Raman study of $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$ superlattices

A. P. Litvinchuk,* C. Thomsen, I. E. Trofimov,† H.-U. Habermeier,
and M. Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany
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We report Raman measurements on c-axis-oriented high-T_c $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$ superlattices. The assignment of the observed phonon lines is obtained from a comparison of the Raman spectra of these superlattices, bulk $YBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$ and also of an $(Y/Pr)Ba_2Cu_3O_{7-\delta}$ mixed crystal. Vibrational peaks were found corresponding to confined phonons as well as extended excitations. We find also a pronounced softening of the B_{1g}-like phonon localized in the Y layers (out-of-plane bending vibration of CuO_2-plane oxygen) below the superconducting transition temperature T_c, a property characteristic of $YBa_2Cu_3O_{7-\delta}$ superconductors, while phonons localized in $PrBa_2Cu_3O_{7-\delta}$ show no such effect.

I. INTRODUCTION

In spite of the complex crystallographic structure of $RBa_2Cu_3O_{7-\delta}$ (R = rare earth) superconductors, artificially layered structures of these materials have recently become available.[1–4] Improved layer by layer growth techniques enable one to manufacture oriented superlattices with thicknesses of alternating layers down to a single unit cell (about 12 Å in c direction). A number of physical properties of these superlattices have been studied, both experimentally and theoretically. Particular attention was paid (see, e.g., Ref. 5) to the investigation of the effect of layer thickness on the transition temperature T_c for superlattices consisting of superconducting (e.g., $YBa_2Cu_3O_{7-\delta}$) and nonsuperconducting ($PrBa_2Cu_3O_{7-\delta}$) materials.

We report here results of a study of vibrational modes of well-characterized $(Y/Pr)Ba_2Cu_3O_{7-\delta}$ superlattices with layer thicknesses in the range 7–14 monolayers (ML), corresponding to 84–168 Å, by means of Raman spectroscopy. To reach the phonon mode assignment we compare the Raman spectra of superlattices with those of bulk $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ materials and of an $(Y/Pr)Ba_2Cu_3O_{7-\delta}$ alloy. We analyze also superconductivity-induced phonon self-energy effects.

II. GROWTH AND CHARACTERIZATION OF SUPERLATTICES

$(Y/Pr)Ba_2Cu_3O_{7-\delta}$ superlattices were grown by a standard *in situ* pulsed-laser deposition technique, which has been described elsewhere.[6] Stochiometric $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ targets were mounted on a multitarget holder that permits individual rotation of the targets as well as their exchange during the deposition process. The superlattices were grown on $SrTiO_3(100)$ and $LaAlO_3(100)$ substrates at a deposition rate of 1.0 Å per pulse and 2 Hz in an ambient O_2 pressure of 1 mbar, with a substrate temperature of 790 °C. The pulsed KrF ($\lambda = 248$ nm) excimer laser produced an energy density in the targets of about 1.5 J/cm^2. The substrate-target distance was kept at 4 cm. After the growth procedure the superlattices were cooled within 30 minutes to room temperature at an oxygen pressure of 1 atm.

The structure of the superlattices was examined by means of x-ray diffraction; in Fig. 1 diffraction patterns for one of them are shown. Only $(00l)$ diffraction peaks were observed, indicating complete c-axis texturing. The presence of satellite peaks on both sides of the main peaks demonstrates the additional periodicity in the film produced by the superlattice layers. This modulation wavelength Λ can be calculated from the separation of satellite peaks as follows:[7]

$$\Lambda = (\lambda/2)[\sin\Theta_i - \sin\Theta_{i-1}]^{-1},$$

where λ is x-ray wavelength (1.542 Å in our case) and Θ_i are the positions of two adjacent x-ray peaks. We found Λ = 161.5, 184.3, and 246.5 Å for the superlattices

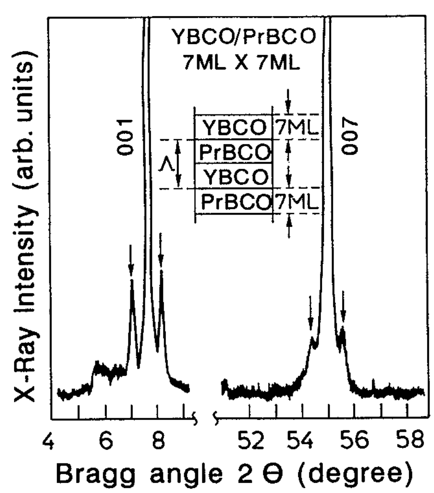

FIG. 1. X-ray diffraction patterns for the (Y_7Pr_7)BCO superlattice with $\Lambda = 161.5$ Å.

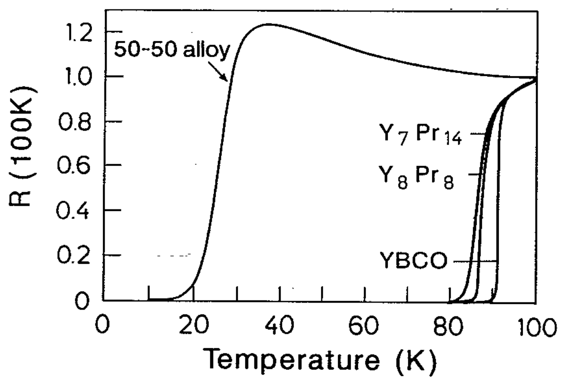

FIG. 2. Temperature dependence of the normalized resistance for a YBCO film, a $(Y_{0.5}Pr_{0.5})BCO$ alloy film, and $(Y_8Pr_8)BCO$, $(Y_7Pr_{14})BCO$ superlattices.

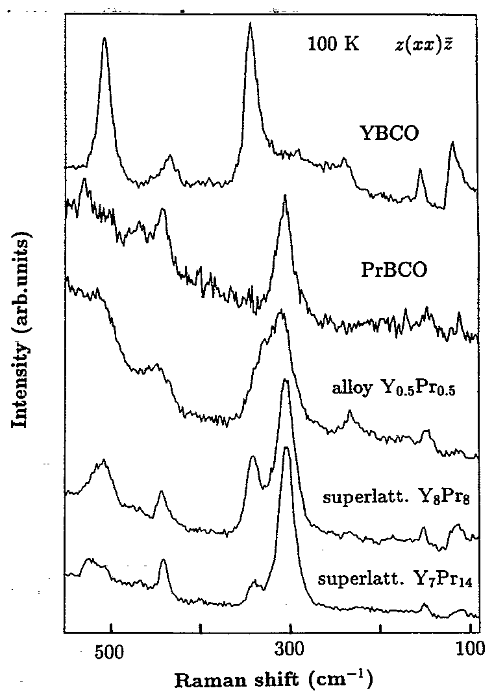

FIG. 3. Raman spectra of bulk YBCO, PrBCO, $(Y_{0.5}Pr_{0.5})BCO$ alloy, and $(Y_8Pr_8)BCO$, $(Y_7Pr_{14})BCO$ superlattices taken at 100 K in the $z(xx)\bar{z}$ geometry.

Y_7Pr_7, Y_8Pr_8, and Y_7Pr_{14}, respectively (here and for the rest of the paper the subscripts denote the superlattice layer thickness in monolayers, ML).

Resistivity measurements (Fig. 2) reveal the well-known[2,3] decrease of T_c and the increase of the transition width with decreasing of layer thicknesses. The values of T_c ($\varrho = 0$) were found to be 83.5 K for Y_7Pr_7, 85 K for Y_8Pr_8, and 82.5 K for Y_7Pr_{14} superlattice.

III. EXPERIMENT

Raman measurements in polarized light were performed in back-scattering geometry with a Dilor XY triple spectrometer. The samples were attached to the cold finger of a temperature-variable cryostat. The 5145-Å line (10 mW) of an Ar^+ laser was used for excitation. The values of phonon frequencies reported here as well as the linewidths were obtained by fits of the experimental spectra to either Lorentzian or Fano line shapes.

IV. RESULTS AND DISCUSSION

The Raman spectra of $RBa_2Cu_3O_{7-\delta}$ compounds have been studied extensively (see Ref. 8 and references therein). They exhibit five strong Raman-active phonons of which four are fully symmetric (A_{1g} symmetry in tetragonal notation to which we will adhere in this paper) and one has B_{1g} symmetry. It was shown that the frequencies of these modes for $RBa_2Cu_3O_{7-\delta}$ vary nearly linearly with the ionic radius of the rare-earth ion R (Refs. 9–11) due to the change of interatomic distances in the crystallographic unit cell.

In Fig. 3 spectra of $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ c-axis films taken in $z(xx)\bar{z}$ geometry at $T = 100$ K are shown (upper two curves), where both A_{1g} and B_{1g} modes are allowed by symmetry.[8] One can see all five phonon lines in each spectrum corresponding, in order of increasing frequency, to Ba, Cu, out-of and in-phase plane oxygen [O(2), O(3)], and apical oxygen [O(4)] vibrations, respectively. As can be seen from Table I, the frequencies of metal-ion and in-phase plane oxygen vibrations are very similar in the two materials discussed. The frequency difference ($\Delta\nu = \nu_{Pr} - \nu_Y$) of the apical-oxygen mode between the R=Pr and R=Y compound ($\Delta\nu = 22$ cm^{-1}) and especially that of the out-of-phase out-of-plane bending-oxygen vibration ($\Delta\nu \approx -41$ cm^{-1}) are considerably larger.

TABLE I. Frequencies and (in brackets) linewidths of the Raman-active vibrations obtained from fits to Fano [Ba and O(2)-O(3) modes] and Lorentz (all other modes) in bulk YBCO, PrBCO, the $(Y_{0.5}/Pr_{0.5})BCO$ alloy, and the $(Y_8Pr_8)BCO$ superlattice at 100 K. All values are given in cm^{-1}. The typical accuracy of the data in frequency is 1 cm^{-1} and in linewidth 1–3 cm^{-1}. Asterisks mark room-temperature data from Ref. 12.

Mode	Bulk YBCO	Bulk PrBCO	(Y/Pr) alloy	(Y_8Pr_8) superlatt.
Ba	121 (14)	115	120*	120 (16)
Cu	151 (12)	150	147*	151 (11)
O(2)–O(3)	347 (15)	306 (20)	331(27); 309(25)	344(15); 304(22)
O(2)+O(3)	432 (17)	442 (13)	440 (28)	442 (11)
O(4)	507 (15)	529 (13)	512 (22)	509 (28)

The A_{1g} modes of $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ alloys have been found to exhibit one-mode behavior, i.e., the frequency of these modes varies smoothly with alloy composition x.[11–13] There is no general consensus on the behavior of the B_{1g} mode: both one-mode[11,13] as well as two-mode behavior[12] have been reported to date. In the latter case phonons of both Y and Pr components were seen in the mixed crystals (with frequencies shifted up to 15 cm^{-1} from their pure, bulk values). This is also what we observe in the spectrum of $(Y_{0.5}Pr_{0.5})Ba_2Cu_3O_{7-\delta}$ film, shown in Fig. 3, middle curve: the broad asymmetric peak around 320 cm^{-1} seems to consist of two lines. Note the considerable broadening of the phonon lines in the spectrum of the alloy (see also Table I), especially for the highest-frequency vibrations, which can be related to the self-energy associated with the disorder.[14,15]

Having presented data for $YBa_2Cu_3O_{7-\delta}$, $PrBa_2Cu_3O_{7-\delta}$, and their 50/50 alloy, let us discuss the results for the $(Y/Pr)Ba_2Cu_3O_{7-\delta}$ superlattices. Can we expect the appearance of phonon confinement effects similar to those known for III-V semiconductor superlattices?[16] We have to note here that for the $RBa_2Cu_3O_{7-\delta}$ compounds phonon dispersion is vanishing (with the exception of the low-frequency Ba mode) in the growth direction z.[17] Thus, confinement may appear for the phonons in the neighboring layers if their frequency separation is larger, at least, than their half widths Γ. Otherwise one deals with extended excitations. The former seems to be the case for the B_{1g} modes which are well separated in frequency ($\Delta\nu$ is two times larger than the phonon linewidths, Table I) and, probably, for the high-frequency apical-oxygen mode ($\Delta\nu \approx \Gamma$). Note that frequencies of acoustic phonons along the z axis are below 50 cm^{-1} (Ref. 17) and thus one may expect the appearance of folded acoustic modes in the range $0 < \nu \leq 50$ cm^{-1}.

In Fig. 3 experimental spectra are shown for two of the superlattices studied (lower curves) which differ in the ratio of Y- to Pr-layer thicknesses. One can see all four A_{1g} modes, like in the alloy. It appears as if the modes do not feel the new periodicity introduced by the superlattice formation. However, unlike in the alloy, we find sharp phonon lines at 304 and 344 cm^{-1} which correspond to confined B_{1g} phonons in both the Pr and Y layers, respectively. It is important to note that the half widths and frequencies of these two lines are the same within experimental error as for pure, bulk $PrBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ materials (compare to upper curves in Fig. 3 and Table I). This indicates the absence of detectable interdiffusion at the layer interfaces. A variation of the relative layer thicknesses in the superlattices in the range studied (7 to 14 ML) does not change Raman spectra qualitatively; it influences only the relative intensities of the confined-phonon modes.

Important information on the lattice dynamics and on electron-phonon interaction in superconductors may be obtained also from the investigation of the temperature dependence of the phonon parameters. Phonon frequencies, linewidths, and intensities are strongly affected by the superconducting transition in $RBa_2Cu_3O_{7-\delta}$ providing information on the position of the superconductivity-related gap.[18,19] In this sense a comparison of the data for $RBa_2Cu_3O_{7-\delta}$ bulk materials and high-T_c superlattices is of interest.

The Raman-scattering spectra for one of the superlattices investigated are shown in Fig. 4 for different temperatures and the temperature dependence of the phonon frequencies and linewidths is summarized in Fig. 5 for the oxygen-related vibrations. An important feature is the softening below T_c of the B_{1g} phonon localized in the Y layers, which is a typical property of bulk superconducting $YBa_2Cu_3O_{7-\delta}$. The same softenings were also found for two other superlattices studied (Y_7Pr_7 and Y_7Pr_{14}). The absolute value of the softening (~ 4 cm^{-1}) is about half of what we observed for the fully oxidized $YBa_2Cu_3O_{7-\delta}$ film, also previously reported for single crystals.[20,21] For small reductions in the oxygen content ($\delta \approx 0.05$) it was recently found that the softening in single crystals is reduced to about half without affecting the superconducting transition temperature significantly ($\Delta T_c \approx 1$ K). A similar effect of oxygen content on the imaginary part of the superconducting self-energy (i.e., phonon linewidth) exists in single crystals[20,21] as well as in our superlattices [Fig. 5(b)]. It is thus a possibility that the oxygen content in our superlattice layers is slightly reduced, a fact which should have little effect on T_c. The other reason for the reduction in self-energy effects could be a diminishing of the electron-phonon coupling strength because of hole depletion from the superconducting $YBa_2Cu_3O_{7-\delta}$ lay-

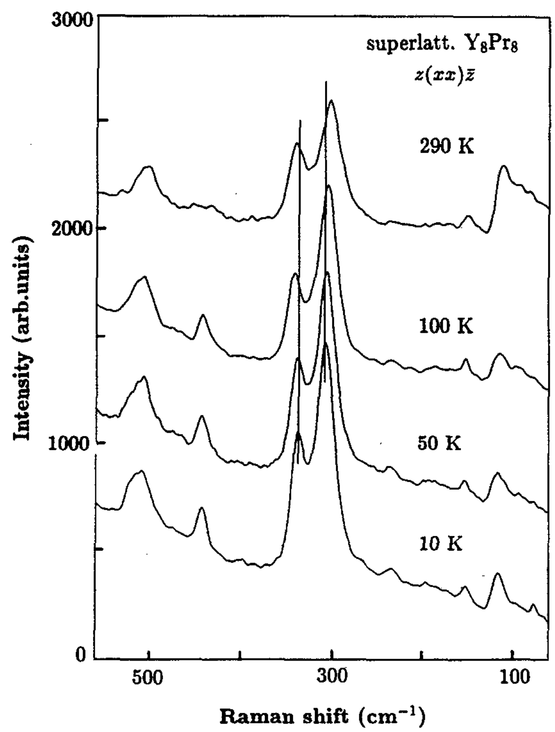

FIG. 4. Raman spectra of (Y_8Pr_8)BCO superlattice in the $z(xx)\bar{z}$ geometry at room temperature, 100, 50, and 10 K. The curves are shifted by 500 on the vertical scale. Solid lines mark the low-temperature position of the confined Y- and Pr-like B_{1g} modes.

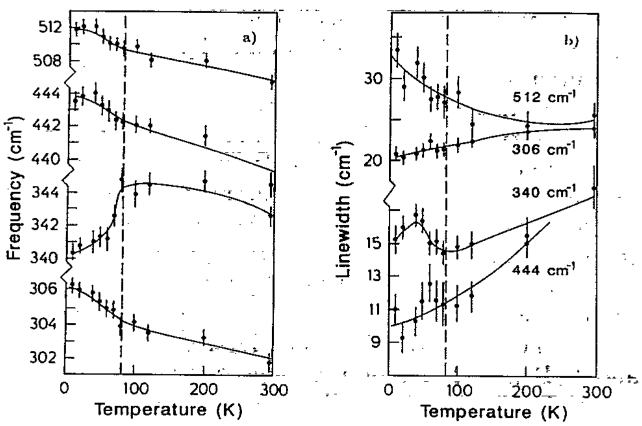

FIG. 5. Temperature dependence of phonon frequencies (a) and linewidths (b) for the (Y_8Pr_8)BCO superlattice. Vertical dashed lines mark T_c.

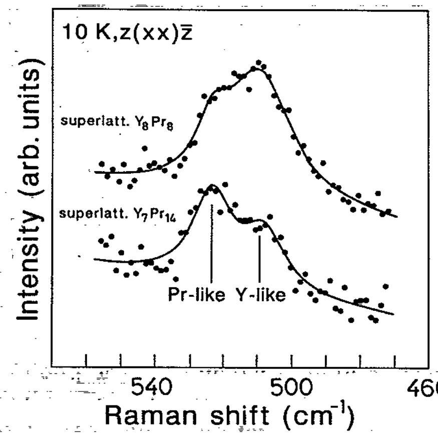

FIG. 6. Raman spectra of (Y_8Pr_8)BCO and (Y_7Pr_{14}) BCO superlattices taken at 10 K in the $z(xx)\bar{z}$ geometry. Solid lines are the fits to two Lorentzians. Note the variation of relative line intensities.

ers by the adjacent nonsuperconducting $PrBa_2Cu_3O_{7-\delta}$. This influences strongly the superconducting properties of thin-layer superlattices $(Y/Pr)Ba_2Cu_3O_{7-\delta}$.[22] However, because of screening effects and the relatively large layer thicknesses of the superlattices studied here, this effect seems to be too small to account for the variation of strength of the electron-phonon coupling by a factor of 2.

The softening does not occur for the B_{1g} mode confined in the nonsuperconducting $PrBa_2Cu_3O_{7-\delta}$ layers. This mode shows the usual anharmonicity-related hardening with decreasing temperature saturating at low T. If the Pr layers were superconducting and the coupling strength similar to the equivalent mode in $YBa_2Cu_3O_{7-\delta}$ one would, according to the Zeyher-Zwicknagl calculations of the self-energies,[23] expect a softening of about half (≈ 2 cm^{-1}) for the 304 cm^{-1} mode. Similarly, its linewidth should decrease as the phonon frequency is below the bulk value $2\Delta_{YBCO} \approx 320$ cm^{-1}.[18] As it is seen in Fig. 5, however, there is neither a softening nor a narrowing of the mode localized in the Pr layers. Thus, for the Pr-layer thicknesses studied (7 to 14 ML), no influence of the superconducting $YBa_2Cu_3O_{7-\delta}$ layers on the nonsuperconducting $PrBa_2Cu_3O_{7-\delta}$ is found. For sufficiently thin Pr layers one might expect this to happen due to the proximity to the superconducting layers. The preparation of these layers is under way.

It is now interesting to look at the influence of superconductivity on the extended oxygen mode (Fig. 5) at 444 cm^{-1}. It shows a slight hardening (≈ 2 cm^{-1}) in the superconducting state, comparable to the behavior in bulk material.[24] This behavior is typical of an above-gap phonon and shows that a phonon extended through the entire superlattice still couples to the gap in the superconductor. The linewidth of the phonon shows no change at T_c within the error of our data.

The phonon line with the highest frequency, corresponding to the O(4) vibration, also exhibits similar hardening below T_c and, at the same time, an unusual increase of the linewidths upon cooling. This effect cannot be understood within the self-energy picture, because for phonons well above the gap superconductivity-induced broadening should decrease with phonon frequency,[23] i.e., the effect should be smaller than for the 444 cm^{-1} phonon. Instead, we believe that there is a splitting of this line at low temperatures. The reason for this is the localization of O(4) vibrations in the Y and Pr layers of the superlattice. At low temperatures one can indeed identify two lines in the range of interest with frequencies of 509 and 523 cm^{-1} and linewidths of about 15 cm^{-1}, corresponding to these confined modes (Fig. 6). The variation of the relative layer thickness in the two superlattices gives rise to corresponding changes of the line intensities: the low-frequency peak of the Y-like phonon becomes stronger for the Y_8Pr_8 superlattice with respect to the Y_7Pr_{14} one. Thus, phonon confinement is responsible for the apparent broadening with decreasing temperature of the high-frequency line in the Raman spectrum.

V. CONCLUSIONS

We have reported the observation of confined and extended optical phonon modes in $YBa_2Cu_3O_{7-\delta}$/$PrBa_2Cu_3O_{7-\delta}$ superconducting superlattices. The self-energy effects typical for the pure bulk superconductors were found for modes confined in the superconductor and for extended modes. Modes confined in the insulator showed no self-energy effects.

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*On leave from the Institute of Semiconductors, Ukrainian Academy of Sciences, 252650 Kiev-28, Ukraine.

†Permanent address: P.N. Lebedev Physical Institute, 117924 Moscow, Russia.

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