

## Dynamics of the $c$ -polarized infrared-active modes in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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(Received 18 April 1997)

We have studied the  $c$ -polarized optical phonons of high quality single crystals of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with doping concentrations ranging from the underdoped to the overdoped regime ( $x=0.1,0.12,0.15,0.18,0.2$ ) at temperatures between 10 and 300 K. We discuss the dependence of all observed phonon modes on temperature as well as on doping. We find no indication for a coupling of the zone-center phonons to the electronic continuum, either in the normal or in the superconducting state. [S0163-1829(97)08734-1]

### I. INTRODUCTION

The  $c$ -polarized infrared response of high- $T_c$  cuprates is composed of two contributions; one is of electronic origin, the other is given by the infrared-active vibrational modes causing a dipole moment along the  $c$  axis. As a consequence of the strong ionicity<sup>1</sup> and the anomalously small dc conductivity along the  $c$  axis, in particular in underdoped compounds, the phonon contribution to the optical conductivity usually exceeds the electronic contribution. For an unambiguous separation of the electronic response, which is the contribution to the optical conductivity of main interest concerning the phenomenon of superconductivity, a detailed knowledge of the phonon response, in particular its dependence on temperature and doping, is a prerequisite.

The role of phonons in high-temperature superconducting cuprates is still an open question. Especially for the double-layer compounds, such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , abrupt changes of the frequencies and linewidths of some phonons at  $T_c$  have been detected by Raman<sup>2</sup> as well as by infrared spectroscopy.<sup>3-6</sup> These anomalies have been attributed to the opening of a superconducting gap. Anomalies detected above  $T_c$  for underdoped samples have been related to the opening of a pseudogap or spin gap.<sup>4,7</sup> It is, therefore, of considerable interest to determine whether such anomalies are also present in other high- $T_c$  superconductors, in particular in single layer compounds.  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  has one of the simplest crystal structures among the high- $T_c$  cuprates (the so-called  $T$  structure). Therefore one would expect this system to be ideal from the theoretical as well as from the experimental point of view. Indeed, large, high quality single crystals are available with various doping concentrations, which are required for a detailed study of the  $c$ -axis properties.<sup>8</sup> However, the situation is complicated by a structural phase transition from the low-temperature orthorhombic phase to the high-temperature tetragonal phase.<sup>9</sup> Moreover, the transition temperature decreases with increasing doping. Both these phenomena complicate the analysis of the phonon response. While the infrared-active phonons for the undoped compound  $\text{La}_2\text{CuO}_4$  and their temperature dependence have been studied systematically and compared with theoretical calculations,<sup>10</sup> to our knowledge no systematic study of the infrared-active phonon modes for the Sr doped

compounds has been presented so far.

In this paper we report the temperature dependence as well as the doping dependence of the  $c$ -polarized infrared-active phonon modes measured by far infrared ellipsometry, a method which allows us to determine the dielectric function directly.

### II. EXPERIMENTAL DETAILS, SAMPLE PREPARATION, AND DATA EVALUATION

The measurements were partly performed with a home-built ellipsometer attached to a Bruker 113v Fourier transform IR spectrometer<sup>11</sup> and with the same ellipsometer attached to a Nicolet Impact 400 vacuum Fourier spectrometer at the beam line U4IR of the National Synchrotron Light Source (NSLS) in Brookhaven.<sup>12</sup> The ellipsometer is basically a rotating analyzer setup, where the polarization ellipse of the light after reflection on the sample is determined by monitoring for each frequency the detected intensity as a function of the analyzer angle  $A$ . For a perfect setup, the detected light intensity  $I$  is expected to be modulated like<sup>13</sup>

$$I(A) = I_0(1 + \alpha \cos(2A) + \beta \sin(2A)), \quad (2.1)$$

where  $\alpha$  and  $\beta$  are the so-called Fourier coefficients. From these coefficients one can directly determine the complex reflectance ratio<sup>13</sup>

$$\tilde{\rho}(\omega, \phi) = \frac{\tilde{r}_p(\omega, \phi)}{\tilde{r}_s(\omega, \phi)}, \quad (2.2)$$

where  $\phi$  is the angle of incidence (in our experiment  $80^\circ$ , with a beam divergence of  $\pm 1.7^\circ$ ) and  $\tilde{r}_p$  and  $\tilde{r}_s$  are the Fresnel reflection coefficients for  $p$ - and  $s$ -polarized light, respectively.<sup>13</sup> The inversion of Eq. (2.2) yields the complex dielectric function:

$$\tilde{\epsilon}(\omega) = \left( \frac{1 - \tilde{\rho}(\omega, \phi)}{1 + \tilde{\rho}(\omega, \phi)} \right)^2 \tan^2 \phi \sin^2 \phi + \sin^2 \phi. \quad (2.3)$$

This relation assumes an isotropic, clean, and homogeneous sample-ambient interface. For an anisotropic sample different dielectric tensor elements contribute to  $\tilde{\rho}(\omega, \phi)$ . In such

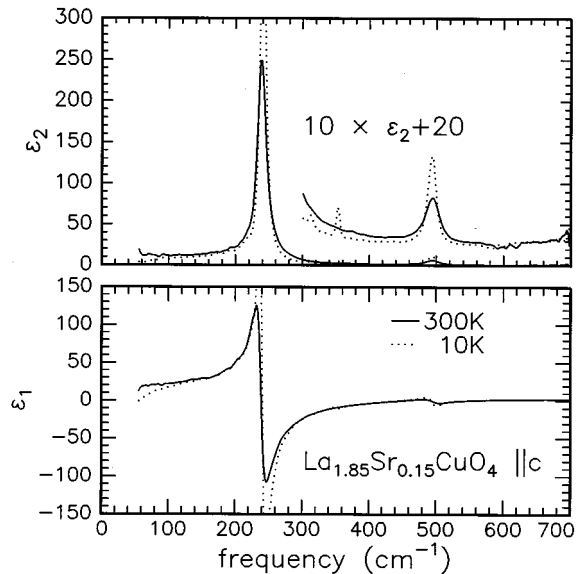


FIG. 1. The real (lower panel) and imaginary part (upper panel) of the  $c$  component of the dielectric function of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  at 300 K (solid line) and 10 K (dotted line). The upper panel also displays  $\epsilon_2(\omega)$  with the vertical scale enlarged by a factor 10 and shifted by 20.

case, the function  $\langle \tilde{\epsilon}(\omega) \rangle$  obtained with Eq. (2.3) is called pseudodielectric function.<sup>14</sup> For a uniaxial material, like  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , we can obtain the dielectric tensor components  $\tilde{\epsilon}^{aa}(\omega)$  and  $\tilde{\epsilon}^{cc}(\omega)$  by fitting the Fresnel equations for a uniaxial material to two experimental spectra of  $\tilde{\rho}(\omega, \phi)$ , taken with the  $c$ -axis parallel and perpendicular to the plane of incidence.<sup>15,16</sup> Such calculations reveal in many scenarios the differences between the pseudodielectric function and the tensor element along the line of intersection between the plane of incidence and the sample surface to be small.<sup>14</sup> Since fits obtained for the  $c$ -axis response of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  using the full anisotropic tensor elements did not significantly alter the results while degrading the signal-to-noise ratio due to noisy  $a$ -axis data, the  $\tilde{\epsilon}^{cc}(\omega)$  data presented in this paper are pseudodielectric functions measured with the  $c$  axis of the sample aligned along the line of intersection between the plane of incidence and the sample surface.

The  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  crystals investigated, with  $x=0.1, 0.12, 0.15, 0.18,$  and  $0.2$ , were grown at the University of Tokyo by the traveling floating-zone method.<sup>17</sup> Their growth and characterization is described elsewhere.<sup>8,18</sup> The measurements were performed on mechanically polished (100) surfaces with dimensions of about  $4 \times 5 \text{ mm}^2$ . The thickness of the samples was above 1 mm, sufficient to make them opaque throughout the entire measured frequency range. The samples were mounted on the cold finger of a He cryostat and the temperature was measured with a Si diode placed close to the sample.

### III. RESULTS AND DISCUSSION

In Fig. 1 we have displayed the real and imaginary part of the out-of-plane component of the dielectric function,  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ , obtained by far infrared ellipsometry for

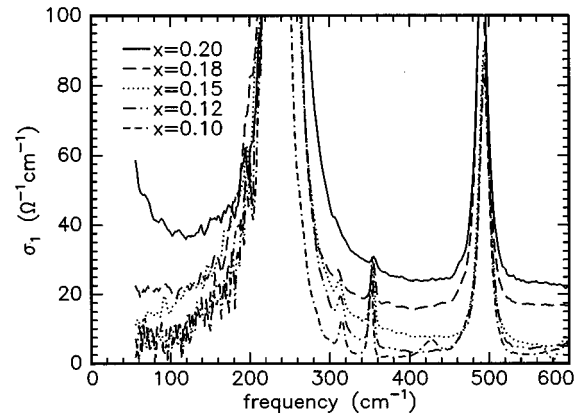


FIG. 2. Real part of the optical conductivity  $\sigma_1(\omega)$  obtained at 50 K for different doping concentrations  $x$  ranging from underdoped to overdoped.

the optimally doped  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  crystal. In addition to the 300 K data we show the dielectric function obtained at 10 K. Consistent with the low dc conductivity of the material and its strong ionic character, the  $c$ -axis response is mostly of phononic origin. For doping concentrations between  $x=0.1$  and  $x=0.2$  the real part of the optical conductivity  $\sigma_1(\omega)$  obtained at 50 K is shown in Fig. 2. While increasing the doping concentration to  $x=0.2$ , the phonon response remains dominant; even at this high doping level, the phonon contribution to the optical conductivity exceeds the electronic background by more than one order of magnitude. The optical conductivities determined by far infrared ellipsometry are in very good agreement with earlier data obtained from reflectance measurements on the same crystals.<sup>8</sup>

All modes contributing to the dielectric function for  $c$ -polarized electric fields can be described by Lorentzian profiles. Therefore we find no indication for an interaction of the phonons with the electronic continuum, which in many cases leads to an asymmetric profile of the phonon structures.

#### A. Assignment of the modes

In the low-temperature optical conductivity (Fig. 2) we observe in total four phonon modes. We note that, contrary to our earlier reports,<sup>10,19</sup> for the Sr doped samples we do not observe a splitting of the strongest mode at  $235 \text{ cm}^{-1}$ . We attribute this difference to a lower quality of the crystal used in the previous work. This conclusion is supported by significantly smaller line widths observed for the phonon modes of the samples discussed in this work.

Based on the fact that the modes at  $310 \text{ cm}^{-1}$  and  $350 \text{ cm}^{-1}$  only appear in the low temperature spectra (see Fig. 1), it has been concluded that they arise from the Brillouin zone folding produced by the orthorhombic distortion of the crystal.<sup>10,19</sup> Consistent with the small orthorhombic distortion, both modes have a small oscillator strength. The two stronger modes at  $235 \text{ cm}^{-1}$  and  $500 \text{ cm}^{-1}$  are already present in the tetragonal high-temperature phase and represent two of the three expected  $c$ -polarized, infrared-active  $A_{2u}$  modes for the tetragonal phase (for the orthorhombic phase six infrared-active modes having  $c$  polarization, corre-

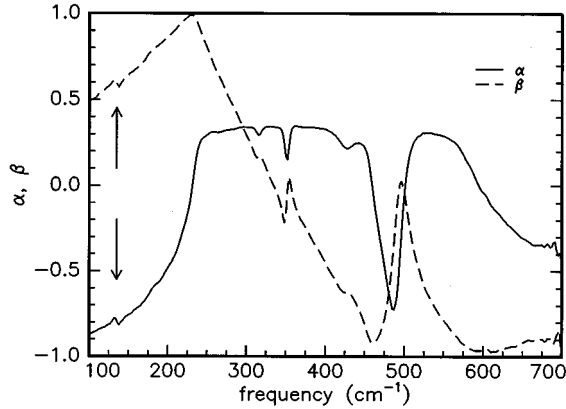


FIG. 3. Fourier coefficients  $\alpha(\omega)$  and  $\beta(\omega)$  determined at 10 K for the  $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$  sample. The arrows mark the weak structures, which we attribute to a  $A_{2u}$  mode at  $135\text{ cm}^{-1}$ . From simulations we can estimate the oscillator strength of this mode to be approximately  $S=0.025$ .

sponding to  $B_{1u}$  symmetry, are predicted based on symmetry considerations).<sup>9</sup> So far only two of the three modes expected for the tetragonal phase and four of the six predicted for the orthorhombic phase have been detected in the infrared spectra for *c* polarization.<sup>10</sup> Based on phonon calculations, and on data obtained by inelastic neutron scattering, the ‘‘missing’’ modes are expected to have frequencies smaller than that of the strong mode at  $235\text{ cm}^{-1}$ .<sup>10,20</sup>

For samples in the underdoped regime ( $x=0,0.1,0.12$ ) we observe at low temperatures a weak structure in the measured Fourier coefficients around  $135\text{ cm}^{-1}$ , see Fig. 3, which we attribute to the ‘‘missing’’  $A_{2u}$  mode. The oscillator strength of this mode was predicted to be very weak.<sup>10</sup> The increased phonon lifetime at low temperatures, together with the small conductivity, allow this mode to show up in the Fourier coefficients. The mode may not be observable for the samples with higher doping because of the increased conductivity and the concomitant noise. As a consequence of the nonlinear relation between the Fourier coefficients and the dielectric function, noise is strongly enhanced in the low frequency regime, a fact which makes it difficult to locate the  $135\text{ cm}^{-1}$  mode in the dielectric function. In a recent publication Bazhenov *et al.*<sup>21</sup> observed an indication for a  $A_{2u}$  mode at  $175\text{ cm}^{-1}$  in  $\text{La}_2\text{CuO}_4$ . However, the phonons measured by this group are very broad, a fact which may indicate a lower quality of their sample which is probably affecting this feature. The frequency of  $135\text{ cm}^{-1}$  observed by us is very close to the frequency of the corresponding mode in the related  $T'$  structure; for  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  a frequency of  $134\text{ cm}^{-1}$  has been reported.<sup>22,23</sup> By simulating the ellipsometric Fourier coefficients we can estimate the oscillator strength of this mode to be approximately  $S=0.025$ .

Because of the small orthorhombic distortion, the ‘‘missing’’  $B_{1u}$  mode is expected to be even weaker than the  $A_{2u}$  mode found at  $135\text{ cm}^{-1}$ . This may explain why we do not see it.

Based on phonon calculations for the tetragonal phase, and on measured oscillator strengths, we have analyzed the eigenvectors of the  $A_{2u}$  modes. The details of this procedure

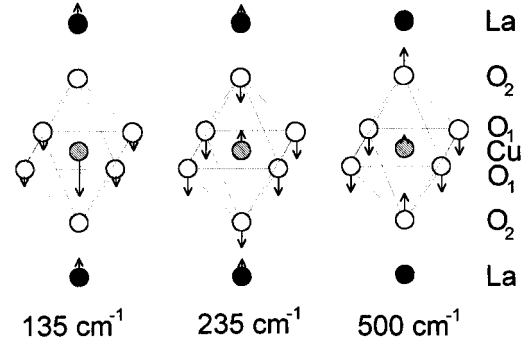


FIG. 4. Eigenvectors, obtained from phonon calculations of the infrared-active  $A_{2u}$  modes, having *c* polarization in tetragonal  $\text{La}_2\text{CuO}_4$ . These eigenvectors have been discussed in more detail in Ref. 10. Note that the corresponding atomic displacements are obtained by dividing the vectors shown here by the square root of the corresponding mass.

are described in a previous publication.<sup>10</sup> The eigenvectors extracted from this analysis are sketched in Fig. 4.

### B. Temperature dependence of the phonon parameters

The temperature dependence of the TO frequency, the linewidth (FWHM) and the oscillator strength for the infrared active modes with *c* polarization is given in Fig. 5 for an underdoped sample ( $x=0.1$ ), in Fig. 6 for the optimally doped one ( $x=0.15$ ), and in Fig. 7 for an overdoped sample ( $x=0.2$ ). The TO frequency, the linewidth  $\Gamma$ , and the oscillator strength  $S$  correspond to the Lorentz parameters obtained from simultaneous least square fits of Lorentzian line shapes to  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ . The temperature dependence of the modes observed is the same for all samples (independent of the dopant concentration) and agrees with the temperature dependence found for the undoped compound.<sup>10</sup>

When analyzing the modes originating from the orthorhombic distortion of the crystal structure one has to be aware of the fact that the temperature at which the orthorhombic-tetragonal phase transition takes place shifts from about 275 K for  $x=0.1$  to about 50 K for  $x=0.2$ .<sup>9</sup> Therefore the temperature dependence of these modes is strongly affected by the phase transition. In particular the oscillator strengths of these modes extrapolate to zero for temperatures close to that where the phase transition takes place. Especially for the overdoped samples, the modes at  $310\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$  appear very weak only in the measured low-temperature dielectric function. In fact, for the crystal with  $x=0.2$  the modes show up so weak, that they cannot be reliably fitted. Therefore, for this sample the frequency of the  $350\text{ cm}^{-1}$  mode has been determined from the maximum in  $\epsilon_2(\omega)$ . The observation, that these two modes seem to become weaker in the spectra with increased doping (see Fig. 2) has its origin in an increase of the linewidth of these modes while the oscillator strength does not show significant changes.

The temperature dependence of the linewidths and the TO frequencies of the modes of tetragonal origin at  $235\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$  follow the temperature dependence expected for an anharmonic decay of the TO mode into two

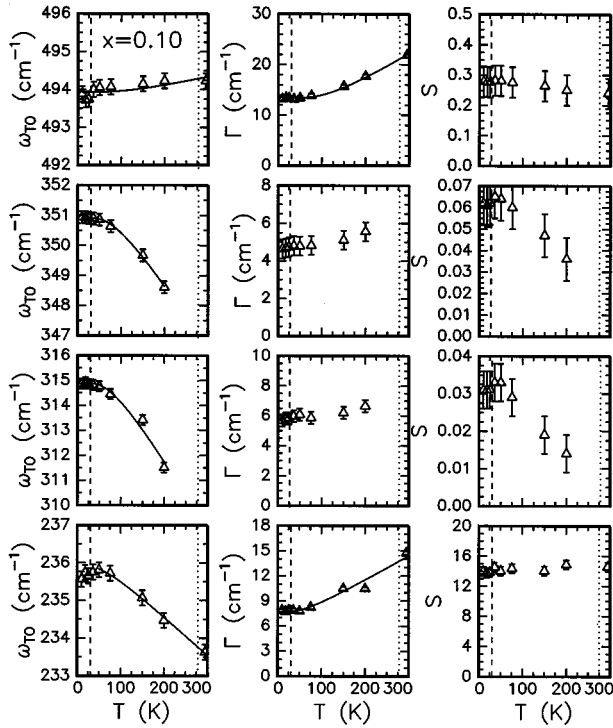


FIG. 5. Temperature dependence of the phonon parameters obtained for the underdoped  $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$  sample by fitting Lorentzian profiles simultaneously to  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ . The critical temperature ( $T_c = 28$  K) is indicated by the dashed lines. The solid lines indicate the temperature dependence expected for an anharmonic decay process into two modes. The dotted lines indicate the temperature of the tetragonal  $\rightarrow$  orthorhombic transition. Note that the oscillator strength of the modes at  $350\text{ cm}^{-1}$  and  $310\text{ cm}^{-1}$  tends to zero as the temperature reaches the temperature of the phase transition.

modes with equal frequency  $\omega_{\text{T0}}/2$  and opposite  $\mathbf{k}$  (in order to fulfill wave vector conservation), as discussed for the undoped compound.<sup>10</sup>

All modes, except that at  $500\text{ cm}^{-1}$ , show a hardening with decreasing temperature. This kind of behavior is usually observed for phonons and corresponds, in part, to the contraction of the lattice parameters  $a$  and  $c$ . The mode at  $500\text{ cm}^{-1}$  behaves differently; for all doping concentrations this mode softens slightly with decreasing temperature. This softening may result from specific structure in the two-phonon density of states involved in the anharmonic coupling in the energy range around the phonon frequency.<sup>24</sup> Depending on the energy of this structure relative to the phonon frequency one might expect either a frequency hardening or a softening. In order to explain a softening a peak in the two-phonon density of states has to appear just below the phonon mode frequency. We are not aware of any published two-phonon densities of states for the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system. However, the dispersion curves measured by inelastic neutron scattering,<sup>1</sup> reveal some flat branches around  $7.2\text{ THz}$  ( $\approx 240\text{ cm}^{-1}$ ), which may cause a peak in the two-phonon density of states just below the  $500\text{ cm}^{-1}$  mode. A two-phonon density of states obtained from lattice dynamical calculations should help to clarify the origin of the anomalous temperature dependence of the  $500\text{ cm}^{-1}$  mode.

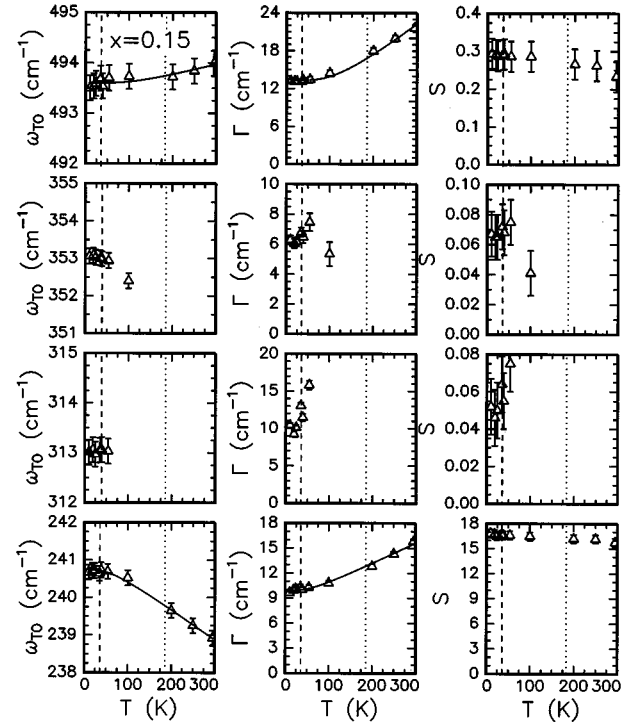


FIG. 6. Temperature dependence of the phonon parameters obtained for the optimally doped  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  sample by fitting Lorentzian profiles simultaneously to  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ . The critical temperature ( $T_c = 37$  K) is marked by the dashed lines. The dotted lines indicate the temperature of the tetragonal  $\rightarrow$  orthorhombic transition. The solid lines indicate the temperature dependence expected for an anharmonic decay process into two modes. Note that the oscillator strength of the  $350\text{ cm}^{-1}$  mode tends to zero as the temperature reaches the temperature of the phase transition. The  $310\text{ cm}^{-1}$  mode is too weak to see this trend.

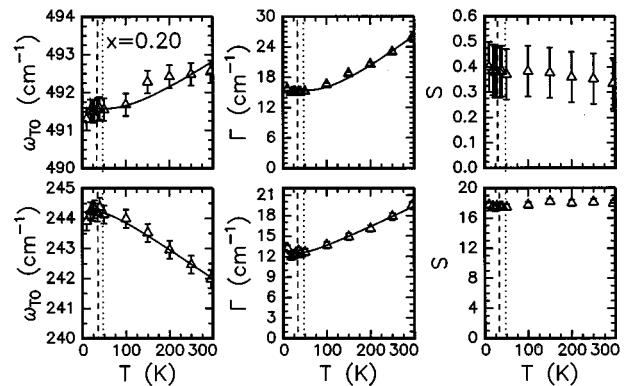


FIG. 7. Temperature dependence of the phonon parameters obtained for the overdoped  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  sample by fitting Lorentzian profiles simultaneously to  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ . The critical temperature ( $T_c = 30.5$  K) is marked by the dashed lines. The dotted lines indicate the temperature of the tetragonal  $\rightarrow$  orthorhombic transition. The solid lines indicate the temperature dependence expected for an anharmonic decay process into two modes. (The modes at  $310\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$  of the orthorhombic phase appear too weak to be meaningfully fitted.)

Contrary to the situation in the double-layer compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , where strong anomalies are observed in the temperature dependence of the frequency and the linewidth of some of the infrared active, *c*-polarized modes,<sup>3-6</sup> no anomalies are detectable for the single layer compound  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . Several arguments have been put forward, why phonon anomalies should be very weak in the single layer compound  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , or why they should not be present at all. Superconductivity induced anomalies of the self-energy were calculated by Zeyher and Zwicknagel using weak-coupling as well as strong-coupling theory.<sup>25</sup> Their calculation described the self-energy related to excitations across the superconducting gap, which are of even parity within the free electron approximation. For the high- $T_c$  cuprates having a center of inversion even parity corresponds to the symmetry of Raman-active modes only.<sup>26,27</sup> However, Tajima argues that this mechanism might account for the observed anomalies of the infrared active modes in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  as well if one considers that the symmetry is broken by the structural disorder due to the oxygen deficiency of the samples investigated.<sup>28</sup> This interpretation implies that no anomaly should be observed at  $T_c$  for the perfect crystal structure. For the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system, where La is partially replaced by Sr, one also has a disordered crystal structure. For the scenario just described, one might expect phonon self-energy effects to show up at  $T_c$  for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  as well. They may, however, be small because of the weak electronic background seen in the infrared absorption spectrum.<sup>28</sup>

The coupling of the infrared-active modes to charge fluctuations between neighboring  $\text{CuO}_2$  planes in a double layered compound provides a second mechanism to explain phonon anomalies at  $T_c$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . In a double-layer compound the electronic coupling between two neighboring  $\text{CuO}_2$  planes leads to two approximately parallel conduction bands; one of them is even when parity applies, the other odd. Odd vibrational modes, which correspond to the infrared-active phonons, couple to interband transitions between these bands, and thus experience a renormalization of their self-energy.<sup>29</sup> This mechanism can account for the anomalies observed at  $T_c$  in several infrared-active modes of double-layer compounds. For a single-layer compound, like  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , there is only one band crossing the Fermi surface and, as a consequence, there are no interband transitions which can couple to the phonon modes. Independently of the strength of the electronic background, one would not expect any superconductivity-induced anomaly of the infrared modes at  $T_c$ .

There is another argument which has to be considered: Since  $T_c$  for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is about 30% of that for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , we would expect the superconducting gap  $2\Delta$  to be roughly 30% of that in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $2\Delta \approx 316 \text{ cm}^{-1}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  according to Ref. 2). Since phonon shifts only occur when the phonon frequency is close to  $2\Delta$ ,<sup>30</sup> and no infrared-active modes are observed at such low energies, no pronounced phonon anomalies are expected. The fact that no anomalies are observed for the  $T'$  structure agrees with the results for the  $T$  structure, where for the Raman active modes no anomalies have been observed either.<sup>24</sup>

Anomalies in the phonon parameters observed *above*  $T_c$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have been related to the opening of a spin

TABLE I. Lattice parameters  $a$ ,  $b$ , and  $c$  for various dopant concentrations  $x$  obtained from different sources in the literature. We have multiplied the  $a$  and  $b$  axis by  $\sqrt{2}$  for the tetragonal structures (\*) for easy comparison with the twice as large unit cell of the orthorhombic structure.

$x$	$a$ [Å]	$b$ [Å]	$c$ [Å]	Symmetry	Source
0	5.357	5.389	13.175	<i>Bmab</i>	Ref. 34
0.1	5.364*	5.364*	13.201	<i>I4/mmm</i>	Ref. 35
0.15	5.345*	5.345*	13.226	<i>I4/mmm</i>	Ref. 36
0.2	5.333*	5.333*	13.251	<i>I4/mmm</i>	Ref. 37

or pseudogap.<sup>4,7</sup> The presence of a spin gap in underdoped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is still not clear.<sup>8,31</sup> Our measurements do not reveal any phonon anomaly possibly related to a spin gap in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . However, the absence of such anomalies does not necessarily indicate the absence of a spin gap. One can again argue that no anomalies are observed as a result of the weak electronic background for *c* polarization and not because of the absence of a spin gap.

### C. Dependence of the phonon parameters on doping

In the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system trivalent  $\text{La}^{3+}$  ions are replaced by  $\text{Sr}^{2+}$  ions which have an almost equal ionic radius<sup>32</sup> and lead to an increase of the number of holes in the  $\text{CuO}_2$  planes. While the lattice parameter  $c$  is found to increase with increasing  $x$ , the lattice parameter  $a$  decreases. Published values of the lattice parameters  $a$  and  $c$  for different dopant concentrations  $x$  are given in Table I.

The dependence of the phonon parameters on the doping level is displayed in Fig. 8. We find clear and systematic shifts of the TO frequencies with doping, which can in principle be used for the determination of the doping concentration. While the TO frequencies of the  $235 \text{ cm}^{-1}$  and  $350 \text{ cm}^{-1}$  modes increase with increasing  $x$ , we observe a softening of the TO frequencies of the  $310 \text{ cm}^{-1}$  and the  $500 \text{ cm}^{-1}$  modes. By analyzing the ellipsometric Fourier coefficients, we observe also for the TO frequency of the  $135 \text{ cm}^{-1}$  mode a tendency to decrease with increased doping (from  $\approx 135 \text{ cm}^{-1}$  for  $x=0$  to  $\approx 133 \text{ cm}^{-1}$  for  $x=0.12$ ).

The softening of phonon modes is expected from the expansion of the *c*-axis lattice parameter. In this connection we can assume that the frequencies are approximately proportional to the inverse of the third power of the lattice parameter.<sup>33</sup> However, the different doping dependence of the  $a$  and  $c$  axis leads to deviations from this simple power law which is also observed in the experiment. For the modes which soften we find that the frequency shift is *larger* than predicted by the power law. Changes in the bond lengths, and especially in the bond angles between atoms involved in the vibrations, may account for this phenomenon (a large effect of the bond angles would imply a significant covalent contribution to the bonds). Reduced restoring forces as a

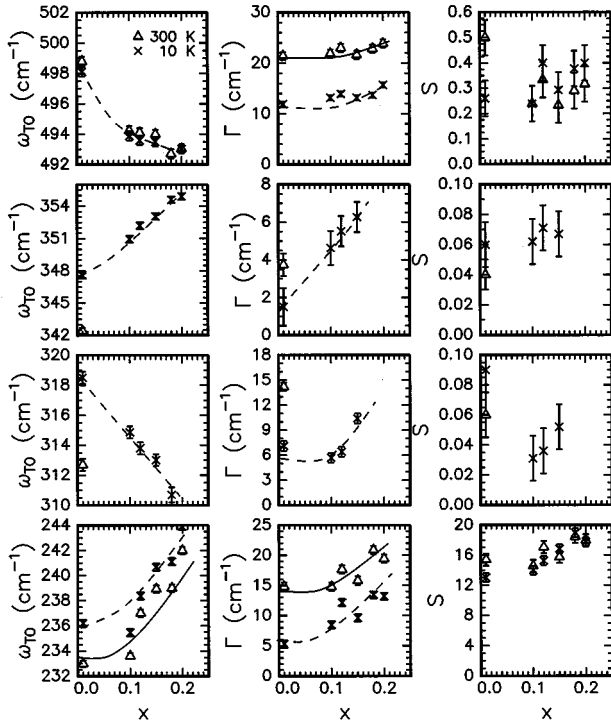


FIG. 8. Dependence of the phonon parameters on doping  $x$  obtained for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  from Lorentzian profiles fitted simultaneously to  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ . The crosses correspond to the 10 K data, while the triangles indicate the 300 K results. All lines are guides to the eye.

result of interaction of the phonons with the free carriers are not believed to be responsible for the strong softening since the corresponding electronic optical conductivity remains very small over the whole doping regime under investigation. In that case one would expect the oscillator strength to decrease systematically with increasing doping, which is not observed.

Considering that one replaces La atoms by Sr, which has a significantly smaller atomic mass than La ( $m_{\text{La}}=138.91; m_{\text{Sr}}=87.62$ ), and neglecting the different effective charges of these atoms, one might expect the modes to which the La sites contribute to become harder with increasing  $x$ . In the simplest picture, for a pure La vibration, one would expect the mode frequency to scale with  $1/\sqrt{m}$ , where  $m$  corresponds to the average mass on the La sites. This relation certainly overestimates the expected effect since other sites also have to contribute to the vibrational mode in order to fulfill the conservation of the center of mass.<sup>6</sup> However, even these crude assumptions clearly exceeding the realistic influence of the mass replacement, cannot fully account for the observed hardening. Therefore, one has to consider an additional mechanism. The analysis of the eigenvectors of the  $235\text{ cm}^{-1}$  mode, Fig. 4, suggests that the forces between the Cu ions and the in-plane oxygen ions might play an important role for the dynamics of this mode. In such a case the frequency of this mode would scale with the elementary cell  $a$  axis instead of its  $c$  axis. Then, with increasing doping, the contraction of the  $a$  axis should result in the mode hardening observed in the experiment. It is tempting to assume that a similar mechanism also works for

TABLE II. Effective Grüneisen parameters calculated for the modes scaling with the  $a$  axis ( $\gamma_a$ ) and for the modes scaling with the  $c$  axis ( $\gamma_c$ ). The calculations have been performed with the frequencies measured at 10 K.  $\omega$ ,  $a$ , and  $c$  are given for  $x=0$ .  $\Delta\omega$ ,  $\Delta a$ , and  $\Delta c$  represent the differences of the corresponding values for  $x=0.2$  and  $x=0$ , except for the  $310\text{ cm}^{-1}$  mode (\*) where the differences are given between  $x=0.15$  and  $x=0$ .

$\omega$ [ $\text{cm}^{-1}$ ]	$\Delta\omega$ [ $\text{cm}^{-1}$ ]	$a$ [ $\text{\AA}$ ]	$\Delta a$ [ $\text{\AA}$ ]	$c$ [ $\text{\AA}$ ]	$\Delta c$ [ $\text{\AA}$ ]	$\gamma_a$	$\gamma_c$
236.2	7.7	5.373	-0.040			2.19	
318.5	-5.5*			13.175	0.051*		4.45*
347.6	7.3	5.373	-0.040			1.41	
498.1	-6.8			13.175	0.075		2.40

the  $350\text{ cm}^{-1}$  phonon. However, the eigenvectors of that mode are not very well established since hardly any lattice dynamical calculations have been performed for the orthorhombic phase.<sup>21</sup>

The differences in the dependence on doping of the TO frequencies are attributed to the modes scaling with the lattice parameters along different crystal axes. Under this assumption one can estimate from the observed frequency shifts and the changes of the lattice parameters the Grüneisen parameters of the different phonon modes. Since the Grüneisen parameter [ $\gamma = -\partial \ln \omega / \partial \ln V \approx -(\Delta\omega/\omega)(V/\Delta V)$ ] describes the change of the phonon frequency with the variation of the volume of the crystal, we have to relate the change in volume to the variation of the lattice parameters. For a tetragonal crystal the volume of a unit cell is given by  $V=a^2c$ . We shall consider two limiting cases for an empirical treatment of the tetragonal anisotropy: (1) the volume changes because the lattice parameter  $a$  varies, while  $c$  is unchanged ( $\Delta V=2ac\Delta a$ ) and (2) the volume changes because the lattice parameter  $c$  changes while  $a$  remains constant ( $\Delta V=a^2\Delta c$ ). Substitution of  $\Delta V$  by the corresponding expression yields expressions for the two extreme cases concerning the Grüneisen parameter:

$$\gamma_a = -\frac{1}{2} \frac{\Delta\omega}{\omega} \frac{a}{\Delta a}$$

and

$$\gamma_c = -\frac{\Delta\omega}{\omega} \frac{c}{\Delta c}.$$

Applying these relations to the phonon modes assumed to scale with the different axes leads to values for the corresponding Grüneisen parameters in the order of two (see Table II), which fall within the typical range for this parameter.

For all modes the linewidth seems to increase slightly with increasing doping, a fact which is most likely related to the increasing disorder in the La layers because of the substitution by Sr.

#### IV. CONCLUSION

We have studied the  $c$ -polarized far-infrared response of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , with doping concentrations  $x$  ranging from the underdoped to the overdoped regime. We focused on the observed infrared-active modes and discussed their temperature dependence as well as their dependence on doping. The temperature dependence of the observed zone-center optical phonons can be described in a first approximation by anharmonic decay of these modes into two phonons, while the dependence on doping show that the  $c$ -polarized phonons scale partly with the  $a$  and partly with the  $c$  lattice parameter. We do not observe any anomalies of the phonon param-

eters, which could be related to the opening of either a superconducting gap or a spin gap or any other kind of pseudogap in the normal state for the underdoped compounds.

#### ACKNOWLEDGMENTS

We are indebted to D. Böhme for technical help and acknowledge the support of D. van Campen, L. Carr, and G. Williams at the beam line U4IR at the NSLS in Brookhaven. A.W. acknowledges the support of a KBN grant under Project No. 2P03B7011.

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