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Raman scattering from single crystals of the 84-K superconductor $Bi_{2.2}Ca_{0.8}Sr_2Cu_2O_{8+\delta}$

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We report the Raman spectrum of single crystals of $Bi_{2.2}Ca_{0.8}Sr_2Cu_2O_{8+\delta}$. The most prominent features are at 120, 295, 462, and 625 cm^{-1}. The 462-cm^{-1} mode is tentatively assigned to axial O(3) symmetric stretching. The 625-cm^{-1} mode is assigned to planar Cu-O(1) bond stretching. The 120-cm^{-1} mode shows a strong *a*-*b* anisotropy. The effect of the *b*-axis superstructure upon the Raman spectrum is emphasized.

Superconductivity with a T_c near 120 K has been reported recently for multiphase samples of copper oxide systems containing bismuth, calcium, and strontium.[1-3] Within this class of materials, single-phase material with the stoichiometric composition $Bi_2CaSr_2Cu_2O_8$ (Bi-Ca-Sr-Cu-O) that shows bulk superconductivity at 84 K has been prepared and characterized.[4-8] Here, we report a Raman-scattering study of single crystals[5] of this material and make a preliminary assignment of the vibrational features.

The early Raman studies of high-T_c ceramics, for example, $Ba_2YCu_3O_x$, showed discrepancies[9-13] due to the appearance of bands that were not intrinsic to the superconducting materials. Questions concerning which modes were intrinsic and their assignments were settled only after single crystals became available.[14,15] For the new Bi-Ca-Sr-Cu-O compound, both ceramics and single crystals are available so that there can be confidence that Raman features are indeed intrinsic. Further, polarization selection rules are essential to confirm the assignments of the vibrational features.

The structure of Bi-Ca-Sr-Cu-O has been examined by x-ray and neutron diffraction.[4,6-8] There is a complicated superlattice of orthorhombic subunits with a stoichiometric composition of $Bi_2CaSr_2Cu_2O_8$. These orthorhombic subunits can be approximated by a body-centered-tetragonal structure ($I4/mmm$ or D_{4h}^{17}) with the primitive cell shown in Fig. 1 (see Ref. 16) which we consider in the discussion of the Raman spectra. As in previous high-T_c oxides, there are CuO_2 planes which are separated by Ca much as the planes in $Ba_2YCu_3O_x$ were separated by Y. The in-plane Cu-O(1) distance is 1.91 Å. The novel feature of this structure is the presence of an edge-shared bismuth oxide double layer. The Bi coordination is octahedral with Bi-O(2) distances of 2.71 Å. The copper-oxygen coordination polyhedron shares its apical O(3) with the Bi octahedron. The Cu-O(3) and Bi-O(3) distances are 2.65 and 1.89 Å, respectively. (Bond lengths are taken from Ref. 8.)

For our experiments, single crystals of $Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_{8+\delta}$ with a layered morphology and dimensions of several $mm^2 \times \sim 2$ μm were grown from an alkali chloride flux.[5] The *c* axis is normal to the layer. Such crystals show bulk superconductivity at 84 K. A description of their physical properties is reported elsewhere.[4] The crystals used here were verified to be superconducting at 77 K by their deflection in a magnetic field. Two crystal morphologies, thin foils with areas of several mm^2 and with no well-defined crystallographic edges, and thin rectangular samples with square edges, were examined. While x-ray diffraction shows that the former have large mosaics, the latter are indeed ordered single crystals. Several of the measurements reported here were performed on an oriented single crystal with an area of $\sim 1 \times 4$ mm^2. The long axis was along a ⟨110⟩ direction and the *a* and *b* axes were distinguished (the superstructure is along *b*). Pellets of the Bi-Ca-Sr-Cu-O have been prepared by standard ceramic techniques. Spectra were measured for compositions $Bi_{2.2}Ca_{1.1}Sr_{1.7}Cu_2O_{8+\delta}$, $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_{8+\delta}$, and $Bi_2Ca_{1.25}Sr_{1.75}Cu_2O_{8+\delta}$, which gave similar results.

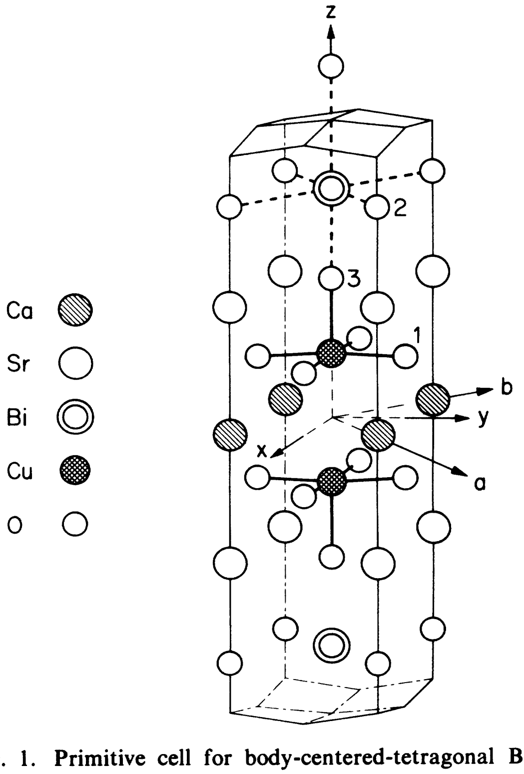

FIG. 1. Primitive cell for body-centered-tetragonal $Bi_2CaSr_2Cu_3O_8$. The *a* and *b* axes at 45° to *x* and *y* are shown and the three inequivalent oxygen sites are labeled.

For our Raman experiments, we have used an Ar^+ laser and an ISA scanning double spectrometer equipped with photon counting detection. The laser power was less than 40 mW and the spectral resolution was 5 cm^{-1}. All measurements on crystals were done in a 90° scattering geometry with the laser light incident on the *c* face at a grazing angle.

Figure 2 shows Raman spectra taken for ceramic samples of $Bi_{2.2}Sr_{1.7}Ca_{1.1}Cu_2O_{8+\delta}$ and $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ and a thin foil of $Bi_{2.2}Ca_{0.8}Sr_2Cu_2O_{8+\delta}$. Comparison of the spectra for ceramics and crystals show that there are no high-frequency Raman modes ($\omega > 300$ cm^{-1}) that are absent because of polarization selection rules for the crystals in this scattering geometry. (The 500-cm^{-1} mode in $Ba_2YCu_3O_7$ crystals was not allowed in the grazing incidence geometry.[14]) The prominent features are at 625, 462, 295, 195, and 120 cm^{-1}. Most of these features are very broad and it is possible that there is an unresolved band between 295 and 462 cm^{-1} where the spectrum is filled in. Spectra taken with polarized light for an oriented single crystal are shown in Fig. 3. Foils and crystals showed the same spectral features.

There are 15 atoms in the unit cell shown in Fig. 1 and, hence, 42 optic modes. Of these, 21 are Raman active. A factor-group analysis (point group D_{4h}) shows that there are $6A_{1g}$, $1B_{1g}$, and 7 doubly degenerate E_g Raman modes. Many of the normal vibrations for the unit cell shown in Fig. 1 are similar to the modes in $Ba_2YCu_3O_x$.[14,15] The six A_{1g} modes all involve symmetric stretching motions along *z*. For example, there will be an A_{1g} mode that involves the axial motion of primarily the O(3) atoms. There will also be A_{1g} modes that involve the axial motions of the O(2), Cu, Sr, and Bi atoms. The remaining A_{1g} and B_{1g} mode involve Cu-O(1) bending motions. For in-phase motion of the O(1) atoms in a Cu plane (in concert with the similar motion in the other Cu plane), the mode has A_{1g} symmetry, while if the motion of the O(1) atoms along *x* and *y* are out of phase, the mode has B_{1g} symmetry. Generally, motions in the *a*-*b* plane of pairs of atoms, one above the Ca plane and one below, give rise to the E_g modes. The motion of the atom above the Ca plane has the opposite phase as that below (the E_g modes have the same symmetry as rotations about *x* or *y*). The A_{1g} and B_{1g} modes are the modes observed strongly in $Ba_2YCu_3O_x$. No E_g motions are observed.[14,15]

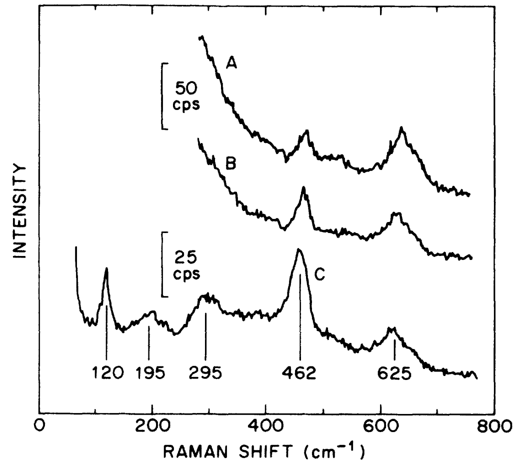

FIG. 2. Raman spectra of Bi-Ca-Sr-Cu-O. Spectra labeled *A* and *B* are for ceramics with compositions $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_{8+\delta}$ and $Bi_{2.2}Ca_{1.1}Sr_{1.7}Cu_2O_{8+\delta}$, respectively. The spectrum labeled *C* is for a thin-foil polycrystal of $Bi_{2.2}Ca_{0.8}Sr_2Cu_2O_{8+\delta}$.

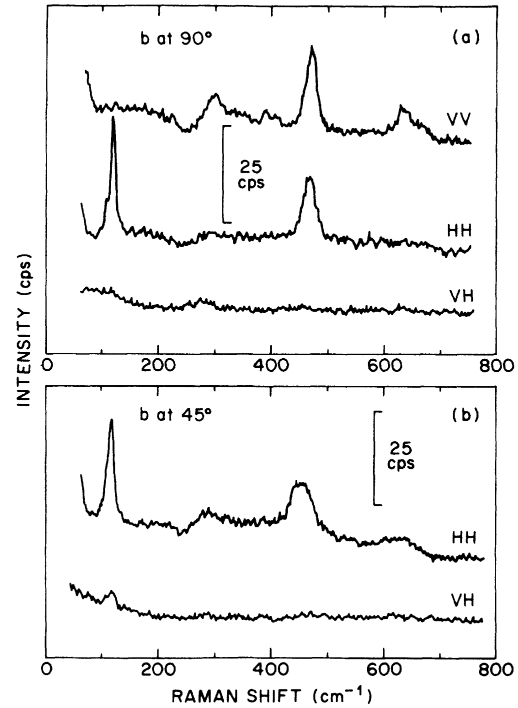

FIG. 3. Raman spectra of single crystal $Bi_{2.2}Ca_{0.8}Sr_2Cu_2O_{8+\delta}$. The excitation beam is incident on the *c* face at a grazing angle and the scattered light is collected at 90°. Light polarized perpendicular (parallel) to the scattering plane is denoted V (H). (a) Spectra taken with the *b* axis of the crystal at 90° to the scattering plane and with the *c* axis in the scattering plane. (b) Spectra taken with the *b* axis of the crystal at 45° to the scattering plane and with the *c* axis in the scattering plane.

Several aspects of the real crystal structure of Bi-Ca-Sr-Cu-O complicate the analysis of the Raman spectrum. There is an incommensurate, *b*-axis superstructure and there can be compositional disorder of the Bi, Ca, and Sr atoms, all of which can add features to the Raman spectra by breaking the selection rules derived for the tetragonal cell shown in Fig. 1. These distortions most likely produce a symmetry of *Fmmm*, however, there is additional evidence that $h = 2n$ peaks that are not allowed by *Fmmm* appear in the x-ray diffraction, further reducing the symmetry to *Ammm*. Changes in composition effect the relative intensity of the 462 and 625 cm^{-1} bands for spectra *A* and *B* in Fig. 2 suggesting that compositional disorder effects the intensities of these features. The vibrational features are broad and the bands are not well resolved between 200 and 500 cm^{-1}, (spectrum *C* in Fig. 2) suggesting that the superstructure and compositional disorder might break the $k = 0$ selection rule for the tetragonal cell and permit scattering from modes at other points in the Brillouin zone. Lastly, there is a pronounced *a*-*b* anisotropy observed for the 120-cm^{-1} band in Fig. 3(a) and also for all the other modes to some degree except the 462-cm^{-1} band. (The degree of *a*-*b* anisotropy in modes other than the 120-cm^{-1} band was sample dependent.) The orthorhombic distortion and the superstructure will lift the degeneracy of the E_g modes of the tetragonal cell and also lead to additional modes that might give rise to the anisotropic scattering. In spite of these complexities, we have chosen to discuss the Raman spectrum in terms of the tetragonal cell shown in Fig. 1 to facilitate comparison with $Ba_2YCu_3O_x$ and because it is not yet clear which symmetry lowering effects are responsible for specific spectral characteristics.

We make tentative assignments of the spectral features. We expect the highest frequency 625-cm^{-1} mode in Bi-Ca-Sr-Cu-O to be associated with the planar Cu-O(1) stretching motions because of the short bond lengths and the light oxygen mass. For the tetragonal cell there is an E_g mode that involves planar Cu-O(1) stretching. However, the effects described in the previous paragraph will make additional Cu-O(1) bond stretching modes allowed. The planar Cu-O stretching motions and Cu-O chain modes give rise to the highest-frequency vibration observed in $Ba_2YCu_3O_x$ and it has been suggested that they are allowed by vacancy disorder.[14,15]

We suggest that the prominent 462-cm^{-1} band can be assigned to axial symmetric stretching of the O(3) atoms by analogy with the 500-cm^{-1} mode of $Ba_2YCu_3O_7$. This band has no strong *a*-*b* anisotropy or depolarized scattering, consistent with A_{1g} symmetry. The vibrational frequency depends on the force constants (and hence bond lengths) associated with both the Bi-O(3) and Cu-O(3) bonds. The Bi-Cu distance[8] of 4.54 Å is consistent with a lower vibrational frequency for O(3) axial stretching when compared to the shorter Cu(1)-Cu(2) distance of 4.14 Å for the 500-cm^{-1} axial stretching mode[17] of the bridging O(1) in $Ba_2YCu_3O_7$. (We use the notation and bond lengths of Ref. 18 for $Ba_2YCu_3O_7$.)

At lower frequency (i.e., between 300 and 400 cm^{-1}) we expect to find the modes due to Cu-O(1) bond bending and Bi-O(2) bond stretching. In $Ba_2YCu_3O_7$, the Cu-O(2,3) bond bending modes were observed at 435 and 340 cm^{-1} and were assigned to A_{1g} and B_{1g} vibrations, respectively.[14,15] For our Bi-Ca-Sr-Cu-O samples, no mode is observed with clear B_{1g} symmetry. [We would have expected only depolarized scattering from a B_{1g} mode[15] for the crystal orientation shown in Fig. 3(a). There is no strong depolarized scattering observed in either of the crystal orientations we have examined.] In $BaBiO_3$, the $Bi\text{-}O_6$ breathing mode is at 569 cm^{-1} (Ref. 19). For Bi-Ca-Sr-Cu-O, the planar Bi-O(2) bonds are much longer[8] ($\sim$2.7 Å) as compared to the Bi-O bonds in $BaBiO_3$ (average bond lengths[20] of 2.28 and 2.12 Å), hence, we expect the planar Bi-O(2) vibrations to appear at lower frequency here. Because of the spectral congestion and lack of definitive polarization information, we do not propose specific mode assignments in this region.

The band at 120 cm^{-1} has a strong *a*-*b* anisotropy as is shown in Fig. 3(a). Further, there is no strong depolarized scattering observed, even when the crystal is rotated about the *c* axis [Fig. 3(b)]. Hence, this mode cannot be due to an A_g mode with an *a*-*b* anisotropy for an orthorhombic cell because rotation about the *c* axis would give rise to off-diagonal elements in the polarizability tensor and, hence, depolarized scattering. For the HH scattering geometry, the incident and scattered light have components of their polarization along the *c* axis (z). We conclude that the 120-cm^{-1} band can only arise from $x'z$ and zx' components of the polarizability tensor (x' is along the *a* axis). A problem with this interpretation is that when the crystal is rotated by 90° from the orientation shown in Fig. 3(a) (i.e., with the *b* axis in the scattering plane) the 120-cm^{-1} band is observed in the VV scattering geometry, where there should be no *z* polariation components, and not in HH. The intensity of the 120-cm^{-1} band (relative to the 462-cm^{-1} band) is reduced by at least a factor of 2 in this VV geometry, hence, we explain this contradictory result by noting that the thin crystals are not flat and that for this nonideal case even the VV geometry can contain small *z* polarization components. Further evidence for $x'z$ scattering is provided by spectra taken with the *c* axis of the crystal intentionally rotated by a few degrees out of the scattering plane. In this case, the 120-cm^{-1} mode was observed for HH, VV, and HV geometries, presumably because these geometries all include $x'z$ scattering components when the *c* axis is not in the scattering plane. We recall that the 140-cm^{-1} and 116-cm^{-1} vibrations observed in $Ba_2YCu_3O_x$ were assigned to axial stretching of the Cu and Ba planes, respectively.[15] Similarly, we suggest that the 120-cm^{-1} vibration in Bi-Ca-Sr-Cu-O is due to Sr or Cu motions and that the vibrations associated with the heavier Bi atom should be at lower frequency.

In conclusion, we have reported polarized Raman spectra for single crystals of the $Bi_2CaSr_2Cu_2O_8$ class of superconductors. Tentative assignments of the vibrational bands have been proposed. Unlike $Ba_2YCu_3O_x$, the crystals are untwinned and several of the Raman features show strong *a*-*b* anisotropy, presumably due to the *b*-axis superstructure. Lattice dynamics calculations and studies of structurally related materials such as the new Tl compounds[21,22] will lead to more complete, definitive assignments. The identification and assignment of the vibrational features are essential first steps towards material characterization by Raman techniques and towards studies of interactions of phonons with electronic or spin excitations for this new class of high-T_c cuprates.

Note added in proof. We have measured Raman spectra of polycrystals of the Bi-Sr-Cu-O compound with a single Cu-O layer (stoichiometric composition $Bi_2Sr_2CuO_6$). The spectrum is remarkably similar to that shown in Fig. 2 here. This implies that the 120-cm^1 band is due to a Bi or Sr axial vibration because an axial Cu vibration is not allowed for the structure with a single Cu-O layer. The shoulder at 295 cm^{-1} in spectrum *C* of Fig. 2 is weaker in the single-layer material. This result supports the recent assignment by Cardona *et al.* [Solid State Commun. **66**, 1225 (1988)] of the 295-cm^{-1} feature to Cu-O(1) bond bending because this mode should also be absent for the structure with a single Cu-O layer.

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