



Far Infrared Spectroscopy of Single Crystal $\text{YBa}_2\text{Cu}_3\text{O}_6$

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We report infrared (IR) reflectivity measurements of single crystal $\text{YBa}_2\text{Cu}_3\text{O}_6$, the semiconducting version of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (i.e., $\delta = 1$). The near normal incidence ab-plane reflectivity clearly exhibits five of the six allowed E_u modes. Based on normal modes in K_2NiF_4 -type materials, we offer a possible explanation for the unobserved E_u mode. Combining the single crystal data with our previously reported data on isomorphically and isotopically (^{18}O) substituted ceramic $\text{YBa}_2\text{Cu}_3\text{O}_6$, we determine the A_{2u} modes. Thus, a fairly complete picture of the IR active phonons is obtained. The phonon assignments are discussed.

Introduction. The phonons in high temperature superconductors have been studied with IR, Raman and neutron techniques^{1,2}. Although single crystal Raman measurements of the phonons in $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been made, there has not been a comparable single crystal IR study of the phonons in this system. The reason for this is that $\text{YBa}_2\text{Cu}_3\text{O}_7$ has a growth habit which yields small ab plate-like crystals with very small dimension along the c axis. The size constraints limit IR measurements to the ab face. Further, in $\text{YBa}_2\text{Cu}_3\text{O}_7$, the ab plane free-carrier plasma couples to the ab plane polarized phonons, making them difficult to observe. Thus, observations of phonons in $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been limited to ceramic samples, where only phonons polarized in the c direction are measurable. In semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$ there is no free-carrier plasma so IR measurements can probe the $5A_{2u} + 6E_u$ infrared active phonons^{3a}. Measurements on ceramics do not, however, separate these two polarizations.

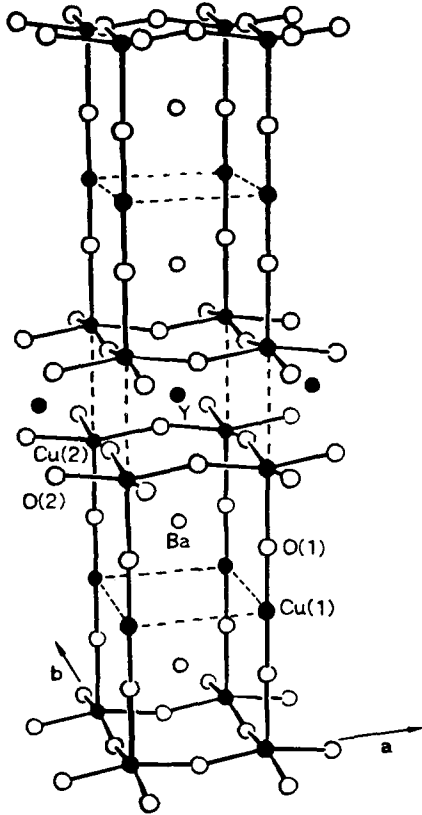
Here we report IR measurements of a $\text{YBa}_2\text{Cu}_3\text{O}_6$ single crystal. These results clearly and unambiguously give the E_u modes. We then compare these results to the ceramic data^{3,4} and thereby determine the A_{2u} modes. From these results, and results⁴ on ^{18}O exchanged $\text{YBa}_2\text{Cu}_3\text{O}_6$, a more accurate picture of the lattice dynamics in this material is obtained³⁻⁵.

Experiment. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal was grown by methods described previously⁶.

The as-grown crystal was reduced in flowing He for 3 days at 700°C, yielding $\text{YBa}_2\text{Cu}_3\text{O}_6$. The IR data acquisition was also described previously⁴. The ceramic data given here for $\text{YBa}_2\text{Cu}_3\text{O}_6$ were corrected for geometric scattering by depositing ~ 1,000 Å of Al on the pellet after data acquisition and using the coated pellet as a reference, while the single crystal data given here were referenced to a front surface Al mirror.

Results and Discussion. The space group of the $\text{YBa}_2\text{Cu}_3\text{O}_6$ structure (Fig. 1) is $P4/mmm - D_{4h}^1$ and, using group theory, we determine^{3a} that there are eleven infrared active phonons which transform as $5A_{2u} + 6E_u$ irreducible representations of the point group $4/mmm - D_{4h}$. The E_u modes are doubly degenerate. For phonons that transform as A_{2u} the ions vibrate along the c axis. These vibrations interact with IR radiation for which the electric field is parallel to the c axis. Due to the small single crystal dimension (~ 100 μm) in the c direction, these IR phonons cannot be directly measured. For the phonons which transform as E_u the ions vibrate in the ab plane. These vibrations interact with IR radiation for which the electric field is perpendicular to the c axis. We can measure only the E_u modes in our single crystal study.

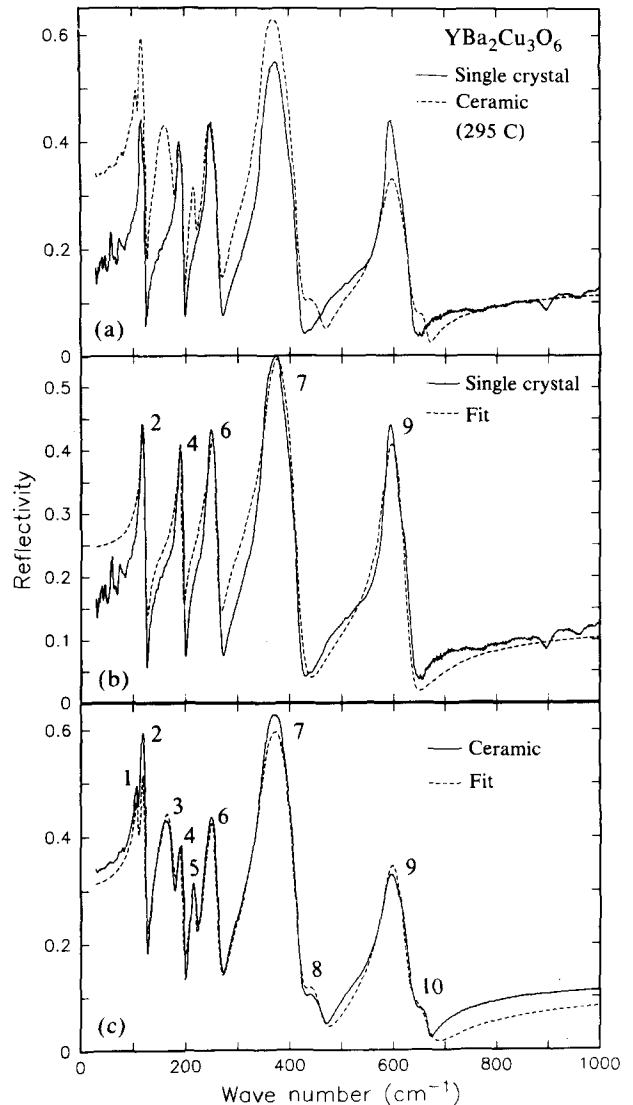
In Fig. 2a we show with the solid line the room temperature infrared reflectance from the ab plane of an oriented single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_6$. (The dashed line is the ceramic data and, as can be seen,



1. Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_6$, space group $P4/mmm-D_{4h}^1$.

five of the phonons appear in both single crystal and ceramic data.) Despite the fact that group theory predicts six E_u modes, only five strong vibrations are seen in the single crystal data. The remaining vibration must either have a very small oscillator strength or be located near in energy to, and thereby hidden from view by, another E_u mode.

It is tempting to associate the missing E_u mode with one that has a very small effective charge, leading to a very small TO-LO splitting, similar to a mode of E_u symmetry found in insulating materials which have the related K_2NiF_4 structure. A variety of such materials have been studied by Geick and colleagues⁷⁻¹⁰. They show, both experimentally and theoretically, that one of the E_u modes involves predominantly oxygen motion and therefore has a very small effective charge and TO-LO splitting. For some crystals (e.g., K_2MnF_4 and Rb_2MnF_4) this splitting is so small that the mode is not observed at room temperature. This mode involves mostly vibration of oxygen ions in the Cu-O planes against the axial oxygen ions above and below the Cu-O planes (O_z ions). Since the oxygen ions have approximately the same charge, the very small net dipole moment for this vibration leads to a very small TO-LO splitting. A picture of this mode can be found in reference 7. This mode has also been discussed more recently in connection with the phonons in



2. (a) Far infrared reflectance of single crystal and ceramic $\text{YBa}_2\text{Cu}_3\text{O}_6$.

(b) Comparison of far infrared reflectance and results of an oscillator fit for single crystal $\text{YBa}_2\text{Cu}_3\text{O}_6$. Solid line is the data.

(c) Comparison of far infrared reflectance and results of an oscillator fit for ceramic $\text{YBa}_2\text{Cu}_3\text{O}_6$. Solid line is the data.

($\text{La,Sr})_2\text{CuO}_4$ ¹¹. In $\text{YBa}_2\text{Cu}_3\text{O}_6$ a similar mode might exist involving in-plane vibration of oxygen ions in adjacent Cu-O planes [O(2)] against the two apical oxygen ions [O(1)]. Although this explanation could account for the sixth E_u mode, we find it at odds with the ^{18}O results⁴ in ceramic $\text{YBa}_2\text{Cu}_3\text{O}_6$, which we discuss below.

In Table 1 are shown the E_u mode TO and LO frequencies from the single crystal $\text{YBa}_2\text{Cu}_3\text{O}_6$ determined by an oscillator fit^{3b} to the reflectance data. The fit can be seen in Fig. 2b. The modes are

Table 1 Transverse-optic (ω_{TO}) energies, longitudinal-optic (ω_{LO}) energies, and damping constants ($\gamma = \gamma_{\text{TO}} = \gamma_{\text{LO}}$), all in cm^{-1} , obtained from an oscillator fit to single crystal and ceramic data for $\text{YBa}_2\text{Cu}_3\text{O}_6$.

Single Crystal				Ceramic			
Mode No.	ω_{TO}	ω_{LO}	γ	Mode No.	ω_{TO}	ω_{LO}	γ
-	-	-	-	1	107	109	5
2	118	124	7	2	118	124	7
-	-	-	-	3	154	180	25
4	190	195	7	4	190	195	9
-	-	-	-	5	217	220	9
6	251	263	15	6	248	264	18
7	361	422	33	7	352	418	33
-	-	-	-	8	442	458	42
9	588	630	29	9	589	628	37
-	-	-	-	10	648	663	45

numbered in Fig. 2b and Table 1 to facilitate comparison to the ceramic data.

Fig. 2a shows the IR reflectivity results for an $\text{YBa}_2\text{Cu}_3\text{O}_6$ ceramic pellet. Results of an oscillator fit to the data can be seen in Fig. 2c and the parameters are given in Table 1. The data and oscillator fits are in excellent agreement with our previously published results^{3,4}. We now compare the single crystal and ceramic data.

First, the $5E_u$ modes observed in the single crystal data are in excellent correspondence with five reststrahlen bands observed in the ceramic data (Fig. 2a). This demonstrates that accurate phonon parameters can be obtained from ceramic reflectance data for $\text{YBa}_2\text{Cu}_3\text{O}_6$, although small particle effects (e.g., surface modes) have been found to cause differences, attributed to particle shape, between ceramic and single crystal data in other materials¹². In ceramic data, of course, the A_{2u} and E_u modes are not separated and may overlap in frequency¹¹.

Second, by comparing the ceramic data to the single crystal data, we deduce the A_{2u} modes, yielding a more complete picture of the phonons in $\text{YBa}_2\text{Cu}_3\text{O}_6$.

Third, in the ceramic data there are two narrow pairs of phonons of A_{2u} and E_u symmetry, one pair at 107 cm^{-1} (A_{2u}) and 118 cm^{-1} (E_u), the other pair at 190 cm^{-1} (E_u) and 217 cm^{-1} (A_{2u}). The E_u modes have a larger TO-LO splitting than the A_{2u} modes. These pairs of modes are assigned as phonons which involve mostly Ba^{2+} and Y^{3+} motion, respectively. These assignments are based upon the results of replacing Y^{3+} with other rare earths, Ba^{2+} with Sr^{2+} , and ^{16}O with ^{18}O (references 3-5). Rare earth substitution for Y^{3+} causes the $190, 217 \text{ cm}^{-1}$ pair to shift by a larger amount than the phonon pair at $108, 118 \text{ cm}^{-1}$.

In Table 2 we summarize our phonon assignments for $\text{YBa}_2\text{Cu}_3\text{O}_6$ based upon single crystal and ceramic data. The phonon symmetry results from this single crystal work lead to some

Table 2 Assignments of the phonons for $\text{YBa}_2\text{Cu}_3\text{O}_6$. The energy units are cm^{-1} .

Energy	Symmetry*	Assignment
107	A_{2u}	Ba translation along c axis
118	E_u	Ba translation in ab plane
154	A_{2u}	O(1)-Cu(1)-O(1) translation along c axis
190	E_u	Y translation in ab plane
217	A_{2u}	Y translation along c axis
251	E_u	O(1)-Cu(1)-O(1) bond bending parallel to ab plane
361	E_u	O(2)-Cu(2)-O(2) bond bending parallel to ab plane
442	A_{2u}	Cu(2)-O(2) bond bending parallel to c axis
589	E_u	Cu(2)-O(2) stretch
648	A_{2u}	Cu(1)-O(1) stretch along c axis

* Determined by comparison of single crystal (E_u) spectrum to ceramic (A_{2u} and E_u) spectrum. One E_u mode is missing.

Note: besides the acoustic phonons, the remaining phonons in $\text{YBa}_2\text{Cu}_3\text{O}_6$ are Raman active ($4A_{1g} + B_{1g} + 5E_g$) and silent (B_{2u}). The B_{1g} and B_{2u} phonons both involve only the oxygen ions in the Cu-O planes.

modifications of previous assignments³⁻⁵, although many of our earlier assignments are supported by the new data. The modes near 600 cm^{-1} involve predominantly Cu-O bond stretching, whereas those near 300 cm^{-1} are predominantly due to Cu-O bond bending vibrations. Based upon the polarized single crystal data given in Table 1, we can more accurately apply the Teller-Redlich product rule to the ^{18}O frequency shifts measured for the A_{2u} and E_u modes (see reference 4 and references therein for the ^{18}O data and a complete description of the Teller-Redlich product rule). The product rule is nearly satisfied for both the A_{2u} modes and the E_u modes. This implies that the missing E_u mode should involve little, if any, oxygen ion vibration, which disagrees with our speculation attributing the missing mode to an essentially pure oxygen vibration. It may be that the missing E_u mode is primarily a Cu(1) or Cu(2) vibration and does not involve significant oxygen motion. This point, however, requires further study.

Finally, we discuss our results in comparison to lattice dynamics calculations^{5,13} for $\text{YBa}_2\text{Cu}_3\text{O}_6$. These calculations appear to agree more closely with Raman measurements than with IR measurements. In general, IR active modes can involve motion of every ion in the unit cell, whereas Raman active modes are restricted by symmetry to involve motion of certain ions only. For example, the chain Cu(1) ion and the Y^{3+} ion do not move in any Raman active mode, and only the O(2) ions in the Cu-O sheets move in the B_{1g} Raman mode. Thus, the Raman modes are simpler in form than the IR modes. Although the calculations predict IR active phonon frequencies which are similar to the measured frequencies, the ionic participation

observed for each mode often disagrees with calculations. The ionic motions which occur in each phonon may be inferred from the changes in phonon frequency due to isomorphic and, most important, isotopic substitution⁴. For example, we find the Ba A_{2u} (108 cm^{-1}) and Ba E_u (118 cm^{-1}) vibrations exhibit very little frequency shift after ^{18}O exchange, whereas calculation¹³ predicts a sizable vibrational amplitude for oxygen in this mode. (It would be useful if these calculations were done for both oxygen isotopes.) Thus, single crystal experimental data, combined with isotope studies, can yield further insight into the lattice dynamics, and thereby stimulate increasingly accurate calculations. This

will lead to a better assessment of the role played by phonons in the phenomenon of high temperature superconductivity.

In conclusion, we report a far infrared reflectivity study of the ab plane phonons in a single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_6$. Unambiguous symmetry assignments have been given for the infrared active phonons and, in combination with previously published isotopic and isomorphic substitution data, individual phonons have been associated with various structural elements of the unit cell.

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