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Phonons in $YBa_2Cu_3O_{7-\delta}$-type materials

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We have report infrared reflectivity measurements on $YBa_2Cu_3O_{7-\delta}$ and $SmBa_2Cu_3O_{7-\delta}$ in the tetragonal semiconducting phase. Ten of the eleven symmetry-allowed modes are seen, and the eleventh is probably observed in the Sm material. When Sm replaces Y, two of the phonons at ≈ 200 cm^{-1} shift to lower energy by 22 and 27 cm^{-1}. These modes, and the two at ≈ 110 cm^{-1}, which undoubtedly involve Ba motions, are very sharp. From Sm-atom substitution, we can surmise which of the two high-frequency Cu-against-O modes is the planar E_u mode, and which is the chain A_{2u} mode. Surprisingly, with Sm replacing Y, the planar mode shifts down in frequency by 25 cm^{-1} (and the chain mode is hardly effected). Other aspects of the data are discussed.

Superconducting materials were once thought to be limited to transition temperatures below $T_c \approx 25$ K, but now, with $YBa_2Cu_3O_{7-\delta}$, values larger than 90 K can be reached.[1] $YBa_2Cu_3O_{7-\delta}$ forms a previously unknown structure[2] shown in Fig. 1. In the superconducting state it is orthorhombic with space group $Pmmm$-D_{2h}^1. The two aspects of the structure that are thought to be important for the superconductivity are (a) the Cu(2*g*)-O(4*i*) square-planar, corner-linked layers that form two-dimensional planar (*ab* plane) networks of Cu—O—Cu bonds; and (b) the Cu(1*a*)-O square building blocks, linked in only one direction, that form one-dimensional chains (or ribbons) along the orthorhombic *b* axis.

Infrared[3] and Raman[4] measurements of the ($k \approx 0$) phonons in this material have been studied extensively. The interest is intrinsic, as well as with the objective of observing signs of the electron-phonon interaction, which may act as the "glue" for the Cooper pairs.

One of the many interesting aspects of this structure is that δ can be varied over a large range[2,5] while the orthorhombic structure and superconductivity are maintained. Moreover, the oxygen atoms that are removable come from the Cu—O chain $O_s(2f)$ oxygens (Fig. 1), which in the orthorhombic structure Wyckoff notation[2,6] are called O(1*e*) or sometimes just O(4). For approximately $0 < \delta < 0.5$ the material is orthorhombic, while for $0.5 < \delta < 1$ it is tetragonal with space group $P4/mmm - D_{4h}^1$. This variation of oxygen content is completely reversible with the superconductivity completely recoverable. However, in the tetragonal phase the material behaves like a semiconductor.[7] Since the structure for both the orthorhombic and tetragonal material is essentially the same, Fig. 1 can be used for both, as clarified in the figure caption.

We have previously studied the phonons in the tetragonal semiconductor phase of $YBa_2Cu_3O_{7-\delta}$, with δ close to unity, by infrared and Raman techniques.[6] Studying these materials in the semiconducting or insulating phases[8] is easier than in the metallic superconducting phases because of the lack of interference with the free-electron plasma. Here, we report and discuss infrared reflectivity results of tetragonal, semiconducting $YBa_2Cu_3O_{7-\delta}$ and compare it to the semiconducting $SmBa_2Cu_3O_{7-\delta}$.

In Fig. 2(a) the infrared reflectivities for ceramic $YBa_2Cu_3O_{7-\delta}$ and $SmBa_2Cu_3O_{7-\delta}$ in the semiconducting tetragonal phase are shown. The materials are obtained by heating above the orthorhombic-tetragonal transition temperature and then cooling in argon gas.[7,9] For such samples the resistance always increases as the temperature is lowered (see the inset to Fig. 1 in Ref. 7). The reflectivity data in Fig. 2(a) were fit to a frequency-dependent dielectric constant of the form

$$\frac{\epsilon(\omega)}{\epsilon_\infty} = \prod_i \frac{(\omega_{\mathrm{LO}i}^2 - \omega^2) - i\omega\gamma_{\mathrm{LO}i}}{(\omega_{\mathrm{TO}i}^2 - \omega^2) - i\omega\gamma_{\mathrm{TO}i}} , \tag{1}$$

where ω_{TO} and ω_{LO} (and their corresponding dampings γ_i) are the transverse-optic and longitudinal-optic modes, respectively. The dielectric constant above the phonon frequency is summarized in $\epsilon_\infty (=4)$, and the product is over the 11 allowed infrared modes.[6]

We clearly resolve 10 infrared reststrahlen bands for both of the materials studied [Fig. 2(a)]. The frequencies, given in Table I, are obtained [via Eq. (1)] by fitting the reflectivity data. The fit is very sensitive to ω_{TO}, ω_{LO}, and γ; a one-wave-number difference is noticeable for the sharper bands. In Fig. 2(b), the fit for the Sm material is shown. As will be discussed later, in the Sm material, possibly the eleventh mode is observed, which would then ac-

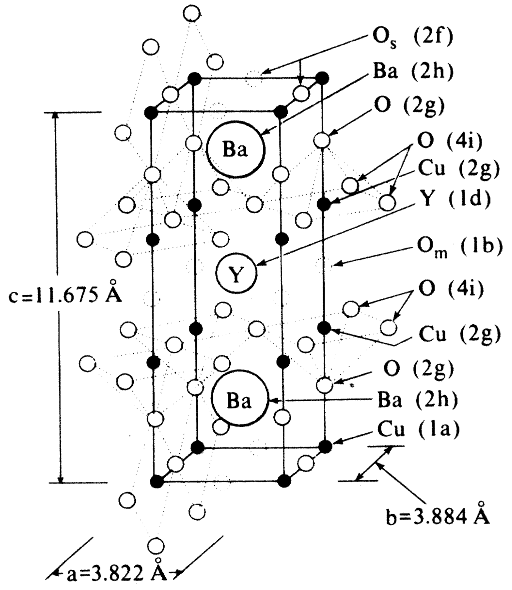

FIG. 1. Structure of $YBa_2Cu_3O_{7-\delta}$. Since the structure for both the orthorhombic and tetragonal materials is very similar, this figure may be used for both. The Wyckoff notation of the atom positions is given for the tetragonal material, but the unit-cell dimensions are given for the orthorhombic material. The only fundamental difference between these materials is that in the tetragonal structure both oxygen atoms labeled $O_s(2f)$ are found to be missing, or at least the occupation of this site is very low. In the orthorhombic structure only one of these sites is occupied; it is the site along the *b* axis, as indicated with a solid circle.

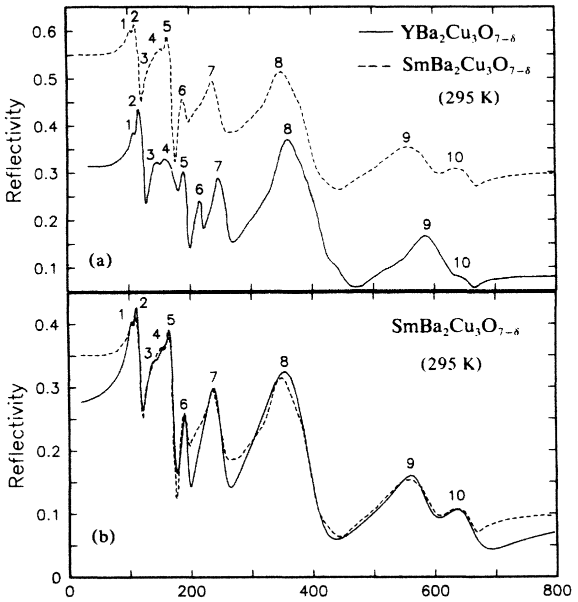

FIG. 2. (a) Measured infrared results for both the Y and Sm material in the semiconducting phase. The magnitude of the reflectivity for the Sm material is shifted by 0.20 for ease of observation. The reflectivity bands are labeled 1, 2, 3, . . . , 10 for comparison purposes. (b) Measured and oscillator fit reflectivity results for the Sm material. Values for the parameters in the oscillator fit are given in Table I. The dashed line is the data and the solid line is the fit.

count for all 11 allowed infrared modes.[6] We discuss important aspects of the data.

First, as already mentioned, almost all of the symmetry-allowed[6] modes are observed. Thus, the infrared results seem to yield phonon spectra that are simpler to interpret than those found in the infrared[3] and Raman measurements,[4] which have been made on the metallic (superconducting) materials, where the electron plasma has a strong reflectivity. In the metallic phase, the plasma may be confined to the *ab* plane, in which case it will tend to screen the infrared phonon modes whose vibrations are in this plane.[10] Thus, only modes in which the vibrational motion is perpendicular to this plane will be observed easily. For the tetragonal phase, if the material were metallic, this would mean that the infrared E_u modes would then tend to be screened, and the A_{2u} modes would be more easily observed. The tetragonal doubly degenerate E_u modes, when in the orthorhombic structure, split into two singly degenerate B_{2u} and B_{3u} modes which should be screened. Infrared results[10(b)] on superconducting single-crystal arrays seem to show this screening behavior.

Second, the splittings between the LO and TO modes are determined[11] by the effective charges, Q, and effective masses, m, of the vibrations. The relationship is $\omega_{LO}^2 - \omega_{TO}^2 \propto Q^2/m$. For the materials shown in Fig. 2, this difference is relatively small for most of the modes, making the reflectivity bands relatively sharp. This also is the case for the $(La,Sr)_2CuO_4$ superconductors, which can be directly compared to other more ionic compounds with the same structure.[8(c)] Since in these systems the effective masses of the individual normal modes probably do not vary strongly, it appears that small effective charges may be a general feature of Cu—O bonds.

Third, the Y atoms (or Sm atoms) vibrate in infrared-active modes that transform as the A_{2u} and E_u irreducible representations,[6] the former involving motion along the *c* axis, and the latter doubly degenerate modes involving

TABLE I. The transverse-optic (TO) frequencies, longitudinal-optic (LO) frequencies, and damping constants $\gamma = \gamma_{TO} = \gamma_{LO}$ obtained from the fit. All of the values are given in cm^{-1}.

	$YBa_2Cu_3O_{7-\delta}$				$SmBa_2Cu_3O_{7-\delta}$		
No.	ω_{TO}	ω_{LO}	γ	No.	ω_{TO}	ω_{LO}	γ
1	108	109	9	1	105	106	9
2	118	124	10	2	113	118	10
3	147	151	22	3	139	143	24
4	164	176	25	4	155	165	27
5	190	195	10	5	167	172	10
6	217	220	10	6	191	195	10
7	249	261	23	7	239	254	28
8	360	422	55	8	348	407	65
9	593	612	55	9	568	588	60
10	648	663	65	10	646	664	60

atomic motion in the *ab* plane. In principle, motion of the Y atom can be involved in all $5A_{2u}$ as well as all $6E_u$ allowed infrared-active modes. However, in practice this is rarely the case for structures that contain specific structural elements (such as the $Cu-O_4$ planes and other $Cu-O_4$ chains). Typically, the motion of a given atom is confined principally to a few normal modes. This situation seems to be the case here. Modes numbered 5 and 6 shift sharply to lower frequency (by 22 and 27 cm^{-1}, respectively) when Y atoms are replaced by the heavier Sm atoms [Fig. 2(a) and Table I]. Presumably, one of these modes is an A_{2u} and one is an E_u mode. This approximate isotropy of the down shift is consistent with the structure (Fig. 1), where the Y atom, which is in between the two $Cu-O_4$ planes, is cubicly (eight neighbors) surrounded by oxygen atoms in a manner that is approximately isotropic.

Fourth, with the replacement of the Y atoms by the heavier Sm atoms, we observe a surprisingly large downshift [25 cm^{-1}, Fig. 2(a) and Table I] in the high-frequency mode, labeled No. 9. In our previous work,[6] the two high-frequency modes (Nos. 9 and 10) were related to modes that involve motion of the lightest atoms (the O atoms) directly against Cu atoms. The motion for one of these modes is the in-planar Cu(2*g*)-O(4*i*) vibrations (E_u mode). The other motion is that of Cu(1*a*) atoms in the chains against the O(2*g*) atoms in the chains, both moving along *c* axis (A_{2u} mode). With the replacement of Y atoms by Sm atoms, mode No. 10 hardly shifts, but No. 9 downshifts 25 cm^{-1}. This shift, along with the fact that the Y atom is very close to the Cu—O planes (Fig. 1) and relatively distant from the Cu—O chains, enables us to assign mode No. 10 to the high-frequency Cu—O motion in the chain. The in-planar Cu(2*g*) against O(4*i*) motion is then assigned to mode No. 9.

With the replacement of Y with Sm atoms, mode No. 8 moves down in frequency by 12 cm^{-1} (Table I), which is also a reasonably large shift. We assign this mode to the low-frequency in-plane Cu(2*g*)-O(4*i*), E_u mode.[6,12] This is a bond-bending mode and therefore lower in frequency than the Cu against O motion in mode No. 9, as discussed above.

This assignment of the high-frequency zone-center modes, and the fact that T_c does not vary with the replacement of Y atoms by rare-earth atoms (with the corresponding decrease of high-frequency Cu-O planar vibrations), is consistent with the approximate lack of isotope effect in these materials.[1]

Fifth, with the assignments of some of the midfrequency modes (Nos. 5 and 6), we can consider the lower-frequency modes. Undoubtedly, the normal modes are complicated, and a trustworthy lattice-dynamics calculation would be helpful. However, it seems certain that the heavy Ba atoms are involved in these modes. Ba-atom motion is involved in A_{2u} and E_u modes,[6] and it is possible that this atom is primarily involved in the normal modes Nos. 1 and 2. Partial or complete substitution for the Ba atoms could clarify this point.

It is interesting to note that these two lowest-frequency modes and the two associated with the Y atoms (or Sm atoms) have the smallest damping constants (Table I). This is consistent with the structure, in that both the Ba and Y atoms appear to be loosely coupled to the other atoms.

Sixth, it is possible that in the Sm material we observe the eleventh allowed infrared mode. It is weak, at ≈ 210 cm^{-1} (Fig. 2), and is observed when mode No. 6 moves to lower frequency due to the rare-earth substitution.

In comparing our data to infrared reflectivity results in $YBa_2Cu_3O_{7-\delta}$ superconductors,[3] there does not appear to be a clear one-to-one comparison. Most of the infrared results in these superconductors are in reasonable agreement with the early work of Bonn *et al.*[3(a)] who find three pairs of lines whose frequencies are approximately at 151, 191, 279, 310, 548, and 609 cm^{-1}. Others[3(d),3(h)] also report a mode at ≈ 230 cm^{-1}. One could argue that due to coupling with a two-dimensional (*ab* plane) electron plasma, the E_u modes would be screened and hence much weaker than the A_{2u} modes; this has been observed in single crystals.[10] Therefore, only the $5A_{2u}$-type modes might be observable in the superconductors. However, if this is the case, we are left with a dilemma. If the two highest-frequency modes (548 and 609 cm^{-1}) are associated with the Cu-O inplanar vibrations, then one must be an E_u mode, as discussed. Also, if no modes are observed at ≈ 110 cm^{-1} (corresponding to our No. 1 and No. 2 modes, one of which is an A_{2u} mode), then the counting is wrong.

One aspect of the comparison to the superconducting materials is, however, satisfactory. The mode observed at 191 cm^{-1} in the Y superconductors is found to shift[3(j)] to ≈ 166 cm^{-1} in the rare-earth materials. Therefore, this mode is probably an A_{2u} mode, as discussed above. Furthermore, the shift is in good agreement with our results (Table I). On the other hand, the mode observed at ≈ 575 cm^{-1} in the superconductor does not shift when rare-earth atoms are substituted for Y atoms[3(j)] as is observed here. The planar Cu-O distances remain very similar in the tetragonal and orthorhombic phases, so it is reasonable to compare the infrared results. However, for the chains the Cu-O distances and environment are rather different in the two phases,[5(b)] so a comparison has less meaning.

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[12] As pictured in Ref. 6, the high-frequency E_u, in-plane Cu(2g)-O(4i) mode approximately has these atoms moving against one another. The lower-frequency E_u mode has Cu atoms moving colinearly with two of its neighboring O atoms, and the other two oxygen atoms moving in the opposite direction; this causes a change in the O—Cu—O bond angle. Motion in the other Cu-O plane is in phase.