a conversion of part of the superconducting (metallic) volume into a nonsuperconducting (semiconducting) one, *the latter corresponding to different phases* for changes of x and δ, respectively. As the conductivity $\sigma(T) = 1/\rho(T)$ is determined by mainly the metallic phase, the nature of the nonsuperconducting phase is of lesser importance. In contrast, all phases contribute to the Raman scattering and, hence, within a multiphase model the x and δ are Raman spectroscopically inequivalent.

Recent resonant Raman scattering experiments on oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0.6$) (Ref. 20) have given evidence for the coexistence of microstructures corresponding to ortho-I, ortho-II, and tetragonal phases. The spectra in this case are a superposition of spec-

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tra of the coexisting phases, their relative weight being determined by their abundance and Raman cross sections. Further evidence for the same phase separation has been obtained from inelastic neutron scattering of $\mathrm{ErBa_2Cu_3O_{7-\delta}}$ $(0 \leq \delta \leq 1)$,[21] where the observed energy spectra have been interpreted as a superposition of two different metallic components and a semiconducting one, the relative weight of each component being extremely dependent upon δ. Moreover, it has been concluded in the latter study that the superconductivity results from the formation of a two-dimensional network, with the two-plateau structure of T_c being directly related to the variation of the proportions of the different cluster types versus δ. A model for the separation of Pr and R atoms in Pr-rich and R-rich microstructures (clusters) has also been used to explain the T_c dependence on the radius difference Δr of R^{3+} and Pr^{3+} in $R_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O_{7-\delta}}$ ($R =$ Sm, Gd, Y, Er, Tm; $\delta \sim 0$).[4] It has been argued in Ref. 4 that the larger Δr favor the formation of Pr-rich and R-rich regions, separated by boundaries with the Pr-R connections. For the case of smaller Δr the size of the R-rich regions and Pr-rich regions decreases and the one with Pr-R connections increases. As both the Pr-Pr and Pr-R connections are detrimental to superconductivity, the critical concentration for the destruction of superconductivity is lower.

Unlike the pair $\mathrm{YBa_2Cu_3O_6}$-$\mathrm{YBa_2Cu_3O_7}$ the Raman spectra of $R\mathrm{Ba_2Cu_3O_7}$ ($R =$ Y, rare earth) compounds are very similar. It is not clear *a priori* whether the formation of R-rich and Pr-rich microregions in mixed $R_{1-x}\mathrm{Pr}_x1237$ crystals would result in detectable changes in the Raman spectra due to phonon confinement. An indication that the latter could be the case is given by the results of comparative Raman studies of c-axis-oriented $\mathrm{Y_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}}$ thin film and $\mathrm{(Y/Pr)Ba_2Cu_3O_{7-\delta}}$ superlattices with a relatively large individual layer thickness ($d \sim 8$ unit cells or ~ 100 Å).[22] While two-mode behavior of the B_{1g}-like mode, and to a lesser extent of the O(4) mode, has clearly been observed in the latter case, in the former case such a behavior is less obvious with frequencies intermediate to these of $\mathrm{YBa_2Cu_3O_7}$ and $\mathrm{PrBa_2Cu_3O_7}$.

In this work we report results of polarized Raman scattering experiments on the $\mathrm{R_{0.5}Pr_{0.5}Ba_2Cu_3O_7}$ series, which undergoes a superconductor-to-nonsuperconductor transition with decreasing Δr. While two-mode behavior of the B_{1g} band was observed at higher Δr, the A_g modes exhibited one-mode behavior. It was also established that the $\mathrm{Ba}(A_g)$ mode exhibits in the xx spectra a Fano shape for all R. The origin of the Fano interference and the variations with Δr of the phonon parameters are discussed.

II. SAMPLES AND EXPERIMENT

The ceramic samples of $R_{0.5}\mathrm{Pr_{0.5}Ba_2Cu_3O_{7-\delta}}$ ($R =$ La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Tm, Yb, and Lu) were prepared by the standard solid state reaction technique. To avoid the formation of spurious phases, the purity of the starting materials was of major concern. Namely, the oxides (better than 99.99%) were heated in flowing oxygen at about 800 °C and the carbonates (99.99%) were dried at 200 °C. After mixing and firing, the samples in the form of pellets were annealed in four successive steps (time duration 10 h each) at 920, 930, 940, and 950 °C with intermediate grindings. For achieving the melting of $\mathrm{BaCuO_2}$, which usually appears as impurity phase in the R-1:2:3 compounds, we performed twice the "cycle": annealing in flowing oxygen at 450 °C for 12 h, in flowing helium gas at 920 °C for 20 h, and finally in oxygen at 450 °C for 12 h. The oxygenation was done in flowing oxygen at 450 °C for 24 h.

The x-ray diffraction (XRD) spectra (Siemens D500) Cu $K\alpha$ showed that the samples were of orthorhombic symmetry (space group $P4mmm$). The unit cell dimensions were calculated by the RIETVELD program.[23] The variations of the unit cell parameters as a function of the average R-Pr ionic radius for the series $\mathrm{R_{0.5}Pr_{0.5}Ba_2Cu_3O_7}$ are presented in Fig. 1. One notes that $c/3$ is shorter than b in the $R_{0.5}\mathrm{Pr_{0.5}}1237$ series although in the R-1:2:3:7 series it is the opposite. A similar behavior of the $c/3$ has been observed in the $\mathrm{Y_{1-x}Pr_xBa_2Cu_3O_7}$ series too.[24] It is also worth noticing that the $c/3$ value of Pr-1:2:3:7 does not follow the trend of the R-1:2:3:7 but of the $R_{0.5}\mathrm{Pr_{0.5}}$-1:2:3:7 series. As long as all samples were produced under the same and most favorable conditions for full oxygenation (24 h) we suggest that the oxygen content corresponds to $\delta \sim 0$. The latter is supported by the fact that the a and b parameters of the $R_{0.5}\mathrm{Pr_{0.5}}$ compounds are very close to the lines that describe the trends of the corresponding values of the R-1:2:3:7 series (Fig. 1). The RIETVELD refinement also gave the best results considering the number of oxygen atoms as 7. Figure 2 shows the $\rho(T)/\rho(100)$ dependences which illustrate the change in the type of conductivity between $R =$ Gd and Dy.

The visual observation of the polished surface of the pellets under an optical microscope showed that the size

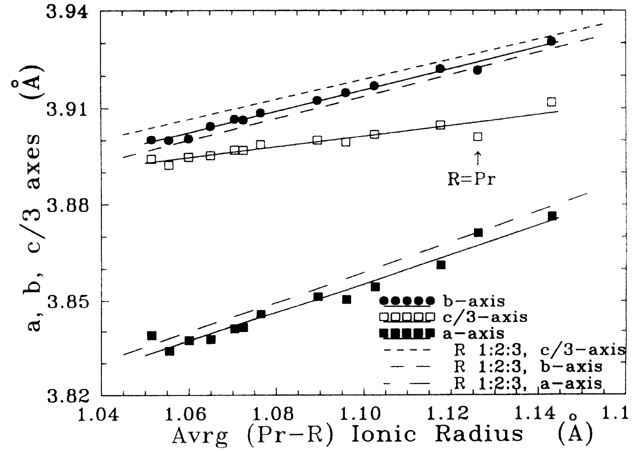

FIG. 1. The variations of the a, b and $c/3$ parameters as function of the average R-Pr ionic radius for the series $R_{0.5}\mathrm{Pr_{0.5}Ba_2Cu_3O_7}$. The dashed lines show the corresponding trends of the same parameters for the $R\mathrm{Ba_2Cu_3O_7}$ series. The values for the trivalent rare-earth ionic radii were taken from Shannon (Ref. 5).

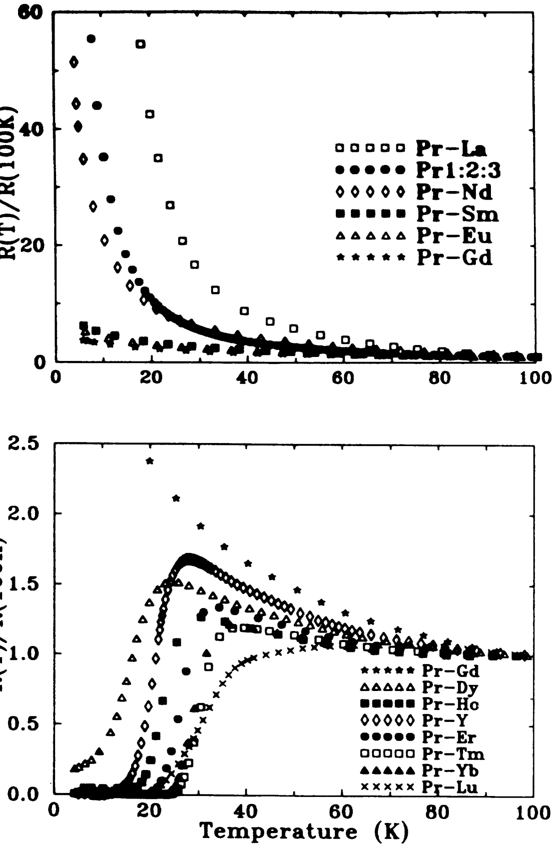

FIG. 2. $R(T)/R(100)$ dependences of the $R_{0.5}$Pr$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ samples used in the Raman experiments as obtained by a dc four-point technique.

of most microcrystals contituting the pellet was between 5 and 40 μm. The elongated projections of the microcrystals were often of the form of rectangles with longer sides corresponding to a direction within the ab plane. The latter assignment is confirmed by comparison of the shapes of Raman spectra taken in polarizations parallel and perpendicular to these edges. Following a procedure described in Ref. 19 it was possible to select microcrystals with zx orientation on the polished surface of each $R_{0.5}$Pr$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ pellet, where z is a direction that nearly coincides with the c axis and x and y are two orthorhombic directions within the ab plane. Thus, the spectra could be measured in the most informative polarizations $y(zz)\bar{y}$ (for the A_g modes), $y(xx)\bar{y}$ (for the A_g and B_{1g}-like modes), and $y(zx)\bar{y}/y(zx)\bar{y}$ (for the "nondiagonal" B_{2g} and B_{3g} modes).

The polarized Raman spectra were measured at room temperature using two different types of triple spectrometers equipped with a microscope (Microdil 28 with a multichannel detector and Jobin-Ivon T64000 with a liquid-nitrogen-cooled CCD detector). The obtained spectra were nearly identical. An objective of 100× magnification was used for both focusing the laser beam ($\lambda_L = 514.5$ nm or 488.0 nm) and collecting the scattered light. The laser power at the focus (2–3 μm diameter of the spot) was kept below 0.2 mW in order to avoid overheating. The typical acquisition times were 2000 s.

III. RESULTS AND DISCUSSION

In Fig. 3 and Fig. 4 are shown the variations with R of the Raman spectra with the $y(zz)\bar{y}$ and $y(xx)\bar{y}$ scattering geometries, respectively. Figure 5 summarizes the results in terms of the phonon mode frequency versus average ionic radius. It follows from Figs. 3 and 5 that except for the weak shift of the Ba, Cu(2), and O(2),O(3) in-phase A_{1g} modes and stronger shift of the O(4) (A_g) mode, the $y(zz)\bar{y}$ spectra are nearly identical for all R. The line shape of the high-frequency band in the $y(zz)\bar{y}$ spectra (Fig. 3) can be fitted by two Lorentzians: We assign them to the O(4) (A_g) and a Raman-forbidden modes respectively. The frequency of the additional zz line is also included in the upper part of Fig. 5. In the $y(xx)\bar{y}$ spectra (Fig. 4) mainly the Ba- and the B_{1g}-like O(2),O(3) out-of-phase modes are pronounced. The Ba mode is of assymmetric Fano shape for all R, its maximum being shifted by 3–5 cm^{-1} towards lower wave numbers if compared to the zz counterpart (Fig. 6).

It is remarkable that the width of the band of B_{1g}-like symmetry (Fig. 5) varies significantly with R. While for R of ionic radius close to that of Pr^{3+} (La,Nd) the bandwidth is comparable with the one of pure Pr-1:2:3:7 ($\sim$30 cm^{-1}), it increases significantly with Δr, reaching

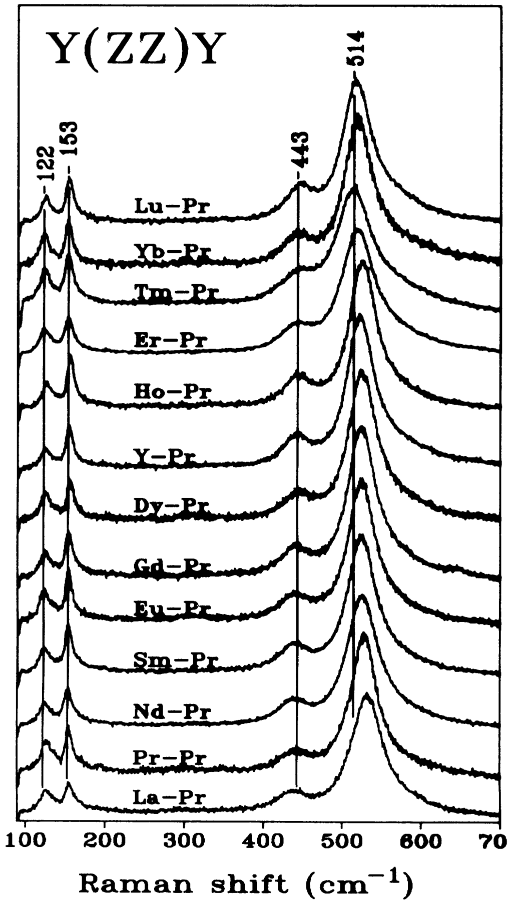

FIG. 3. Raman spectra of $R_{0.5}$Pr$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ as obtained with 514.5 nm excitation at room temperature in the $y(zz)\bar{y}$ scattering geometry.

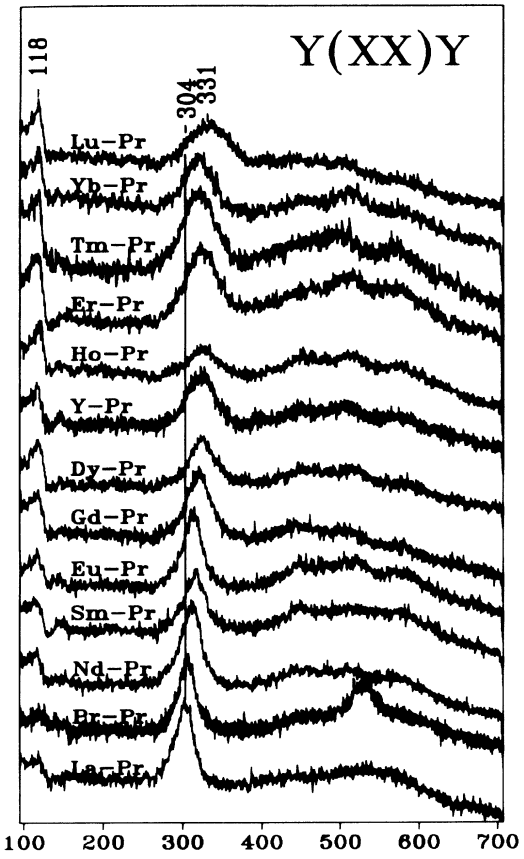

FIG. 4. Raman spectra of $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ as obtained with 514.5 nm excitation at room temperature in the $y(xx)\bar{y}$ scattering geometry.

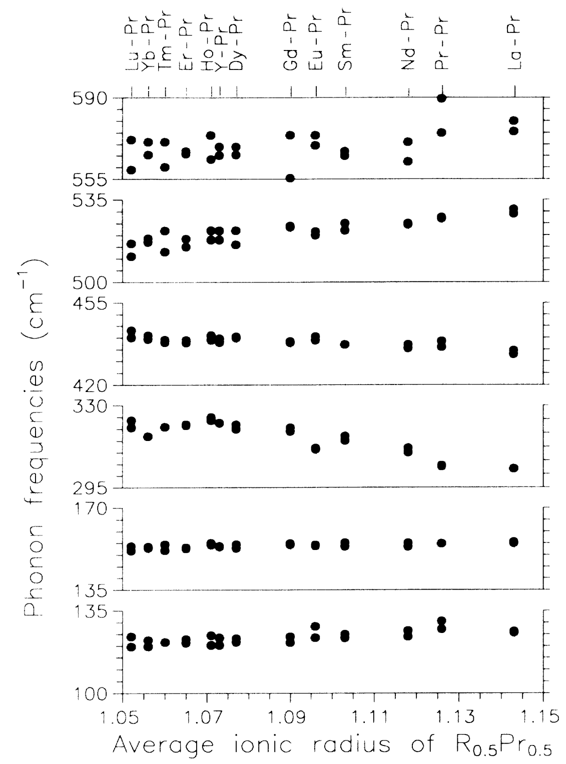

FIG. 5. Variation with the (average) ionic radius of the phonon mode frequencies of $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$. The two sets of data correspond to spectra measured with Microdil 28 (488.0 nm excitation) and Jobin-Ivon T64000 (514.5 nm excitation) spectrometers, respectively. The phonon frequencies were obtained by fit with Lorentzians of the $y(zz)\bar{y}$ spectra. The frequency of the B_{1g}-like mode (at 300–330 cm^{-1}) was obtained by fitting with a single Lorentzian of the corresponding phonon line profile in the $y(xx)\bar{y}$ spectra.

values of about 60–70 cm^{-1} for Lu,Yb,Tm,Er. With increasing Δr the band maximum shifts clearly towards higher wave numbers although for some R the position of the maximum may vary from microcrystal to microcrystal within 5–10 cm^{-1}. In some cases the band was obviously of a complex line shape, the latter suggesting two or more components: an indication for multimode behavior. We note here that the effects of a two-mode behavior or multiphase scattering volume (if any) has to be most clearly pronounced for the B_{1g}-like mode due to the strong variation of its frequency with R.

As long as the frequency of the B_{1g} mode in the R-1:2:3:7 series depends linearly on the rare-earth ionic radius,[11] one expects that in the case of one-mode behavior, the corresponding B_{1g} frequency will follow the same linear dependence on the average $R_{0.5}Pr_{0.5}$ radius for the $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ series too. Figure 7 illustrates that the latter is obviously the case for these $R_{0.5}Pr_{0.5}$ compounds which correspond to lower Δr values (La-Pr, Nd-Pr, Sm-Pr, Eu-Pr, Gd-Pr). With further increase of Δr (beginning from $R_{0.5}Pr_{0.5} = Dy_{0.5}Pr_{0.5}$) the maximum of the B_{1g} band deviates from the $\omega_{B_{1g}}$ versus Δr linear dependence and even decreases. The latter indicates that the "one-mode approximation" may not be valid for larger Δr.

In order to prove the "multimode model" we attempted to fit the B_{1g}-like band for the $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds corresponding to larger values of Δr with two or three Lorentzians (we had in mind that the Lorentzian line shape may be only a rough approximation for a superconducting R-1:2:3:7 local structure as one expects an asymmetrical Fano profile for the B_{1g} line in this case[25]). The $y(xx)\bar{y}$ spectra of at least two $R_{0.5}Pr_{0.5}$ microcrystals for each R were analyzed. The assumption for three B_{1g} components implies a multiphase scattering volume with the main microstructure phases corresponding to $RBa_2Cu_3O_{7-\delta}$, $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$, respectively. In the latter case the Pr-1:2:3:7 component of the B_{1g} band has to be observed near 300 cm^{-1} for all R-Pr samples, which was not supported by our analysis. The results of fitting of the B_{1g} line by two Lorentzians (for R = Dy, Y, Ho, Tm, Yb, and Lu) are given in Fig. 8.

It is difficult at this stage to make a final conclu-

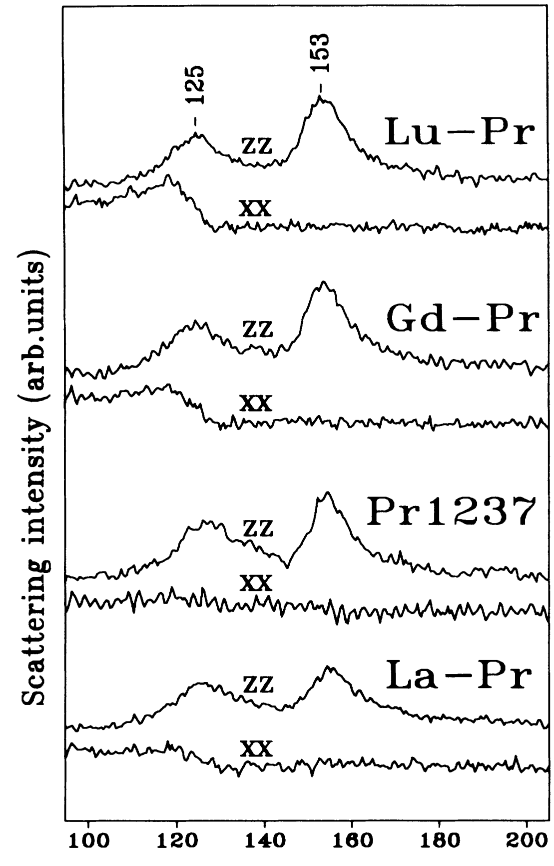

FIG. 6. Comparison of the $y(zz)\bar{y}$ and $y(xx)\bar{y}$ spectra of superconducting $Lu_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ (T_c ~ 40 K) and nonsuperconducting $Gd_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$, $PrBa_2Cu_3O_{7-\delta}$, and $La_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$. The $y(xx)\bar{y}$ intensities are multiplied by a factor of 3. The Fano effect is evident for all samples.

sion for the origin of the two-mode behavior of the B_{1g}-like band at larger Δr. A natural explanation could be the separation with increasing Δr of the $\omega(\mathbf{k})$ branches $[\omega(\mathbf{k}=0)=\omega_{B_{1g}}]$ of the end compounds $PrBa_2Cu_3O_7$ and $RBa_2Cu_3O_7$, supported by the strong variation of the B_{1g}-frequency R-1:2:3:7. An example for such a behavior is the Raman spectrum of mixed $Ga_{1-x}Al_xAs$ crystals.[26] Although in the $RBa_2Cu_3O_7$ compounds the phonon dispersion does vanish along the $[0,0,k_c]$ direction of the Brillouin zone, the $\omega(\mathbf{k})$ dispersion of the particular branch corresponding to the B_{1g}-like phonon is significant along other $\mathbf{k}$ directions (30–40 cm^{-1} for $YBa_2Cu_3O_7$; see, e.g., Refs. 27, 28). We note here that the scattering configuration $y(xx)\bar{y}$ used in this work and in the experiments of McCarty *et al.*[17] on single-domain $Y_{0.56}Pr_{0.44}Ba_2Cu_3O_7$ corresponds to $\mathbf{k}$ values of the dispersive $\omega(\mathbf{k})$ branch and, hence, is less favorable for the two-mode behavior of the B_{1g}-like mode than the $z(xx)\bar{z}$ configuration used in experiments on c-oriented (Y,Pr)-1:2:3:7 thin films.[22] Nevertheless, practically the same width of the B_{1g}-like band (35–40 cm^{-1})

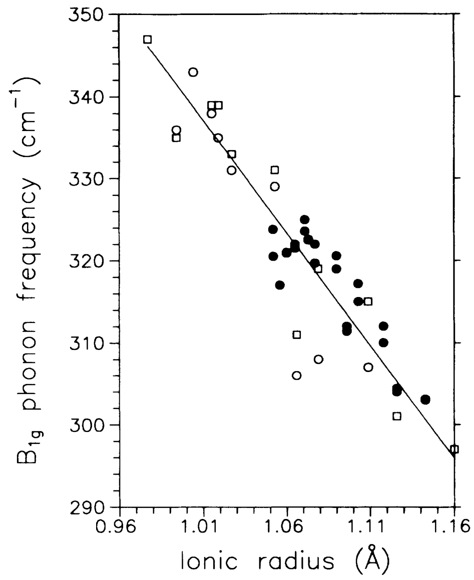

FIG. 7. Variation with the (average) ionic radius of the frequency of the B_{1g}-like mode of $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ (solid circles) and $RBa_2Cu_3O_{7-\delta}$ [open circles (Ref. 14) and squares (Ref. 15)].

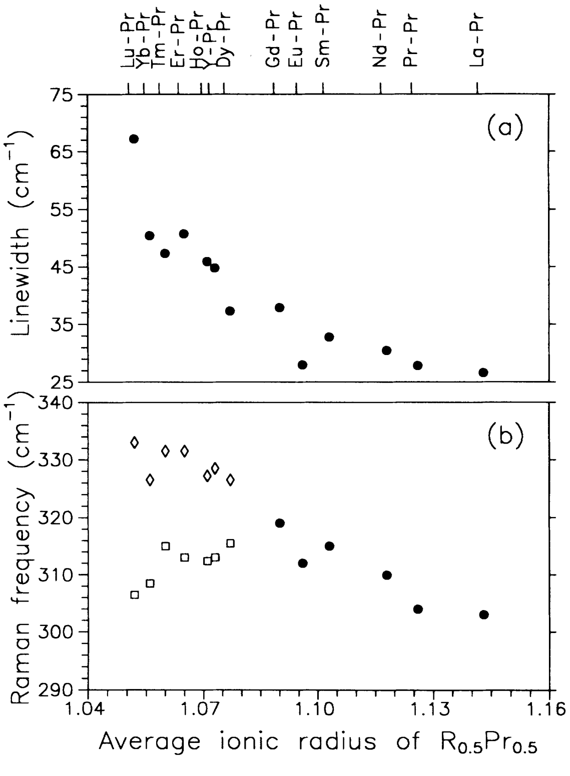

FIG. 8. Variation with the average ionic radius of $R_{0.5}Pr_{0.5}$ of (a) the linewidth of the B_{1g}-like phonon if fitted by one Lorentzian; (b) the frequencies of the B_{1g}-like mode (solid circles) or its two components (open squares and diamonds), as obtained by a fit with two Lorentzians, respectively.

has been found in all measurements on materials close to $Y_{0.5}Pr_{0.5}$1:2:3:7.

Our results can consistently be explained also within the model of formation of *R*-rich and Pr-rich microstructures (clusters) (Ref. 4) as follows: At low Δr the *R* and Pr atoms are statistically distributed and the B_{1g} band exhibits one-mode behavior [favored by the overlapping of frequency ranges of corresponding $\omega(\mathbf{k})$ branches]. With increasing Δr, *R*-rich and Pr-rich microstructures (beyond the sensitivity of XRD) are formed which favors the appearance of superconductivity, B_{1g}-phonon confinement, and thus two-mode behavior. If so, it seems that the separation in Pr-rich and Pr-deficient phases depends also on the sample's growing and annealing procedures. An indication for the latter could be the strong scattering of the data reported by different groups for the $T_c(x)$ dependences in the $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ systems, in particular for the most studied $Y_{1-x}Pr_xBa_2Cu_3O_7$.[2] A careful study of the possibility for the coexistence of different microstructures in $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0$) compounds and their transformations is worth further attention.

The observation of a Fano-shaped Ba line (A_g) in the $y(xx)\bar{y}$ spectra of all $R_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-\delta}$ (Figs. 4 and 6) was an unexpected result. The Fano interference proves the existence of an intrinsic scattering background and an interaction between the elementary excitations causing the background and those phonons which show the Fano effect.[25] It is usually assumed that the background is due to scattering by quasifree carriers and hence the Fano effect has to disappear in the nonsuperconducting samples with low carrier concentration. Indeed, it has been reported that there is no asymmetry of both the Ba(*xx*) and the O(2),O(3) out-of-phase (B_{1g}-like) phonons in semiconducting $YBa_2Cu_3O_6$ (Ref. 29) and of the B_{1g} phonon in nonsuperconducting $PrBa_2Cu_3O_7$.[30] It is under question, however, whether the sample used in the experiments of Ref. 30 has had an oxygen content corresponding to $YBa_2Cu_3O_6$: More recent experiments[31–33] have given evidence that the Ba mode is not observable in the $y(xx)\bar{y}$ scattering geometry for $YBa_2Cu_3O_6$ (see also Ref. 20). As concerns $PrBa_2Cu_3O_7$, there are to our opinion no reliable data on the *xx*-polarized Raman spectra in the frequency range of the Ba phonon. In the $y(xx)\bar{y}$ spectra of $PrBa_2Cu_3O_7$ reported in Ref. 13 the Ba phonon has been not observable.

It is difficult at this stage, at least due to lack of data on the polarized Raman spectra of $R_{1-x}Pr_x$1:2:3:7 samples with various *x* and at low temperatures, to interpret unambiguously the Fano shape of the Ba line in the $R_{0.5}Pr_{0.5}$-1:2:3:7 compounds. Moreover, even for the most studied case of $YBa_2Cu_3O_{7-\delta}$, there is no consensus on either the nature of the continuum required for the Fano interference (electronic[25] or two-phonon[34] one) or whether the origin of the Fano effect is the same for the Ba(xx, A_g), O(2),O(3) out-of-phase(xx, B_{1g}-like), and O4(zz, A_g) phonons. Further we discuss the three possible explanations.

(1) At room temperature the holes in all $R_{0.5}Pr_{0.5}$1:2:3:7 samples are delocalized and the electronic structure becomes similar to that of superconducting *R*-1:2:3:7. The Fano shape is due to interference with intraband electronic transitions near E_F within either the two O(3)(*y*)-Cu(2)(x^2-y^2)-O(2)(*x*)-like antibonding $pd\sigma$ "plane" bands, responsible for the superconductivity, or the dispersive O(4)(*z*)-Cu(1)($y^2 - z^2$)-O(1)(*y*)-like antibonding $pd\sigma$ "chain" band.[35] If the "plane" bands are considered, the Fano effect has to be temperature dependent, in particular at low temperatures, in both the superconducting *R*-rich phases (due to the opening of the superconducting gap) and insulating Pr-rich phases (due to the hole localization and shift of the Fermi level). It was shown, however, that the Fano shape of the Ba phonon is even more pronounced at low temperatures.[36] The vanishing of the Fano shape for the Pr-1:2:3:7 B_{1g}-like phonon (if of the same origin) cannot be explained either, if one takes into account that the electronic band structures of Y-1:2:3:7 and Pr-1:2:3:7 are very similar.[37]

(2) The electronic continuum responsible for the Fano effect could be due to interband (intraband) transitions between (within) the two bands in the vicinity of the Fermi energy near the *S*-*R* line of the Brillouin zone, shown to exist on the basis of *ab initio* band structure calculations for $YBa_2Cu_3O_7$.[35,38] The upper band crosses E_F and has mainly O(4)(p_y) character, with some Ba(p_x), Cu(1)(d_{yz}), and O(1)(p_z) admixture, whereas the lower band is below E_F and has O(4)(p_x) character, with some Ba(p_y) and Cu(1)(d_{xz}) admixture. The bands are separated by ~ 40–45 meV (320–360 cm^{-1}) and have negligible *z* dispersion.[38] Such an origin of the electronic continuum could explain both the anisotropy and the strength of the Fano effect of the Ba phonon. As long as the substitution of Pr for Y does not change significantly the electronic band structure near the *S* point,[37] it is plausible to expect that the latter structure (and hence the electronic continuum) remains nearly the same for all $R_{1-x}Pr_x$-1:2:3:7 composition. No correlation between the observation of Fano interference and opening of the superconducting gap has to exist, provided the holes of the O(4)-Ba band(s) do not couple at low temperatures. We note here that there are some experimental findings that indirectly support the coexistence of an electronic continuum originating from different electronic subsystems; namely, (i) the imaginary response function describing the Raman continuum in $YBa_2Cu_3O_7$ was found to have components with different temperature dependences, one of them with normal-state behavior;[39] (ii) while the *zz* continuum disappears with decreasing oxygen contents, the *xx*/*yy* low-frequency continuum remains nearly the same.[40] A possible effect of the carriers in the Ba-O(4) planes on the Ba and O(4) Raman modes in $Y_{1-x}Pr_x$-1:2:3:7, resulting in a reduction of their intensities in the *xx*/*yy* spectra (if compared to these in Y-1:2:3:7) has been discussed in Ref. 19. The weak intensity of the Ba and O(4) lines in the *xx*-spectra of Fig. 3 may be due to the same effect.

(3) The background continuum in the region 100–1000 cm^{-1} contains significant two-phonon scattering and the Fano line shape is due to an anharmonic phonon – two-phonon interaction. Such a model has recently been proposed by Mihailovic *et al.*[34] to explain the

temperature dependence and the asymmetric line shape of the O(4)(zz, A_g) Raman phonon in $YBa_2Cu_3O_{6.9}$, $TlBa_2CaCu_2O_7$, and $Tl_2Ba_2CaCu_2O_8$. Although the model describes correctly the behavior of the O(4) mode (in particular of Tl-1:2:1:2) it seems to be inapplicable to the Ba- and B_{1g}-like modes in R-1:2:3:7. The Fano effect of the low-frequency modes would be strongly temperature dependent between 10 and 300 K as the two-phonon scattering background depends on the $(n+1)^2$ and/or $n(n+1)$ prefactors, where $n = 1/[\exp(\hbar\omega/k_BT) - 1]$ and would decrease at low temperatures which is obviously not the case. The contribution of two-phonon processes to the Ba-phonon linewidth is discussed in Ref. 41.

It follows from our results on the Ba (xx)-phonon line shape in the $R_{0.5}Pr_{0.5}Ba_2Cu_3O_7$ series that the observation of the Fano effect for all R, including Pr-1:2:3:7, can most consistently be explained assuming the existence of an electron continuum originating from the band(s) of mostly O(4) character crossing the Fermi level near the S point.[38] It seems that the role of the "Ba-O(4)-plane" carriers, so far neglected, is worth more attention.

IV. CONCLUSIONS

The polarized Raman spectra of $R_{0.5}Pr_{0.5}Ba_2Cu_3O_7$ give evidence that the nonsuperconductor-to-superconductor transition that occures with increasing R-Pr radius difference Δr correlates with transition from one- to two-mode behavior of the R-size-sensitive B_{1g} mode of the O(2),O(3) out-of-phase vibrations. The Fano shape of the Ba(xx, A_g) line for all $R_{0.5}Pr_{0.5}$ and its independence of the carrier concentration indicates that the Fano effect for this particular mode may not be related to the superconductivity. Rather, the electronic transitions near E_F between or within the "plane" bands of mainly O(4) character in the vicinity of the S point have to be considered.

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