

## Phonon anomalies in $a$ -axis-oriented $(\text{YBa}_2\text{Cu}_3\text{O}_7)_m(\text{PrBa}_2\text{Cu}_3\text{O}_7)_n$ superconducting superlattices: Evidence for an anisotropic gap function

V. Storozhuk, Kyung-Min Ham, T. Teng, and R. Sooryakumar  
*Department of Physics, The Ohio State University, Columbus, Ohio 43210*

I. Takeuchi, Z. Trajanovic, C. Kwon, Qi Li, and T. Venkatesan  
*Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742*  
 (Received 14 October 1994)

The temperature dependence of phonon self-energies in  $a$ -axis-oriented superconducting superlattice films of  $(\text{YBa}_2\text{Cu}_3\text{O}_7)_m(\text{PrBa}_2\text{Cu}_3\text{O}_7)_n$  reveals several modes associated with the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  layer exhibiting anomalies in their frequencies and linewidths below  $T_c$ . The ability to modify the superconducting properties through choice of  $m$  and  $n$  while not altering important phonon frequencies or the unit-cell atomic composition of the individual layers enable a critical examination of key aspects of the microscopic theory by Zeyher and Zwicky [Z. Phys. B **78**, 175 (1990)] that is often used to account for such renormalizations in bulk samples. While our data cannot be satisfactorily accounted for by this theory when including isotropic  $s$ -wave pairing, the results are in qualitative agreement with a recent extension that considers an anisotropic gap parameter. Further, despite a relatively large value ( $\sim 20 \text{ \AA}$ ) for the superconducting coherence length in the  $\text{CuO}_2$  plane in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , vibrations confined primarily to the Pr layer show no anomalies below  $T_c$  indicating suppression of the order parameter within  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  in these  $a$ -axis-oriented superconducting superlattices.

### I. INTRODUCTION

Anomalies in frequency and linewidths of near zone center optical phonons in the superconducting state constitute an important part of the study of bulk high- $T_c$  superconductors.<sup>1,2</sup> In particular in  $R\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $R$  = rare earth) the determination of the superconducting energy gap value of  $2\Delta/kT_c \sim 5$  has been a striking conclusion.<sup>3,4</sup> In these experiments, depending on the phonon energy relative to the superconducting energy gap, those Raman-active phonons which couple to the electronic states piled up near  $2\Delta$  will broaden or sharpen and shift up or down in frequency as the sample changes from the normal to superconducting state. In the most dramatic data from  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the “340- $\text{cm}^{-1}$ ” phonon which involves the out-of-phase vibrations of the O(2) and O(3) oxygen atoms in the  $\text{CuO}_2$  planes, softens by 4–8  $\text{cm}^{-1}$  and broadens from 13 to 20  $\text{cm}^{-1}$  as the sample is cooled from  $T_c$  (=92 K) to about 70 K.<sup>5–7</sup> Calculations of Zeyher and Zwicky<sup>8</sup> (ZZ) who assume isotropic  $s$ -wave pairing and include strong-coupling effects have become a popular theory to explain such phonon anomalies in  $R\text{Ba}_2\text{Cu}_3\text{O}_7$ .

A key prediction of the ZZ theory and a direct manifestation of an isotropic  $s$ -wave gap is the abrupt transformation in the clean limit of the softening of a phonon lying just below the gap to enhanced hardening as  $\hbar\omega_v/2\Delta(T=0)$  increases only slightly beyond a critical value of  $\sim 1.08$ . Although the extent of such hardening is diminished for finite electron elastic-scattering rates  $h/2\Delta(0)\tau$ , the suppression of the softening nevertheless continues to be very rapid when  $\hbar\omega_v/2\Delta(0)$  approaches 1.08. Early experiments established that the size of the

softening and hardening as well as line width changes when the frequencies of the 340- and 440- $\text{cm}^{-1}$  phonons were tuned by about 10% by replacing Y with rare-earth atoms and replacement<sup>3,4</sup> of  $\text{O}^{16}$  by  $\text{O}^{18}$  agreed reasonably well with predictions of the ZZ theory and enabled an energy gap to be deduced. These experiments however did not change  $T_c$  significantly and thus it was not possible to increase  $\hbar\omega_v/2\Delta(T=0)$  sufficiently to observe the predicted rapid crossover from softening to hardening and swift onset of enhanced broadening of the “near-gap” phonon below  $T_c$ .

In an experiment specifically designed to observe this abrupt transition in the phonon self-energies as  $2\Delta$  was presumably lowered below  $\hbar\omega_v$ , the  $B_{1g}$ -like 340- $\text{cm}^{-1}$  phonon in Ni-doped  $\text{YBa}_2\text{Cu}_3\text{O}_7$  was investigated.<sup>9</sup> Ni was a particularly good dopant in this regard since, while  $T_c$  was reduced systematically with doping, the frequency of the O(2)–O(3) Raman modes was unaffected. It was thus possible to tune  $\hbar\omega_v/2\Delta(0)$  for this mode from 1.03 to 1.3 (assuming  $2\Delta/kT_c \sim 5$ ) and hence adequately cover the range over which a rapid change in the sign of the real part of the phonon self-energy was expected on the basis of the ZZ calculations. However, the softening of the 340- $\text{cm}^{-1}$  phonon was retained from all Ni-doped films with no evidence for its reversal. In fact, for the highest Ni-doping ( $T_c = 71 \text{ K}$ ), the softening occurred well above  $T_c$  and continued smoothly to 10 K. The phonon linewidths did not show any anomalies regardless of the Ni concentration.

Other studies of doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  include oxygen-depleted samples,<sup>10,11</sup> Au substitution for Cu atoms in the  $\text{CuO}$  chains,<sup>12</sup> and Pr doping for Y.<sup>12,13</sup> Au doping increases  $T_c$  slightly, while O depletion, and Pr doping de-

creases  $T_c$ . In all cases the renormalization of the  $340\text{-cm}^{-1}$  phonon linewidth disappears quickly with doping. Phonon softening is slightly more robust and is present in the Au-doped samples ( $T_c > 90$  K) even though the broadening is suppressed, while with oxygen depletion the softening disappears completely for  $T_c \leq 84$  K. It is thus evident that while the Zeyher-Zwiczagl theory captures several aspects of the measured phonon anomalies below  $T_c$  in  $\text{RBa}_2\text{Cu}_3\text{O}_7$ , some key predictions of theory remain to be verified and important observations related to effects of doping are not fully borne out in the calculations. As a qualitative explanation for some of these departures, it has been proposed that different phonons couple most strongly to different segments of the Fermi surface and that the energy gap is anisotropic.<sup>12</sup>

The experiments conducted thus far that allow the predictions of ZZ to be scrutinized are generally all based on site-selective substitutions to modify the material properties. This approach however bears some inherent disadvantages. Doping changes the crystal composition to varying degrees and hence subtle modifications, especially at the Fermi surface, to the electronic properties could influence factors as the normalized elastic-scattering rate  $h/2\Delta(0)\tau$  which are important to the ZZ description. Different dopants also alter  $T_c$  via different mechanisms depending on which site they substitute while their magnetic character, for example, Ni and Zn compared to Cu, may lead to consequences on pair breaking. Further, doping often alters unit-cell lattice constants thereby affecting short-range atomic overlap potentials.

In this paper we utilize  $a$ -axis-oriented superlattices constructed of  $m$  superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $n$  insulating  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  unit-cell blocks (denoted as  $a\text{-Y}_m\text{Pr}_n$ ) seeking to observe the predicted swift change below  $T_c$  in the real part of the phonon self-energy as  $\hbar\omega_v/2\Delta$  increases beyond the critical value. An advantage of utilizing superlattice structures is that the superconducting properties are modified by merely altering the superlattice period while the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  unit-cell composition remains unaltered. Moreover, the frequencies of the Raman phonons that exhibit anomalies below  $T_c$  in bulk layers are largely unaffected in the superlattice thus allowing  $\hbar\omega_v/2\Delta$  to be tuned over the desired range. The specific  $a\text{-Y}_m\text{Pr}_n$  structures for this study were carefully selected exploiting the significant dependence of  $T_c$  on  $m$  and  $n$  as well as the ability to construct high-quality films with optimal oxygen content and sharp interfaces. While impurities are known to affect the phonon linewidths and the superconducting gap there is no significant differences in sample quality and impurity content amongst our samples since they were ablated from the same high-quality target material under identical conditions. In addition, since the in-plane low-temperature superconducting coherence length  $\xi_{a,b}$  ( $\sim 20$  Å) in bulk samples far exceeds the  $a, b$  lattice parameters ( $\sim 4$  Å),<sup>14</sup> a search for proximity-induced superconductivity in the  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  layers via studies of the phonon anomalies will be more amenable in  $a\text{-Y}_m\text{Pr}_n$  than in  $c$ -axis-oriented superlattices.

Our results show that the  $340\text{-cm}^{-1}$   $\text{YBa}_2\text{Cu}_3\text{O}_7$  phonon continues to soften in the superconducting state in

the superlattices when  $T_c$  is reduced to as low as 56 K, while its linewidth broadens slightly in the ordered state in the three superconducting samples with  $T_c \geq 63$  K. The vibration at 440 and  $505\text{ cm}^{-1}$  associated with the O(2)–O(3) atoms and O(4) atoms indicate noticeable additional hardening below  $T_c$  in  $a\text{-Y}_{30}\text{Pr}_{10}$  ( $T_c = 80$  K) and  $a\text{-Y}_{18}\text{Pr}_6$  when  $T_c$  equals 74 K. These results, particularly the sustained softening of the  $340\text{-cm}^{-1}$  mode in films where  $T_c$  has been reduced by over 35% of its bulk value (90 K) cannot be reconciled with the ZZ theory when isotropic  $s$ -wave pairing is assumed. The phonon anomalies are however in qualitative agreement with a recent extension by Nicol, Jiang, and Carbotte<sup>15</sup> that considers an anisotropic superconducting gap function. We also deduce from the normal temperature response of modes confined to the Pr layers in  $a\text{-Y}_m\text{Pr}_n$ , no evidence for proximity-induced superconductivity even in the thinnest (12 Å)  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  layer despite the relatively large value of  $\xi_{a,b}$  in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

## II. EXPERIMENTAL DETAILS

Four superlattice samples of  $a\text{-Y}_m\text{Pr}_n$  [ $a\text{-Y}_{30}\text{Pr}_{10}$  ( $T_c = 80$  K),  $a\text{-Y}_{18}\text{Pr}_6$  ( $T_c = 74$  K),  $a\text{-Y}_{12}\text{Pr}_4$  ( $T_c = 63$  K), and  $a\text{-Y}_9\text{Pr}_3$  ( $T_c = 56$  K)] each about 300 nm thick were made by pulsed-laser deposition on (100)  $\text{LaSrGaO}_4$  substrates as described elsewhere.<sup>16</sup> The samples were characterized by x-ray-diffraction and Fig. 1(a) shows typical diffraction spectra from one sample,  $a\text{-Y}_{18}\text{Pr}_6$ . Satellite peaks due to superlattice modulation are indicated by arrows and their separation provides for the superlattice period which agree with estimates deduced from growth conditions.<sup>17</sup> The transition temperature  $T_c$  of each sample was measured by dc resistivity and the values quoted in this paper refer to the midpoint of the resistive transition. The Raman measurements were made in back scattering utilizing 488.0 and 514.5-nm laser lines with typical power densities of  $50\text{ W/cm}^2$  focused by a cylindrical lens. The temperatures quoted are those recorded by a sensor placed next to the samples.

## III. RESULTS AND DISCUSSION

Figure 1(b) shows Raman spectra at 300 K from  $a\text{-Y}_{18}\text{Pr}_6$  revealing strong polarization selectivity that confirms the very high degree of in-plane orientational order while Fig. 1(c) illustrates selected spectra indicating their temperature dependence. Spectra of similar quality were obtained from the other superlattices. The peaks at 128, 152, 307, 337, 440, and  $505\text{ cm}^{-1}$  are also observed in bulk layers and the principal atoms involved in these vibrations are, respectively, Ba, Cu(2), O(2)–O(3) (out-of-phase) in Pr layer, O(2)–O(3) (out-of-phase) in Y layer, O(2)+O(3) (in-phase) and the bridging oxygen O(4) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>1</sup> The Raman spectra from these  $a\text{-Y}_m\text{Pr}_n$  samples are hence largely accounted for as a superposition of vibrations from the component Y and Pr layers with the frequency of the  $500\text{-cm}^{-1}$  phonon confirming the optimal oxygen content in the Y layers.<sup>18</sup> Vibrations related to the O(4) atom around  $520\text{ cm}^{-1}$  in bulk

PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> softens from 523 to 505 cm<sub>p-1</sub> as  $d_{\text{Pr}}$ , the Pr-layer thickness, is reduced from 40 to 12 Å. This reduction confirms earlier findings<sup>19,20</sup> that, independent of the Y-layer thickness, the O(4) mode in the Pr layer softens when  $d_{\text{Pr}} < 25$  Å. The broad and asymmetric profile of the peak around 500 cm<sup>-1</sup> in Fig. 1(c) arises from the overlap of the two O(4) vibrations associated with the Y and Pr layers in *a*-Y<sub>18</sub>Pr<sub>6</sub>.

The solid curves through the data of Fig. 1(c) are fits based on Fano line shape for the mode at ~340 cm<sup>-1</sup>, while a Lorentzian was used to fit the other phonons. Figures 2 and 3 summarize the temperature dependencies of the phonon frequencies and linewidths for the four superconducting *a*-Y<sub>m</sub>Pr<sub>n</sub> films. The solid line through all data for the half-widths are based<sup>3</sup> on decay into two equal energy phonons chosen to fit the data above  $T_c$  while the lines through the frequency data are a guide to the eye. The phonon at ~340 cm<sup>-1</sup> is found to soften rather rapidly by 3–4 cm<sup>-1</sup> in a narrow temperature range between  $T_c$  and  $2/3T_c$  in the *a*-Y<sub>30</sub>Pr<sub>10</sub> ( $T_c = 80$  K) superlattice. A similar renormalization of this mode is

found in *a*-Y<sub>18</sub>Pr<sub>6</sub> ( $T_c = 74$  K) and *a*-Y<sub>12</sub>Pr<sub>4</sub> ( $T_c = 63$  K) although the data from these films indicate that the softening may be commencing at a temperature (~5–15 K) above  $T_c$ . The magnitude of the overall softening in these three superlattices is typical of bulk YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> films<sup>21</sup> and some crystals<sup>5</sup> although smaller than the ~8-cm<sup>-1</sup> drop reported from other single crystals.<sup>6,7</sup> The softening in *a*-Y<sub>9</sub>Pr<sub>3</sub> ( $T_c = 56$  K) is not as distinct as in the other high- $T_c$  superlattices although it is clear that there is *no* continued hardening of this mode below  $T_c$  in this film. Moreover, while it is difficult to identify an exact temperature for the onset of 340-cm<sup>-1</sup> mode softening in *a*-Y<sub>9</sub>Pr<sub>3</sub> the data in Fig. 2 indicate that the modifications in this film may also commence above  $T_c$ . The linewidth of the 340-cm<sup>-1</sup> mode broadens slightly in the ordered state in all films but *a*-Y<sub>9</sub>Pr<sub>3</sub> ( $T_c = 56$  K). There is also clear evidence in Fig. 3 for an abrupt change near  $T_c$  in the slope of the  $\omega_v$  versus  $T$  curve of the 440- and 505-cm<sup>-1</sup> phonons in *a*-Y<sub>30</sub>Pr<sub>10</sub> and *a*-Y<sub>18</sub>Pr<sub>6</sub> indicating anomalous hardening in the supercon-

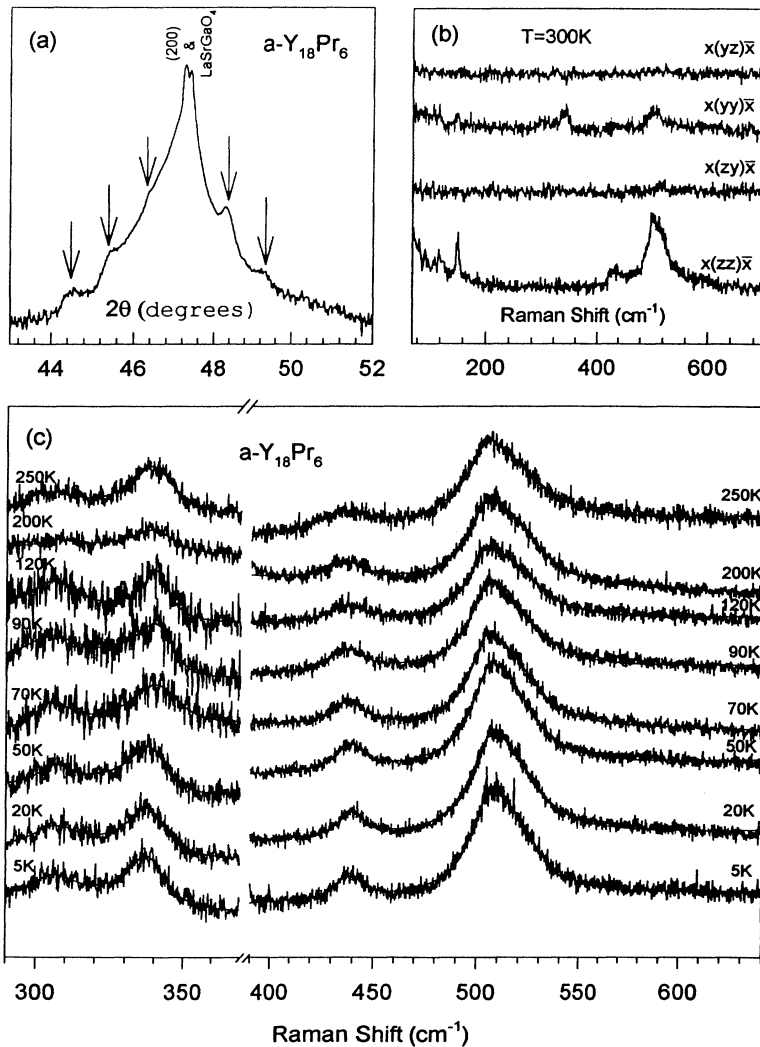


FIG. 1. (a) X-ray-diffraction pattern of *a*-Y<sub>18</sub>Pr<sub>6</sub> superlattice. The satellite peaks around the main (200) peak are superlattice reflections from the modified unit cell. Contributions from the substrate overlap with central (200) peak. The ordinate axis is logarithmic. (b) Raman spectra from *a*-Y<sub>18</sub>Pr<sub>6</sub> at 300 K revealing polarization selectivity of the scattering peaks. In the standard notation  $x(yz)\bar{x}$  directions within brackets indicate the polarizations of the incident ( $y$ ) and back scattered ( $z$ ) photons propagating, respectively, along  $x$  and  $\bar{x}$ . (c) Temperature dependence of several Raman phonons in *a*-Y<sub>18</sub>Pr<sub>6</sub>. The solid line through each spectrum shows a fit based on Lorentzian and Fano line-shape analysis.

ducting state. Such hardening is however absent in the other two superlattices  $a\text{-Y}_{12}\text{Pr}_4$  ( $T_c = 63$  K) and  $a\text{-Y}_9\text{Pr}_3$  ( $T_c = 56$  K). The linewidths of the 435- and 505- $\text{cm}^{-1}$  mode in all four films are well described by standard two-phonon decay over the entire temperature range. The frequency and linewidth of the phonons at 304  $\text{cm}^{-1}$  [O(2)-O(3) vibration in Pr layer] and  $\sim 520$   $\text{cm}^{-1}$  [(O4) vibration in Pr layer] (Fig. 2) as well as the modes at 128  $\text{cm}^{-1}$  (Ba vibration) and 150  $\text{cm}^{-1}$  [Cu(2) vibration] (not shown), behave in a conventional manner.

We now primarily focus on the 340- $\text{cm}^{-1}$  mode where the ratio  $\hbar\omega/2\Delta$  in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$  for this phonon has a magnitude lying close to 1 which hence places it at a critical energy within the ZZ theory.<sup>3,4</sup> Complete suppression of the softening of this mode observed below  $T_c$  should be readily achieved as  $\hbar\omega/2\Delta$  is increased only very slightly to about 1.08 beyond which this phonon

must harden considerably in the ordered state. This reversal in the temperature dependence of the phonon self-energy predicted in Ref. 8 is clearly not evident in our superconducting  $a\text{-Y}_m\text{Pr}_n$  samples. In  $a\text{-Y}_{12}\text{Pr}_4$  ( $T_c = 63$  K) for example for  $2\Delta \sim 5kT_c$ ,  $\hbar\omega/2\Delta$  has now increased beyond 1.5, i.e., well in excess of the critical value, and hence the ZZ calculations predict that this phonon should certainly *not* soften below  $T_c$ . In fact this lattice vibration in  $a\text{-Y}_{12}\text{Pr}_4$  should have hardened considerably below  $T_c$  by a value comparable, for instance, to that observed for the 440- $\text{cm}^{-1}$  phonon in  $a\text{-Y}_{30}\text{Pr}_{10}$ .

The absence of a rapid cross over in the sign for the change in the real part of the 340- $\text{cm}^{-1}$  phonon self-energy suggests that isotropic  $s$ -wave pairing may not be valid for the  $\text{RBa}_2\text{Cu}_3\text{O}_7$  superconductors. Nicol, Jiang, and Carbotte have investigated within a BCS model as

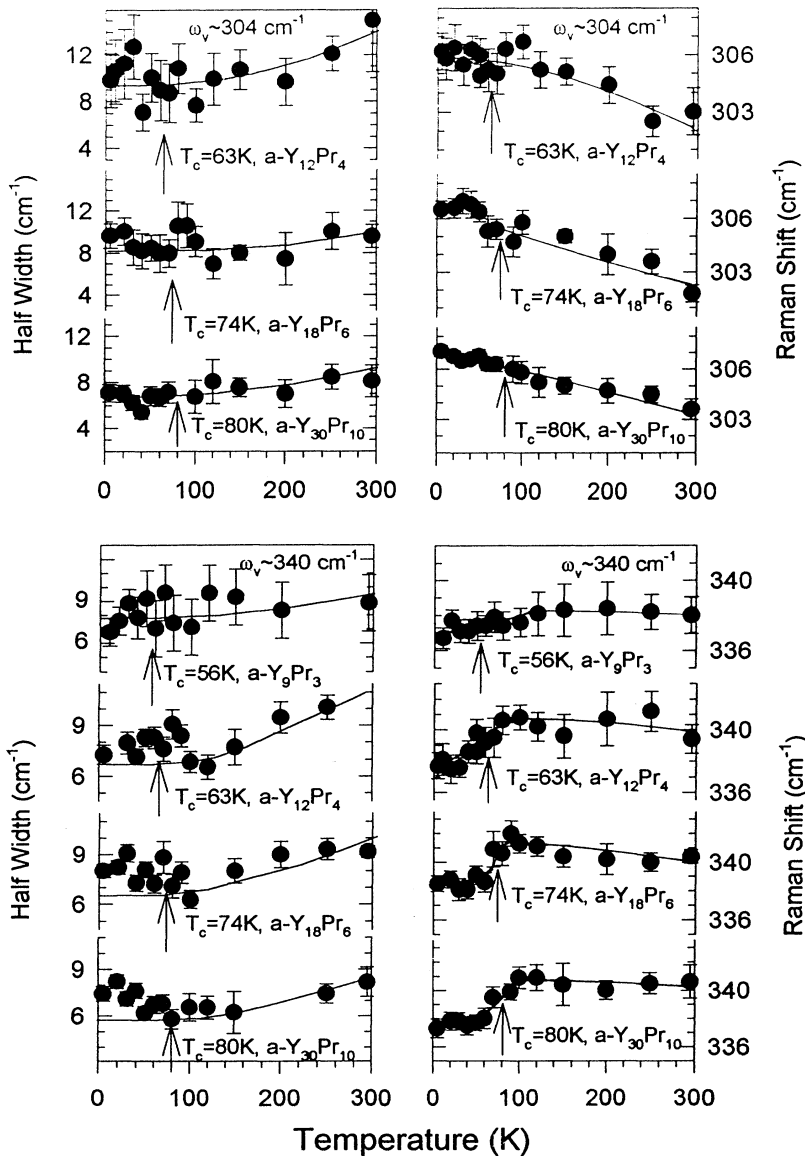


FIG. 2. Half widths and frequencies of the 340- and 300- $\text{cm}^{-1}$  phonon vs  $T$  for the different  $a\text{-Y}_m\text{Pr}_n$  superlattices. The solid lines through data for the half-widths are based on decay into two equal energy phonons chosen to fit data above  $T_c$  while lines through data of frequencies are a guide to the eye.

well as extensions to strong-coupling calculations, the frequency shift and change in linewidth due to superconductivity of zone center Raman phonons with nodes in the gap. They relate their results to a *d*-wave model while a model layered superconductor with large anisotropy is also shown to approximate a gap function with nodes. Among the significant modifications that arise when departing from the isotropic *s*-wave pairing description are the location and abruptness of the crossover from softening to hardening as  $\hbar\omega_v/2\Delta$  increases beyond the critical value of 1.08 in the ZZ calculations. For instance for the layered superconductor with an anisotropic gap function  $\Delta_{Kz} = \Delta[1 + b \cos(K_z c)]$  three distinct regions of behavior are found. For phonon frequencies below twice the minimum gap, the behavior is predicted to be *s*-wave-like with softening accompanied by no change in the phonon linewidth below  $T_c$ . If the frequency lies beyond twice the maximum gap, the behavior is also similar to the *s*-wave case where broadening occurs with hardening of the phonon frequency for  $T < T_c$ . However,

in the region bounded by twice the minimum and maximum gaps, the phonon self-energy behavior is like that for a gap parameter with nodes, where softening with broadening is expected. In this intermediate region not only does the singularity related to the minimum gap leading to frequency softening weaken with increasing gap asymmetry but its location also steadily falls to smaller values of  $\hbar\omega_v/2\Delta$  in comparison to the  $b=0$ , isotropic *s* wave, result. Further, there is a well defined range of frequencies beyond this minimum gap singularity where pronounced phonon softening continues to be sustained before hardening turns on abruptly as  $\hbar\omega_v$  increases beyond the maximum gap. Enhanced broadening is also predicted below  $T_c$  for this finite range of  $\hbar\omega_v/2\Delta$  between the minimum gap singularity and the onset of hardening.

We find that these general trends predicted within the specific anisotropic gap description in Ref. 15 are in qualitative agreement with our results on the 340-cm<sup>-1</sup> phonon. The continued softening of this phonon as well as

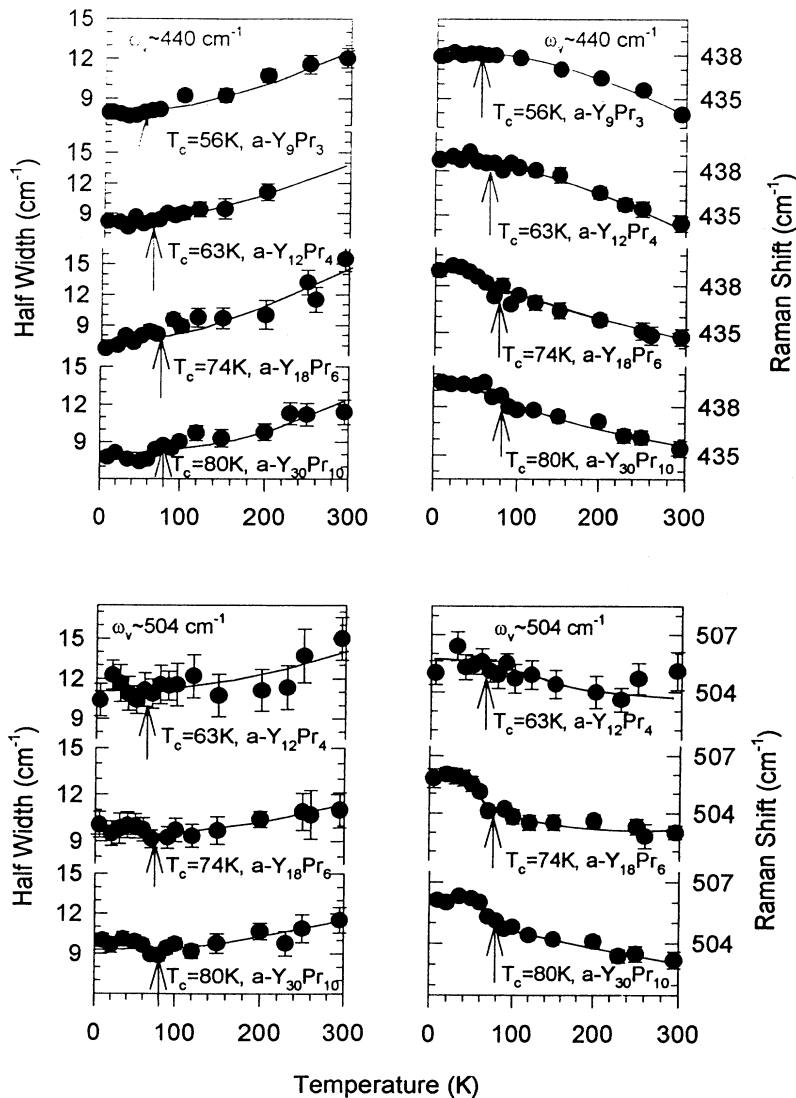


FIG. 3. Half-widths and frequencies of the 440- and ~500-cm<sup>-1</sup> phonon vs  $T$  for the different  $a$ -Y<sub>*m*</sub>Pr<sub>*n*</sub> superlattices. The solid lines through data for the half-widths are based on decay into two equal energy phonons chosen to fit data above  $T_c$  while lines through data of frequencies are a guide to the eye.

its slight broadening below  $T_c$  by approximately the same extent in all our superconducting samples when  $T_c$  drops steadily to 63 K (i.e.,  $\hbar\omega_v/2\Delta \sim 1.53$  for  $2\Delta/kT_c \sim 5$ ) are consistent with these conclusions. In this case, depending on the magnitude of the gap asymmetry (parameter  $b$ ) the hardening of the 440-cm<sup>-1</sup> phonon can also be accounted for within this description since it would lie beyond the maximum gap. As discussed in Ref. 15, the difference between the phonon renormalizations arising from an anisotropic gap  $\Delta_{Kz}$  and that from a gap exhibiting  $d$ -wave symmetry is small and therefore the temperature dependence of the phonon self-energies in our present study is not sufficient to unambiguously identify the precise nature of the gap asymmetry in the  $R\text{Ba}_2\text{Cu}_3\text{O}_7$  superconductors. We however do find that the anomalies *cannot* be satisfactorily described within isotropic  $s$ -wave pairing.

It is indeed significant that the 340-cm<sup>-1</sup> phonon in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  that has been heavily studied in the context of phonon anomalies and gap determination, has not been observed to harden in spite of attempts to alter the relative separation between its energy and the “gap”  $2\Delta$ . Such experiments include Ni doping,<sup>9</sup> application of high pressures,<sup>22</sup> and the present study. Consistent with the notion of an anisotropic gap we therefore conclude as proposed by Thomsen *et al.*<sup>12</sup> that different phonons in the pure material couple to different segments of the gap function. In particular, it appears that the 340-cm<sup>-1</sup> phonon couples with a segment of the gap lying well above this energy, and, on reducing  $T_c$  this portion of the gap function continues to lie above the phonon energy accounting for the absence of hardening in this case. For example we determine from the softening of the 340-cm<sup>-1</sup> phonon in  $a\text{-Y}_{12}\text{Pr}_4$  that  $2\Delta_{\text{max}}/kT_c > 7.8$ . On the other hand the 440- and 500-cm<sup>-1</sup> phonons must lie above the gap to which they couple in order to account for their observed behavior below  $T_c$ . The observed modifications to the phonon self-energies in the  $a\text{-Y}_m\text{Pr}_n$  samples can therefore only be accommodated within an anisotropic gap function for the Y layer.

While there is no definitive consensus for the mechanism for superconductivity in the high- $T_c$  oxides there is growing evidence, theoretical calculations as well as experiments, that suggest an unconventional pairing interaction. Theories include a  $d_{x^2-y^2}$  pairing state that has explained many normal and superconducting properties of the cuprates,<sup>23</sup> anisotropic  $s$ -wave state or complex mixtures of  $s$  and  $d_{x^2-y^2}$ .<sup>24</sup> Experimental evidence for such exotic pairing and support for states in the gap comes from Raman scattering<sup>25</sup> (although, see comment by Krantz and Cardona<sup>26</sup>), point-contact tunneling,<sup>27</sup> penetration depth,<sup>28</sup> and optical conductivity.<sup>29</sup> We note that in the  $a$ -axis superlattices, a periodic modulation of the  $\text{CuO}_2$  planes associated with the Y and Pr layers is introduced. Thus an additional anisotropy, beyond that associated along the  $c$  axis in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$  layers, is interjected by the specific orientation and laminar geometry of these superlattices. Does such an anisotropy manifest in the gap function and the electron-phonon coupling and thus influence our results? An important parameter in

this regard is the inplane superconducting coherence length  $\xi_{a,b}$  which has been measured in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$  to be about 20 Å.<sup>14</sup> Thus the extension of the order parameter in the  $a$  direction is smaller than even the thinnest Y layer (36 Å in  $a\text{-Y}_9\text{Pr}_3$ ) utilized in our experiments which suggest that no additional anisotropies important to this study are likely to be introduced by the specific structures chosen for this investigation.

We now briefly address the finding that the softening of the 340-cm<sup>-1</sup> mode in our superlattices with reduced  $T_c$ 's may be commencing prior to the onset of superconductivity. A similar, though more dramatic, behavior was also observed<sup>9</sup> in bulk  $\text{YBa}_2\text{Cu}_{3(1-x)}\text{Ni}_{3x}\text{O}_7$  when  $T_c$  was reduced from its optimal value of  $\sim 90$  K for the pure ( $x=0$ ) material to 71 K when the Ni concentration was 6 at. %, where the softening commenced at a temperature as high as 140 K ( $\sim 2T_c$ ). Above- $T_c$  anomalies in the phonon frequencies of several *infrared* and Raman-active phonons in oxygen-deficient and ion-substituted  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are now experimentally well established<sup>30</sup> and it has been pointed out that a common feature among the samples where the anomaly in the real part of the phonon self-energy is observed above the superconducting transition temperature is that such samples are generally underdoped with regard to achieving an optimal  $T_c$ .<sup>31</sup> Although a strong correlation has also been found between the occurrence of such phonon anomalies and deviations in the spin susceptibilities,<sup>30</sup> at present there is no microscopic explanation for the above- $T_c$  phonon anomalies.

Finally, unlike data from the Y layers, data associated with the out-of-phase O(2)-O(3) vibrations at  $\sim 300$  cm<sup>-1</sup> and confined to the Pr layer (Fig. 2) shows continued normal hardening below  $T_c$  with the linewidths reminiscent of conventional behavior. If the  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  layers in the superlattice were superconducting and parameters such as the electron phonon coupling and  $\tau^{-1}$ , were similar to that in the neighboring Y layer, then the 300-cm<sup>-1</sup> mode should have softened in the superconducting state. In fact under such conditions this mode in  $a\text{-Y}_{30}\text{Pr}_{10}$  ( $T_c = 80$  K) should have exhibited the largest softening below  $T_c$  and be accompanied by broadening. Further, such softening should be replaced by considerable hardening when  $T_c$  is lowered further to 63 K as in  $a\text{-Y}_{12}\text{Pr}_4$ . The absence of such effects to the  $\sim 300$  cm<sup>-1</sup> phonon hence suggest that there is no influence of the neighboring  $\text{YBa}_2\text{Cu}_3\text{O}_7$  layer on the superconducting properties of the Pr layer. As already noted the superconducting coherence length parallel to the  $\text{CuO}_2$  planes in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is about 20 Å and thus larger than  $d_{\text{Pr}}$ , the Pr-layer thickness in some of the superlattices of this study. The absence of such proximity-induced effects in  $a\text{-Y}_m\text{Pr}_n$  is hence significant and may be due to the interface between the two different layers that intersects the continuously connected  $\text{CuO}_2$  planes associated with  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  cells. In fact, it is believed that the rapid drop in  $T_c$  with decreasing superlattice period in  $a\text{-Y}_m\text{Pr}_n$  relative to that in  $c\text{-Y}_m\text{Pr}_n$  may arise from such disruptions of the  $\text{CuO}_2$  planes at the interface.<sup>32</sup> The 300-cm<sup>-1</sup> mode associated with the Pr layers

in several *c*-axis-oriented  $\text{Y}_m\text{Pr}_n$  superlattices has also been reported<sup>19,20,33</sup> to be unaffected by superconductivity in these structures. This behavior in *c*- $\text{Y}_m\text{Pr}_n$  layers is however less surprising since the coherence length normal to the  $\text{CuO}_2$  planes is only 4 Å and therefore much smaller than the lattice constant (12 Å) in this direction.

#### IV. CONCLUSIONS

In summary, Raman spectra from superconducting  $a$ - $\text{Y}_m\text{Pr}_n$  superlattices have revealed several phonons associated with the Y layer exhibit anomalies in their frequencies and linewidths below  $T_c$ . The ability to modify  $T_c$  with  $m$  and  $n$  that do not concomitantly alter the frequencies of important Raman-active phonons have shown that the deviations, especially of the 340-cm<sup>-1</sup> “near-gap” phonon in the superconducting state cannot

be accounted for by the theory of ZZ when invoking an isotropic *s*-wave pairing interaction in addressing bulk  $\text{RBa}_2\text{Cu}_3\text{O}_7$ . The observed phonon renormalizations are however qualitatively accounted for by a recent theory that considers departures from an isotropic gap function. Vibrations confined primarily to the Pr layer show no anomalies below  $T_c$  and therefore, despite the relatively long coherence length  $\xi_{a,b}$  in bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , the superconducting order parameter is probably strongly suppressed within  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  in these superconducting superlattices.

#### ACKNOWLEDGMENTS

We thank J. P. Carbotte and M. Cardona for a critical reading of this paper. The work at Ohio State University was supported by the National Science Foundation.

- <sup>1</sup>C. Thomsen and M. Cardona, in *Physical Properties of High Temperature Superconductors I*, edited by D. Ginsberg (World Scientific, Singapore, 1989), p. 409.
- <sup>2</sup>C. Thomsen, in *Light Scattering in Solids VI*, edited by M. Cardona and G. Guntherodt, Topics in Applied Physics (Springer-Verlag, Heidelberg, 1991), p. 285.
- <sup>3</sup>B. Friedl, C. Thomsen, and M. Cardona, Phys. Rev. Lett. **65**, 915 (1990).
- <sup>4</sup>C. Thomsen *et al.*, Solid State Commun. **75**, 219 (1990).
- <sup>5</sup>C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and A. Simon, Phys. Rev. B **37**, 9860 (1988).
- <sup>6</sup>S. L. Cooper, F. Slakey, M. V. Klein, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **38**, 11934 (1988).
- <sup>7</sup>S. L. Cooper and M. V. Klein, Comments Condens. Matter Phys. **15**, 99 (1990).
- <sup>8</sup>R. Zeyher and G. Zwicknagl, Z. Phys. B **78**, 175 (1990).
- <sup>9</sup>K.-M. Ham, J.-T. Kim, R. Sooryakumar, and T. R. Lemberger, Phys. Rev. B **47**, 11439 (1993).
- <sup>10</sup>M. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee, Phys. Rev. B **38**, 4992 (1988).
- <sup>11</sup>A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).
- <sup>12</sup>C. Thomsen, B. Friedl, M. Cieplak, and M. Cardona, Solid State Commun. **78**, 727 (1991).
- <sup>13</sup>K.-M. Ham, R. Sooryakumar, and M. B. Maple (unpublished).
- <sup>14</sup>T. K. Worthington, W. J. Gallagher, and T. R. Dinger, Phys. Rev. Lett. **59**, 1160 (1987).
- <sup>15</sup>E. J. Nicol, C. Jiang, and J. P. Carbotte, Phys. Rev. B **47**, 8131 (1993).
- <sup>16</sup>Q. Li *et al.*, Phys. Rev. Lett. **64**, 3086 (1990); I. Takeuchi *et al.* (unpublished).
- <sup>17</sup>Ivan K. Shuller, Phys. Rev. Lett. **44**, 1597 (1980).
- <sup>18</sup>C. Thomsen *et al.*, Solid State Commun. **65**, 55 (1988).
- <sup>19</sup>K.-M. Ham, R. Sooryakumar, Q. Li, C. Kwon, and T. Venkatesan, Phys. Rev. B **48**, 16744 (1993).
- <sup>20</sup>K.-M. Ham, R. Sooryakumar, I. Takeuchi, Z. Trajanovic, C. Kwon, Qi Li, and T. Venkatesan, Phys. Rev. B **50**, 16598 (1994).
- <sup>21</sup>R. Feile, U. Schmitt, P. Leiderer, J. Schnbert, and U. Poppe, Z. Phys. B **72**, 141 (1988); **72**, 161 (1988).
- <sup>22</sup>A. F. Goncharov, V. V. Struzhkin, and K. Syassen, in *High Pressure Science and Technology-1993*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, AIP Conf. Proc. No. 309 (AIP, New York, 1994).
- <sup>23</sup>P. Monthoux, A. Balatsky, and D. Pines, Phys. Rev. B **46**, 14803 (1992).
- <sup>24</sup>S. Chakravarty, A. Sudbo, P. W. Anderson, and S. Strong, Science **261**, 337 (1993); G. Kotliar, Phys. Rev. B **37**, 3664 (1988); Q. P. Li, B. E. Kolteubach, and R. Joynt, *ibid.* **48**, 437 (1993).
- <sup>25</sup>T. P. Devereaux *et al.*, Phys. Rev. Lett. **72**, 396 (1994).
- <sup>26</sup>M. C. Krantz and M. Cardona, Phys. Rev. Lett. **72**, 3290 (1994).
- <sup>27</sup>J. Kane, Q. Chen, K.-W. Ny, and H.-J. Tao, Phys. Rev. Lett. **72**, 128 (1994).
- <sup>28</sup>J. Annett, N. Goldenfeld, and S. R. Renn, Phys. Rev. B **43**, 2778 (1991).
- <sup>29</sup>T. Pham, M. W. Lee, H. D. Drew, V. Welp, and Y. Fang, Phys. Rev. B **44**, 5377 (1991); K. Tamasaku, Y. Nakamura, and S. Uchida, Phys. Rev. Lett. **69**, 1455 (1992).
- <sup>30</sup>A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).
- <sup>31</sup>A. P. Litvinchuk, C. Thomsen, and M. Cardona, in *Physical Properties of High Temperature Superconductors IV*, edited by D. Ginsberg (World Scientific, Singapore, 1993), p. 375.
- <sup>32</sup>C. B. Eom, A. F. Marshall, J.-M. Triscone, B. Wilkens, S. S. Laderman, and T. H. Geballe, Science **251**, 780 (1991).
- <sup>33</sup>A. P. Litvinchuk, C. Thomsen, I. E. Trofimov, H.-U. Habermeier, and M. Cardona, Phys. Rev. B **46**, 14017 (1992).