PHYSICAL REVIEW B VOLUME 39, NUMBER 7 1 MARCH 1989

Vibrational analysis of tetragonal $La_{2-x}M_xCuO_4$ ($M=$Sr,Ba)

V. A. Maroni, T. O. Brun, M. Grimsditch, and C.-K. Loong
Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

(Received 26 August 1988)

A simple valence-bond-type force field has been used to fit the observed Raman and infrared-active zone-center phonons of tetragonal $La_{2-x}M_xCuO_4$ ($M=$Sr, Ba). The phonon frequencies and assignments used in the fitting procedure were culled from a judicious comparison of existing literature data. An excellent fit to the four Raman-active $k=0$ phonons and two (observed) of the seven (expected) infrared-active phonons was obtained using three adjustable parameters (one for each of the discrete near-neighbor bond types, Cu-O, La-O, and Cu-La) and a bond-scaling relationship which correlates the strength of a particular bond type, K^i_{AB} with the length of the bond r_i, i.e., $K^i_{AB}=C_{AB}/r_i^6$, where C_{AB} is a constant. Optimization of the fitting parameters in this approximate force field produced an interestingly large Cu-La interaction, which is taken as evidence for a sizeable attractive force between each lanthanum atom and its nearest copper-oxygen plane. Also, the potential energy distribution indicates that the modes above 250 cm^{-1} are a mixture of Cu-O and La-O stretch, while those below 250 cm^{-1} contain large contributions from the Cu-La interactions.

INTRODUCTION

In a previous paper,[1] we reported the results of a phonon frequency calculation for $La_{1.85}Sr_{0.15}CuO_4$ performed using a simple mechanical model involving near-neighbor interactions. The Raman spectral data employed in that calculation were based on preliminary results from our laboratory and are now known to have included one misassigned frequency. This paper reports the results of further Raman study and vibrational analysis of the tetragonal lanthanum-(strontium or barium)-copper oxide phase (LCO) as well as an assessment of other published Raman and infrared spectra for $La_{1.85}Sr_{0.15}CuO_4$ and for a related oxide phase (Sr_2TiO_4) having the Ni_2CuF_4 structure.

RESULTS AND DISCUSSION

In the LCO series of high-T_c materials, the optimum superconducting properties are achieved at a composition near $La_{2-x}M_xCuO_4$ with $M=$Sr or Ba and $0.1 \leq x \leq 0.2$. At this stoichiometry the structural phase is a tetragonal perovskite having the space group $I4/mmm$ (D^{17}_{4h}) with one formula unit (seven atoms) per unit cell.[2] The representation of the zone-center phonons for this structure is given in Table I. La_2CuO_4 and numerous other related phases[3] have the orthorhombic structure $Cmca$ (D^{18}_{2h}) with fourteen atoms per Bravais unit cell. For purposes of comparison and because it is germane to subsequent discussions, the representation of the zone-center phonons for this structure is also given in Table I.

Raman scattering and infrared (absorption and reflectance) frequencies reported[1,4–19] for tetragonal $La_{1.85}Sr_{0.15}CuO_4$ and related phases over the past two years since the discovery of high-temperature superconductivity in this ceramic oxide are summarized in Table II. In order to consolidate the observations made by the various teams of investigators, values that fall within a frequency range of ±10 cm^{-1} are grouped together for simplicity. This is a reasonable way to present such data since one is dealing with solid-state spectroscopic measurements wherein effects due to oxygen stoichiometry variations, crystalline disorder, mixed phases, attainable signal-to-noise, instrument calibration errors, and variations in technique can easily lead to ±10-cm^{-1} variability in individual peak frequency determinations.

What emerges from this assessment in the case of both the Raman and infrared data is that there is reasonable agreement with regard to the observation and assignment of at least three of the Raman-active vibrational phonons and two of the infrared-active phonons for LCO. Raman bands at 422±10, 218±8, and 145±7 cm^{-1} are seen with good accord by several teams of investigators.[1,4,5] Results of polarization studies[4] give evidence that the "422"- and "145"-cm^{-1} bands are c-axis phonons attri-

TABLE I. Vibrational representations of La_2CuO_4 and $La_{2-x}M_xCuO_4$.

La_2CuO_4 ($Cmca=D^{18}_{2h}$)	$La_{2-x}M_xCuO_4$ ($I4/mmm=D^{17}_{4h}$)
$\Gamma_{tot}=\ 5A_g+4B_{1g}+3B_{2g}+6B_{3g}$	$\Gamma_{tot}=2A_{1g}+2E_g+4A_{2u}+B_{2u}+5E_u$
$4A_u+8B_{1u}+7B_{2u}+5B_{3u}$	$\Gamma_{acou}=A_{2u}+E_u$
$\Gamma_{acou}=B_{1u}+B_{2u}+B_{3u}$	$\Gamma_R=2A_{1g}+2E_g$
$\Gamma_R=\ 5A_g+4B_{1g}+3B_{2g}+6B_{3g}$	$\Gamma_{ir}=3A_{2u}+4E_u$
$\Gamma_{ir}=\ 7B_{1u}+6B_{2u}+4B_{3u}$	

TABLE II. Summary of literature data on observed Raman and infrared phonons for $La_{1.85}Sr_{0.15}CuO_4$.

Raman frequencies (cm^{-1})	Number of reportings/ seven papers[a]	Assignment	Infrared frequencies (cm^{-1})	Number of reportings/ twelve papers[a]	Assignment
422±10	$\frac{6}{7}$	A_{1g}	675±5	$\frac{2}{12}$	c
373±7	$\frac{4}{7}$	b	560	$\frac{1}{12}$	c
218±8	$\frac{3}{7}$	E_g	500±10	$\frac{11}{12}$	A_{2u}
180	$\frac{1}{7}$	b	445	$\frac{1}{12}$	c
145±7	$\frac{4}{7}$	A_{1g}	346±10	$\frac{2}{12}$	c
97±3	$\frac{2}{7}$	E_g	248±8	$\frac{6}{12}$	E_u
			117	$\frac{1}{12}$	c

[a] Some Raman and infrared studies included here do not cover the entire frequency range of the listed bands.

[b] See text.

[c] Not assigned *j* band may be due to orthorombic phase or impurity.

butable to the two A_{1g} modes. The polarization characteristics of the "218"-cm^{-1} band are consistent with its assignment as one of the two expected E_g phonons.[4] There has been at least one observation[6] of a fourth Raman band near 100 cm^{-1} (97±3 cm^{-1}); however, it must be noted that the other observed Raman bands in that particular study are not at assigned Raman frequencies listed in Table II. Instead, the highest-frequency mode is at 380 cm^{-1}, another weak feature is seen near 180 cm^{-1}, and the band observed at 100 cm^{-1} is the most intense of the three. If the spectrum of Blummenroeder *et al.*[6] is indeed due to LCO, it may be that they produced an oxygen deficient phase which shows the same type of behavior discussed recently[20] for $YBa_2Cu_3O_{7-\delta}$ as δ goes from $0 \rightarrow 1$, i.e., a decrease in the highest-frequency totally symmetric phonon. (The possibility that their sample is oxygen deficient is actually mentioned by Blummenroeder *et al.*) Unfortunately, no detailed studies have been found that probe the effect of oxygen stoichiometry on the vibrational modes of LCO; hence, a definitive explanation of the results of Blummenroeder *et al.* cannot be made at this time.

The most revealing Raman study of LCO appears to be the one by Copič *et al.*,[4] which indicated that the 422- and 145-cm^{-1} features have A_{1g} symmetry, while the 218-cm^{-1} band has E_g symmetry. Guided by these results and the information reported by Burns *et al.*[7] for the isomorphic oxide Sr_2TiO_4, it can readily be concluded that the second E_g phonon lies below 145 cm^{-1} and may in fact be the 100-cm^{-1} band reported by Blummenroeder *et al.*[6] To provide some further evidence for this assignment, we show in Fig. 1 the Raman spectrum of a pellet of single phase $La_{1.85}Sr_{0.15}CuO_4$ which has been polished in a slurry of 0.5-μm Al_2O_3-kerosene, rinsed with toluene, and kept in a dry environment prior to study. This spectrum contains evidence of all four features discussed above that have been assigned to the four Raman-active phonons of LCO in Table II. It is important to note here that carefully prepared samples of LCO, i.e., samples showing high tetragonal phase purity by x-ray diffraction, whose surfaces are polished and kept free of moisture, do not show evidence of the previously reported[1] Raman feature at 367 cm^{-1}. Consequently, we no longer feel that this feature is a zone-center phonon of LCO; it may be associated with either the orthorhombic phase or some other impurity species that forms on the surface of LCO samples following exposure to moist atmospheres.

Some additional information that supports the low-frequency Raman observations comes from inelastic neutron scattering (INS) studies of LCO. Both Böni *et al.*[21] and Balakrishnan *et al.*[22] report INS peaks for LCO at around 90 and 150 cm^{-1}. Böni *et al.* connect their findings to the two lowest-frequency Raman-active phonons in the same manner depicted in Table II in terms of both frequency and symmetry assignment.

To add further confirmation to the proposed assign-

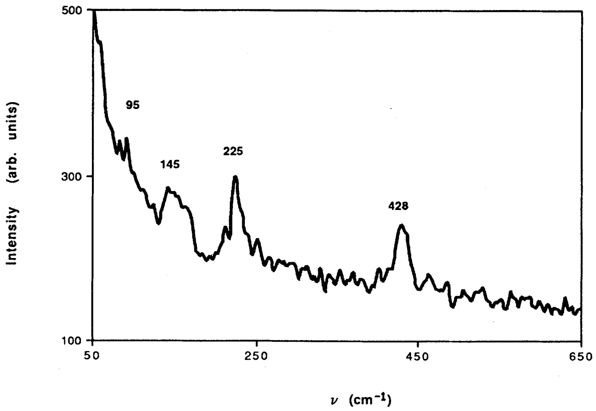

FIG. 1. Backscattered Raman spectrum of a polished sintered pellet of $La_{1.85}Sr_{0.15}CuO_4$ obtained using 100 mW of 514.5 nm radiation.

ments of 422 and 145 cm^{-1} to the A_{1g} phonons and of "218" and "97" cm^{-1} to the E_g phonons of LCO, the correlation chart given in Fig. 2 was prepared. In this chart, the frequency of each observed phonon is ratioed to the highest-frequency A_{1g} phonon, and a plot is made of this relative frequency for both LCO and its isostructural analog Sr_2TiO_4 for which phonon frequencies and assignments are known.[7] A similar correlation diagram based on data for ten rutile compounds[23] (oxides and fluorides) is also presented in Fig. 2. Such diagrams for these tetragonal crystal systems can be expected to provide a representative correlation of *gerade* phonons (which include the Raman-active ones) based on the assumption that the kinetic-energy terms of each phonon are exclusively determined by the mass of the light atom (e.g., oxygen atoms in the oxide compounds). This assumption is strictly correct for the *gerade* phonons of the rutile structure, but only approximately so for the two A_2BO_4 compounds (LCO and Sr_2TiO_4) because there is some motion of the "A" atoms (La or Sr) in the *gerade* modes for this structure. However, the net effect of this motion on the results in Fig. 2 for the LCO and Sr_2TiO_4 comparison should be relatively small (because of the sizeable mass difference between O atoms and La or Sr atoms) and should measurably influence only the lowest-frequency *gerade* modes. The other assumption inherent to these diagrams is that the character of the force field and the proportioning of the corresponding potential constants should be about the same from one isostructural compound to the next. As can be seen in Fig. 2, the correlation of LCO and Sr_2TiO_4 frequencies is impressive.

In the case of the infrared spectroscopy of LCO[10–18] matters are considerably less clear at this time. There is consistent appearance (see Table II) of a sharp infrared transition at 500±10 cm^{-1} and a broader band at 248±10 cm^{-1}. While several other bands are reported in the 330 to 360-cm^{-1} region and at frequencies from 550 to 570 cm^{-1}, there is little firm evidence that these are zone-center phonons of LCO, and the most carefully prepared samples do not as a rule give much indication of such bands.

One revealing observation that has been made in the infrared spectra of tetragonal $La_{2-x}M_xCuO_4$ and orthorhombic La_2CuO_4 is the appearance of a strong infrared absorption near 680 cm^{-1} in the orthorhombic phase which does not appear in the tetragonal phase (both phases show the "500"-cm^{-1} infrared band). This effect, actually first seen by Singh *et al.*[3] for LCO-type perovskites, has been reproduced in several laboratories for La_2CuO_4 and the tetragonal analog produced by doping with barium, strontium, or calcium.[10,13–15] The most logical deduction to be made here is that the 680-cm^{-1} band is a zone-center phonon of the orthorhombic structure that becomes a zone-boundary phonon when the symmetry is raised to tetragonal. The possibility that this mode becomes the inactive B_{2u} phonon of the tetragonal phase seems unlikely, as Prade *et al.*[24] have calculated a value near 200 cm^{-1} for B_{2u} of LCO. Alternatively, the 680-cm^{-1} mode may be an *a*-*b*–plane phonon of the orthorhombic (O) structure that is also infrared active in the tetragonal (T) phase, but is not seen because of enhanced metal-like character in the Cu-O planes following transformation from $O \rightarrow T$. It would follow from this argument that the 500-cm^{-1} band is a *c*-axis phonon since it is seen for both O and T forms. Normal mode calculations for LCO, discussed further on, point to the existence of a high-frequency mode of E_u symmetry that is mainly due to Cu-O stretch in the *a*-*b* plane.

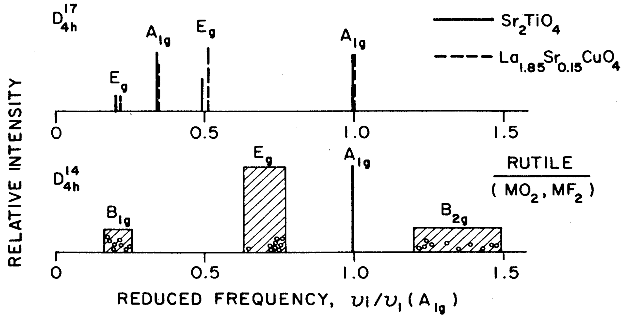

FIG. 2. Frequency correlation diagram for the Raman-active phonons of two tetragonal oxides with the A_2BO_4 ($I4/mmm$) structure and a series of rutile compounds.

An effect similar to the one described above has been observed[8] in the Raman spectra of orthorhombic La_2CuO_4 and tetragonal LCO. The O form has Raman bands at 526 and 422 cm^{-1}, while only the latter is present in the T form. Polarization studies place the eigenvector for the 526-cm^{-1} band in the *a*-*b* plane (i.e., a symmetric stretching mode involving the short Cu-O bonds). Such a mode is a zone-center phonon on the O form, but a zone-boundary phonon of the T-form, thus, it appears in the Raman spectrum of the O form but not the T form. Batlogg *et al.*[9] have studied the effect of isotopic substitution (^{18}O for ^{16}O) in tetragonal LCO. They find a 14.5-cm^{-1} downward shift of the 422-cm^{-1} band upon 52% ^{16}O replacement by ^{18}O and an 18-cm^{-1} shift for 73% ^{16}O replacement. The predicted shift at 422 cm^{-1} for 100% ^{18}O substitution should approach ~ 24 cm^{-1}, i.e., 422 cm^{-1} $x[1-(\frac{16}{18})^{1/2}] \simeq 24$ cm^{-1}. They also see a corresponding distinct lowering of T_c that is proportional to the amount of ^{18}O substitution. These observations provide an important piece of information with regard to the assignment of the LCO Raman bands; they show that the 422-cm^{-1} band originates from an eigenvector that involves mainly oxygen motion. Since polarization studies[4] mark the 422-cm^{-1} band as an A_{1g} mode of LCO, the corresponding oxygen motion must be along the c axis. This body of evidence together with the correlation in Fig. 2 firmly sets the origins of the Raman-active phonons and establishes a basis for detailed lattice mode calculations.

A zero wave-vector lattice-dynamics analysis of the hypothetical phase La_2CuO_4 with $I4/mmm$ symmetry (Ni_2CuF_4 structure) was carried out using the frequencies and assignments in Table II as constraining parameters for iterative derivation of a suitable potential-energy function. The secular equations were set up according to the GF-matrix method described by Shimanouchi *et al.*[25]

and by Decius and Hexter,[26] using the lattice parameters for $La_{1.85}Sr_{0.15}CuO_4$ given by Cava *et al.*[2] The internal coordinate sets chosen were (referring to Fig. 2 of Ref. 1) the Cu-O bonds in the *ab* plane (Cu-O_I), the Cu-O bonds along the *c* axis (Cu-O_{II}), the three shortest La-O bonds (La-O_I, La^c-O^c_{II}, and La^c-$O^{c'}_{II}$, where *c* and *c'* represent adjacent *c* axes, e.g., through 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, 0, respectively), and the shortest Cu^c-$La^{c'}$ interactions, i.e., those between a lanthanum atom and the copper atoms in the nearest copper-oxygen plane. (Note that the designations used here and in Ref. 1 for oxygen atoms O_I and O_{II} are the reverse of those used by Cava *et al.*[2])

The potential-energy function applied in this calculation consisted of a simple diagonal matrix (*F* matrix) formed from the force constants for the six types of interactions described above. In the case of the Cu-O and La-O bonds, a bond-length scaling relationship of the type

$$K'_{mo} = K_{mo}\left[\frac{r_{mo}}{r'_{mo}}\right]^n , \qquad (1)$$

where K_{mo} and K'_{mo} are force constants for bonds between the same types of atoms having bond lengths r_{mo} and r'_{mo}, respectively. This type of bond scaling relationship has been used with success by others in the treatment of condensed phase structures.[23,27–30] It tends to be least accurate when the bond lengths span a wide range of values. Typically, the optimum value of n lies in the range from 5 to 7; $n=6$ was used here since it falls in the middle of the range, but tests at $n=5$ and $n=7$ have indicated that the final results are not overly sensitive to this choice.

Refinement of the force constants and solution of the secular equations was performed with the computer program FPERT.[31] The results of this zero wave-vector refinement based on the approximate force field described above are presented in Table III. With the three adjustable parameters and the scaling relationship, an excellent fit is obtained for the four Raman-active phonons and the two well-confirmed infrared-active phonons (500 and 248 cm^{-1}). The potential energy distribution (PED) over the normal coordinates shows that phonons above 200 cm^{-1} are dominated by metal-oxygen stretching while those below 200 cm^{-1} contain large contributions from the Cu-La coordinate. This result does not strictly confirm that there is a large Cu-La interaction, but it does imply that there are strong forces tying each lanthanum atom to the nearest copper-oxygen plane. Also, the potential energy distribution reveals that it is not correct to refer to any of the observed phonons as being purely Cu-O, La-O, or Cu-La in nature. Similar results have been obtained for $YBa_2Cu_3O_7$ by Bates and Eldridge.[32]

From the calculations summarized in Table III it is not possible to accurately pin down the value of the highest-frequency E_u phonon (E^1_u). This mode is obviously dominated by Cu-O_I stretching in the *a-b* plane. Since the Cu—O_I bond is considerably shorter than Cu—O_{II}, one would expect it to have a much larger force constant than Cu—O_{II}. Using the bond length scaling relationship [Eq. (1)] with $n=6$, we predict a value for E^1_u near 1200 cm^{-1} (probably much too high because of the inaccuracies associated with extending the $1/r^6$ dependence over too wide a range of r). Toning the scaling down by applying

TABLE III. Calculated frequencies [lattice parameters (Ref. 2) used in the calculation were as follows: $a=3.779$ Å, $c=13.226$ Å, $z(La)=0.360$, $z(O_{II})=0.182$, where z is the fractional coordinate along the c axis] and potential energy distributions for tetragonal "La_2CuO_4." Bond lengths (in parentheses) and iteratively determined force constants were as follows: Cu—O_I (1.89 Å) (see footnote a below), Cu—O_{II} (2.41 Å)=1.21 mdyn/Å, La^c—O^c_{II} (2.37 Å)=0.49 mdyn/Å, La—O_I (2.64 Å)=0.24 mdyn/Å, La^c—$O^{c'}_{II}$ (2.73 Å)=0.20 mdyn/Å, Cu^c—$La^{c'}$ (3.25 Å)=0.55 mdyn/Å.

Symmetry	Observed frequency (cm^{-1})	Calculated frequency (cm^{-1})	Calculated potential energy distribution (%) Cu-O	La-O	Cu-La
A_{1g}	422	431	69[b]	31	0
	145	140	6[b]	49	45
E_g	218	218	0	97	3
	97	103	0	29	71
A_{2u}	500	493	79[b]	16	5
		259	1	65	34
		218	0	72	28
E_u		a	99[c]	0	1
	248	245	0	86	14
		216	0	87	13
		189	0	27	73

[a] The calculated Cu-O_I force constant is closely correlated with the value of the highest-frequency E_u phonon, E^1_u (not observed), and is not constrained by any of the observed frequencies. Frequencies ≥ 600 cm^{-1} can be used as input for E^1_u with very little effect on the other force constants, frequencies, or eigenvectors.

[b] All from Cu-O_{II}.

[c] All from Cu-O_I.

bond-length–bond-strength proportions in line with those reported by Siegel,[33] gives $K_{\text{Cu-O}_{\text{I}}} \simeq 2.0\ K_{\text{Cu-O}_{\text{II}}}$ and produces a value for E_u^1 that is around 800 cm^{-1}. This gets closer to the band seen by Singh *et al.*[3] and others[10,13–15] at 680 cm^{-1} in orthorhombic La_2CuO_4 which could come from an eigenvector of the *O* phase that is analogous to the E_u^1 mode of the *T* phase. Failure to observe this mode in infrared spectra of the *T* phase (even above the critical temperature) may be due to a persistent metallic character in the Cu-O_{I} plane of the *T* phase that greatly weakens its capacity to exhibit normal infrared absorption. In fact, in the collected body of Raman and infrared data for LCO and other copper-oxide-containing high-T_c materials there is little concrete evidence that any of the observed bands can be attributed to modes having their eigenvectors in the Cu-O planes.

Although the assignments of the infrared bands at 500 and 248 cm^{-1} were made on a somewhat arbitrary basis, they are supported by the calculations. Note that the 248-cm^{-1} band could just as well be assigned to the second A_{2u} phonon and may, in fact, derive most of its intensity from that mode based on the argument set forth above that the *c*-axis phonons are much more detectable by Raman and infrared spectroscopies than the *a*-*b* plane phonons. The fact that the 422-cm^{-1} Raman band (which has a large contribution from Cu-O_{II} symmetric stretching) and the 500-cm^{-1} infrared band (which is dominated by Cu-O_{II} antisymmetric stretching) are fit so well by the simplified force field is encouraging evidence that the assignment of the 500-cm^{-1} band to A_{2u} is correct.

Our previously reported lattice dynamics analysis of LCO was based on a similar type of valence-bond force field, but several of the observed Raman bands applied in that analysis[1] were not assigned according to the recommended manner in Table II. The force field reported in the earlier paper is considerably different from the one in Table III. Specifically, the one in Table III is dominated by Cu-O interactions, whereas the previous one[1] was dominated by La-O interactions. This difference is largely due to our attempt in the earlier work to fit the band at 367 cm^{-1} into the set of $k=0$ assignments.

Several other groups have carried out lattice dynamics analyses at zero wave-vector and/or phonon density of states calculations for LCO. Prade *et al.*[24] calculated phonon dispersion curves for LCO, but they too did not use all of the recommended assignments as a basis. Mase *et al.*[34] derived phonon dispersion curves for LCO based on force constants deduced from acoustic measurements. Because of certain restrictions due to the nature of their sound velocity data, they conclude that there are no phonons for LCO above ~360 cm^{-1}. This is not in agreement with infrared and Raman studies as can be seen in Table II. Although they did not make specific calculations, Burns *et al.*[7] give a discussion of the eigenvectors for Sr_2TiO_4 and LCO based on a prior normal mode analysis of the isostructural K_2ZnF_4 crystal. They conclude that the eigenvectors for LCO should be considerably different from those for Sr_2TiO_4 and isostructural fluorides of the A_2BX_4 type. In particular, they suggest that the highest frequency A_{1g} mode (422 cm^{-1}) is dominated by La-O_{I} stretching. This is contrary to the results in Table III, which imply that the Cu-O bond force constants and their contributions to the PED for the higher-frequency modes are larger than those for the La-O bonds. Prade *et al.*[24] also find that the Cu-O force constants are at least twice the value of the La-O force constants. Weber[35] too has suggested that the Cu-O forces are major contributors to the high-frequency modes. In fact, his calculated vibrational density of states for LCO shows a surprisingly good correlation with the calculated frequencies in Table III.

There have been several attempts to predict the value of the highest-frequency E_u phonon for LCO at $k=0$. Using a correlation approach, Burns *et al.*[7] place it at 672 cm^{-1}. Cohen *et al.*[36] give a value of 964 cm^{-1} based on the potential induced breathing model. Prade *et al.*[24] calculate that this mode is near 547 cm^{-1} by application of a shell model. Fu and Freeman[37] performed a frozen phonon calculation which gave a value of ~880 cm^{-1} for the Cu-O breathing mode in the *ab* plane. To our knowledge no conclusive infrared observations of E_u^1 have been made to date. Recent neutron inelastic scattering studies in our laboratory[38] suggest that E_u^1 must lie at a frequency that is less than 750 cm^{-1}, as there is no evidence of phonon-induced scattering from LCO above this energy.

ACKNOWLEDGMENTS

We would like to thank B. W. Veal, Jr. for kindly providing the sintered pellet of high-purity $La_{1.85}Sr_{0.15}CuO_4$. This work was performed under the auspices of the Division of Materials Sciences and supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences under Contract No. W-31-109-ENG-28.

---

[1] T. Brun, M. Grimsditch, K. E. Gray, R. Bhadra, V. Maroni, and C. K. Loong, Phys. Rev. B **35**, 8837 (1987).

[2] R. J. Cava, A. Santoro, D. W. Johnson, Jr., and W. W. Rhodes, Phys. Rev. B **35**, 6716 (1987).

[3] K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[4] M. Copič, D. Mihailović, M. Zgonik, M. Prester, K. Biljaković, B. Orel, and N. Brničević, Solid State Commun. **64**, 297 (1987).

[5] B. N. Goshchitskii, S. A. Davydov, M. G. Zemlyanov, A. E. Karkin, V. L. Kozhevnikov, A. V. Mirmelshtein, G. H. Panova, P. P. Parshin, Yu. S. Ponosov, A. A. Fotiev, M. N. Khlopkin, N. A. Chernoplyokov, S. M. Cheshnitskii, and A. A. Shikov, Fiz. Met. Metalloved. **64**, 188 (1987).

[6] S. Blummenroeder, E. Zirngiebl, J. D. Thompson, P. Killough, J. L. Smith, and Z. Fisk, Phys. Rev. B **35**, 8840 (1987).

[7] G. Burns, F. H. Dacol, G. Kliche, W. König, and M. W. Shafer, Phys. Rev. B **37**, 3381 (1988).

[8] G. A. Kourouklis, A. Jayaraman, W. Weber, J. P. Remeika, G. P. Espinosa, A. S. Cooper, and R. G. Maines, Sr., Phys. Rev. B **36**, 7218 (1987).

[9] B. Batlogg, G. Kourouklis, W. Weber, R. J. Cava, A. Jayaraman, A. E. White, K. T. Short, L. W. Rupp, and E. A. Rietman, Phys. Rev. Lett. **59**, 912 (1987).

[10] N. Ogita, K. Ohbayashi, M. Udagawa, Y. Aoki, Y. Maeno, and T. Fujita, Jpn. J. Appl. Phys. **26**, L205 (1987); **26**, L415 (1987); **26**, L420 (1987); **26**, L423 (1987).

[11] D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamarás, C. D. Porter, D. B. Tanner, J. M. Tarascon, W. R. McKinnon, and L. H. Greene, Phys. Rev. B **35**, 8843 (1987).

[12] G. A. Thomas, A. J. Millis, R. N. Bhatt, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 736 (1987).

[13] K. Oh-ishi, M. Kikuchi, Y. Syono, K. Hiraga, and Y. Morioka, Jpn. J. Appl. Phys. **26**, L484 (1987).

[14] H. Sawada, Y. Saito, T. Iwazumi, R. Yoshizaki, Y. Abe, and E. Matsuura, Jpn. J. Appl. Phys. **26**, L426 (1987).

[15] M. Stavola, R. J. Cava, and E. Rietman, Phys. Rev. Lett. **58**, 1571 (1987).

[16] P. E. Sulewski, T. W. Noh, J. T. McWhirter, and A. J. Sievers, Phys. Rev. B **36**, 5735 (1987).

[17] S. Sugai, S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L879 (1987).

[18] S. Sugai, Jpn. J. Appl. Phys. **26**, L1517 (1987).

[19] Z. Schlesinger, R. T. Collins, and M. W. Shafer, Phys. Rev. B **35**, 7232 (1987).

[20] C. Thomsen, R. Liu, M. Bauer, A. Whittlin, L. Genzel, M. Cardona, E. Schönherr, W. Bauhofer, and W. König, Solid State Commun. **65**, 55 (1988).

[21] P. Böni, J. P. Axe, G. Shirane, R. J. Birgeneau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, and T. R. Thurston, Phys. Rev. B **38**, 185 (1988).

[22] G. Balakrishnan, N. R. Bernhoeft, Z. A. Bowden, D. McK. Paul, and A. D. Taylor, Nature **327**, 45 (1987).

[23] V. A. Maroni, J. Phys. Chem. Solids **49**, 307 (1988).

[24] J. Prade, A. D. Kulkarni, F. W. de Wette, W. Kress, M. Cardona, R. Reiger, and U. Schröder, Solid State Commun. **64**, 1267 (1987).

[25] T. Shimanouchi, M. Tsuboi, and T. Miyazawa, J. Chem. Phys. **35**, 1597 (1961).

[26] J. C. Decius and R. M. Hexter, *Molecular Vibrations in Crystals* (McGraw-Hill, New York, 1977).

[27] C. H. D. Clark, Trans. Faraday Soc. **37**, 299 (1941).

[28] J. W. Linnett, Quart. Rev. **1**, 73 (1947).

[29] C. A. Melendres and V. A. Maroni, J. Raman Spectrosc. **15**, 319 (1984).

[30] S. Sunder and H. J. Bernstein, J. Raman Spectrosc. **5**, 351 (1976).

[31] R. G. Snyder and J. H. Schachtschneider, Spectrochim. Acta **19**, 117 (1963).

[32] F. E. Bates and J. E. Eldridge, Solid State Commun. **64**, 1435 (1987).

[33] S. Siegel, J. Inorg. Nucl. Chem. **40**, 275 (1978).

[34] S. Mase, T. Yasuda, Y. Horie, and T. Fukami, Solid State Commun. **65**, 477 (1988).

[35] W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).

[36] R. E. Cohen, W. E. Pickett, H. Krakauer, and L. L. Boyer, Physica B **150**, 61 (1988).

[37] C. L. Fu and A. J. Freeman, Phys. Rev. B **35**, 8861 (1987).

[38] C.-K. Loong (unpublished).