

Raman scattering in single crystals of Tl-Ba-Ca-Cu-O superconductors

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Raman scattering of light by totally symmetric phonons in superconducting single crystals of $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-x}$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-x}$ has been measured. A group-theoretical analysis of the symmetry of phonon modes in $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ has been carried out. The totally symmetric vibrations in the Raman-scattering spectra have been classified.

1. The discovery of bismuth¹ and thallium² superconductors, with a superconducting transition temperature higher than that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, marked the beginning of extensive study of these materials. One of the most important tasks is to determine the common features of all the families of high- T_c superconductors and, in particular, to identify the similarities and the differences in the phonon spectra. The application of Raman scattering makes it possible to study the long-wavelength phonons at the Γ point of the Brillouin zone. The Raman scattering in the compounds $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Refs. 3-5) and La_2CuO_4 (Ref. 6) has been studied in detail. We are reporting here the results of an experimental study of Raman scattering in single crystals of $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-x}$ (Tl-1212) and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-x}$ (Tl-2212).

2. The single crystals were grown by slow cooling from a melt of a stoichiometric composition in flowing oxygen. The rectangular single-crystal wafers with a mirror-finish basal plane had the dimensions $3 \times 3 \times 0.3$ mm. The symmetry of the single crystals was monitored by x-ray diffraction analysis: D_{4h}^{14} ($P4/mmm$), $a = 3.855 \text{ \AA}$, and $c = 12.711 \text{ \AA}$ for Tl-1212 and D_{4h}^{17} ($I4/mmm$), $a = 3.856 \text{ \AA}$, and $c = 29.34 \text{ \AA}$ for Tl-2212. The Tl-1212 and Tl-2212 samples went superconducting at $T = 70 \text{ K}$ and $T = 110 \text{ K}$, respectively.

The Raman-scattering spectra of various single-crystal faces were measured in the backscattering geometry at room temperature, using a spectrometer with a microscope attachment. Light from an Ar^+ laser ($\lambda = 4880 \text{ \AA}$) was focused on a sample in a spot $3 \mu\text{m}$ in diameter. To avoid superheating of the excited region, the power of the laser light was kept at a level no greater than several milliwatts.

3. The Tl-Ba-Ca-Cu-O system has two series of superconducting phases,⁷ $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$. The structures in each series differ in the number n of copper-oxygen layers. The $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ crystals have a body-centered tetragonal structure with two formula units per unit cell (Fig. 1). The primitive cell of these crystals, which is half as large, has only one formula unit. The $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ crystals have a primitive tetragonal structure (Fig. 1) with one formula unit per cell.

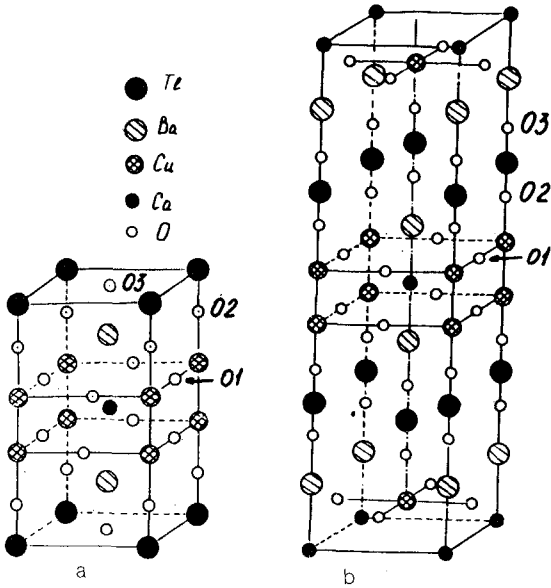


FIG. 1. Unit cells of single crystals. (a) $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ and (b) $\text{TlBa}_2\text{CaCu}_2\text{O}_8$.

The Tl-1212 and Tl-2212 test crystals contain two copper-oxygen layers each, which are divided by Ca-ion planes (Fig. 1). The oxygen ions form an axially extended octahedron around the copper ions. In each structure the Ba ions are situated above and below the Cu-01 layers in the nine-coordinate oxygen surroundings. The Tl ion in each structure links six oxygen ions into a distorted octahedron. The difference in the number of intercalating Tl-O layers sets one structure apart from the other: two layers for D_{4h}^{17} and one layer for D_{4h}^1 .

The number of phonon branches is specified by the number of atoms in the primitive cell. In each structure (Tl-1212 and Tl-2212) the number of phonon branches is determined by the number of atoms in one formula unit. The ions with positional symmetry C_{4v} or C_{2v} cause vibrations which are allowed in Raman scatter-

Table I.

	Lattice symmetry	Vibration symmetry at the Γ point in the Brillouin zone
$\text{Tl}_2\text{BaCuO}_6$	D_{4h}^{17}	$4A_{1g} + 4E_g + 6A_{2u} + B_{2u} + 7E_u$
$\text{Tl}_2\text{Ba}_2\text{CaCuO}_8$	D_{4h}^{17}	$6A_{1g} + B_{1g} + 7E_g + 7A_{2u} + B_{2u} + 8E_u$
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{CuO}_{10}$	D_{4h}^{17}	$7A_{1g} + B_{1g} + 8E_g + 9A_{2u} + 11E_u$
$\text{TlBa}_2\text{CaCuO}_7$	D_{4h}^1	$4A_{1g} + B_{1g} + 5E_g + 7A_{2u} + B_{2u} + 8E_u$
$\text{TlBa}_2\text{Ca}_2\text{CuO}_9$	D_{4h}^1	$5A_{1g} + B_{1g} + 6E_g + 9A_{2u} + 2B_{2u} + 11E_u$

ing: $(A_{1g} + E_g)$ and $(A_{1g} + B_{1g} + 2E_g)$, respectively. The ions with positional symmetry D_{4h} and D_{2h} are not seen in Raman scattering. The total decomposition of both structures with different n is given in Table I. Since the structures have an inversion center, only the even (g -type) modes are active in the Raman scattering.

4. The polarization Raman-scattering spectra of the single-crystals we have studied are shown in Figs. 2 and 3. The Raman-scattering spectra of the Tl-1212 sample reveal four lines with the frequencies 116, 146, 403, and 520 cm^{-1} (Fig. 2). The spectrum of the Tl-2212 sample reveals six clearly resolved lines (109, 132, 158, 410, 495, and 602 cm^{-1}) (Fig. 3). A scanning of the surface of the samples with a laser beam showed that there is a slight difference (no more than 3–4 cm^{-1}) in the frequencies of the lines. In Tl-1212 and Tl-2212 the integrated intensity of the lines in the zz polarization is approximately five times greater than that in the xx polarization. There is also a slight difference in the relative line intensities and the background level in the zz and xx polarizations (Figs. 2 and 3). All of the lines indicated above belong to the totally symmetric A_{1g} vibrations, since no such lines can be seen in a crossed polarization.

The number of A_{1g} modes observed in the Raman-scattering spectra of Tl-1212 and Tl-2212 crystals (four and six, respectively) coincides with the number of A_{1g}

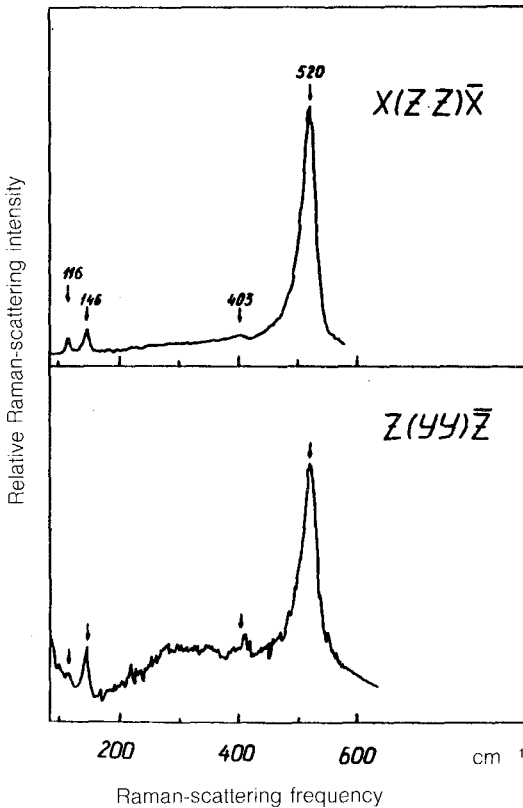


FIG. 2. Raman-scattering spectra of $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-x}$ single crystal.

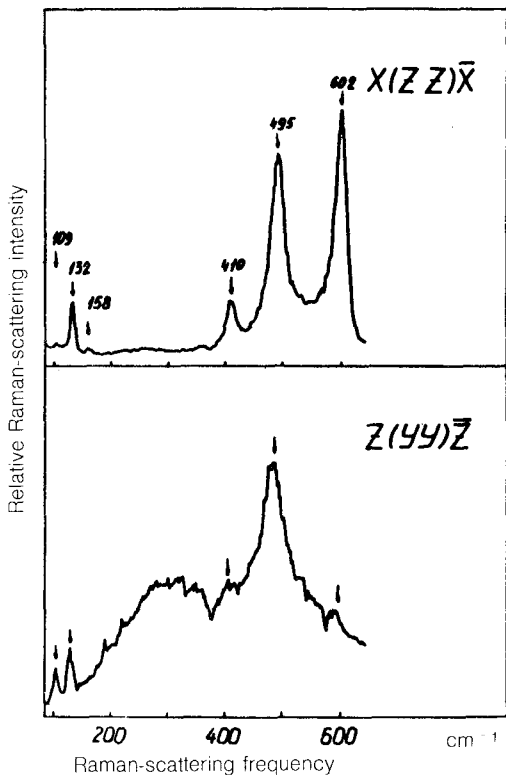


FIG. 3. Raman-scattering spectra of $\text{TlBa}_2\text{CaCu}_3\text{O}_{8-x}$ single crystal.

modes found from the group-theoretical analysis. To correctly classify the vibrations, we must take into account the difference in the masses of the vibrating ions and the difference in the coupling constants for the coupling between various ions. From this viewpoint, it is instructive to draw an analogy between the vibrations in Tl structures and the vibrations in similar structures $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and La_2CuO_4 .

5. A_{1g} vibrations of oxygen ions. The vibrations associated with the oxygen ions, the lightest ions, are expected to occur at frequencies above 300 cm^{-1} . The strongest lines in the zz polarization are identified with the valence vibrations of oxygen. The Tl-1212 structure has one such mode: the valence z vibrations of the O2 ion. The only high-frequency line (at 520 cm^{-1}) in the spectra belongs to this mode (Fig. 2). There are two such modes in Tl-2212: the O2 and O3 ion vibrations. Accordingly, the Raman-scattering spectra (Fig. 3) have two intense high-frequency lines. Taking the bond lengths into account,⁷⁻⁹ we can assign the 602-cm^{-1} line to the O3 vibrations and the 495-cm^{-1} line to the O2 vibrations. Each structure, moreover, has one more mode which is associated with oxygen and which corresponds to in-phase deformation vibrations of the O1 ions. We link with this mode the line at 403 cm^{-1} in the Tl-1212 spectra and the line at 410 cm^{-1} in the Tl-2212 spectra. The difference in the intensities of this mode for Tl-1212 and Tl-2212 (Figs. 2 and 3) may stem from the fact that the activity of the in-phase vibrations of the oxygen ions on the copper-oxygen plane in

the Raman scattering the Tl crystals occurs, as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Refs. 4 and 10), because of their connection with the valence vibrations of the bridge O2 oxygen. This activity strengthens as the difference between the frequencies of these vibrations decreases.

6. A_{1g} vibrations of the metallic ions. In Tl-1212 the z vibrations of Ba and Cu ions belong to these vibrations. We link with these vibrations the two low-frequency vibrations at 116 and 146 cm^{-1} which are observed in the Raman-scattering spectra of these crystals (Fig. 2). Working from the mass ratio of the Ba and Cu ions and the approximate equality of the frequencies of these modes and those measured in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Refs. 3–5), we assign the 116-cm^{-1} line to the A_{1g} vibrations of Ba and the 146-cm^{-1} line to the Cu vibrations.

In the transition from Tl-1212 to Tl-2212 the z vibrations of Tl is added to the vibrations allowed in the Raman scattering. An additional intense line at 130 cm^{-1} in this case appears in the low-frequency region of the Raman-scattering spectrum of Tl-2212 (Fig. 3). We assign this line to the Tl vibrations, since there is no reason to assume that the bond polarizabilities in Tl-1212 and Tl-2212, which determine the intensity of Raman-scattering of Ba and Cu, differ appreciably. The strong activity of the z vibrations of Tl ions in the Raman-scattering spectrum seems to be related to the specific features of the sp hybridization which forms the Tl-O bond. The 109-cm^{-1} and 158-cm^{-1} modes in Tl-2212 are assigned to the Ba and Cu vibrations, respectively. A decrease in the vibration frequency of Ba and an increase in the vibration frequency of Cu in the transition from Tl-1212 to Tl-2212 are in agreement with the change in the distance between the corresponding layers.⁷⁻⁹

7. The large background in the xx -polarization spectra apparently can be explained on the basis of electronic Raman scattering similar to that observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Refs. 4 and 5).

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