

Raman scattering in single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_x$ high-temperature superconductors

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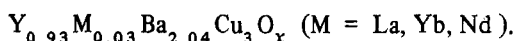
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Polarized spectra of the Raman scattering of tetragonal and orthorhombic single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_x$ have been recorded. The dependence of the frequency of the valence vibration of the Cu(1)-O(1)-Cu(2) bond on the lattice constant c has been established. The nature of the interatomic interaction is shown to depend on the lattice symmetry.

A study of the lattice dynamics of high-temperature superconductors is an exceedingly informative source of data on the structural features and the nature of the interatomic interactions. This information is important for reaching an understanding of the mechanism for the superconducting transition. The physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_x$ compounds are known to depend strongly on the oxygen concentration. In this letter we are reporting the first study of the polarized Raman spectra of several tetragonal and orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystals differing in the lattice constants and thus¹ the value of x .

We studied single-crystal samples from a single lot grown in a platinum crucible from a nonstoichiometric composition at 900–1000 °C. The initial crystals were of tetragonal symmetry ($a = 3.86 \text{ \AA}$, $c = 11.815 \text{ \AA}$) and went superconducting at $T_c = 40\text{--}60 \text{ K}$. Their chemical composition is described by



To obtain a semiconducting tetragonal crystal ($a = 3.86 \text{ \AA}$, $c = 11.864 \text{ \AA}$), we annealed the crystal in flowing helium at 700 °C. Orthorhombic crystals ($a = 3.825 \text{ \AA}$, $b = 3.89 \text{ \AA}$, $c = 11.7\text{--}11.74 \text{ \AA}$) were obtained by annealing the initial crystals in oxygen; they had a transition temperature $T_c = 93 \text{ K}$. The crystals were wafers (with linear dimensions of 1–4 mm and a thickness of 20–80 μm) with mirror-finish faces running parallel to the basal planes. The samples were oriented on an x-ray diffractometer.

The Raman spectra were excited by the beam from an argon laser (514.5 nm) and measured by a multichannel triple spectrometer² over the range 30–700 cm^{-1} with a resolution $\sim 5 \text{ cm}^{-1}$ in the various versions of the scattering geometry which were required in order to study all the components of the Raman-scattering tensor. In the Raman spectra of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystal, the vibrations $5A_g (xx, yy, zz) + 5B_{2g} (xz) + 5B_{3g} (yz)$ are active (the nonvanishing components of the Raman tensor are given in parentheses). In the tetragonal crystal (with $x = 6$), they correspond to the vibrations $4A_{1g} (xx + yy, zz) + B_{1g} (xx - yy) + 5E_g (xz, yz)$.

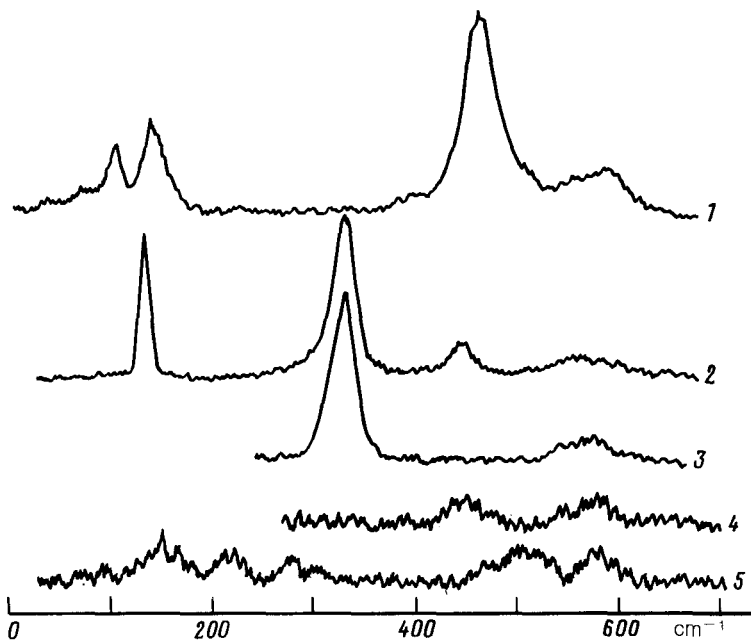


FIG. 1. Polarized Raman spectra of a tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystal for versions of the scattering geometry determined by the following tensor components: 1— zz (A_{1g} vibrations are active); 2— xx ($A_{1g} + B_{1g}$); 3— $x'y'$ (B_{1g}); 4— $x'x'$ (A_{1g}); 5— xz (E_g). The x' and y' axes are rotated 45° from the x and y axes.

Figure 1 shows polarized Raman spectra of the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystal. The bands seen in these spectra have polarization properties which agree with the tetragonal symmetry of the crystal.³ In the spectra we observe four bands of class A_{1g} , with frequencies of 120, 150, 408, and 470 cm^{-1} , detected in the zz geometry; a single band of class B_{1g} , with a frequency of 339 cm^{-1} ; and five bands of symmetry E_g , with frequencies of 152, 212, 275, 506, and 588 cm^{-1} . Furthermore, in the zz geometry we observed a broad band with a frequency of 595 cm^{-1} , whose intensity depended on the quality of the crystal and the conditions under which the spectrum was excited. In the xx geometry we observed bands with frequencies of 140, 450, and 570 cm^{-1} , which were not present in the zz geometry. Since the A_{1g} vibrations of the ideal lattice are axial, we assigned these bands to planar vibrations of the Cu(1) and O(4) atoms, which form chains along the a axis. Their appearance in the Raman spectra can be attributed to changes in the symmetry of the positions of the Cu(1) and O(4) atoms due to the defective state of the crystalline structure.

On the whole, the Raman spectra of the orthorhombic crystals are similar to those of the tetragonal crystals, aside from a few distinctive features. In the first place, the spectra of the orthorhombic crystals generally do not have the broad band at 595 cm^{-1} . In the xx geometry, we also observe some additional bands (including one characteristic of orthorhombic crystals, at 232 cm^{-1}), but their intensities in the

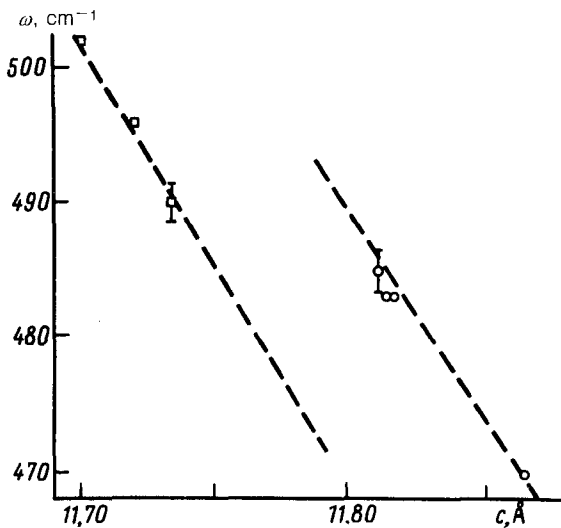


FIG. 2. Frequency of the completely symmetric axial valence vibration of Cu(1)-O(1)-Cu(2) bond in a $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystal as a function of the parameter c . \circ —Tetragonal crystals; \square —orthorhombic crystals. The dashed lines show relation (1) for $n = 3$ and 2.

highest-quality samples were considerably lower than those in the spectra of the tetragonal crystals. This result confirms the interpretation offered above.

An important distinction between the Raman spectra of the orthorhombic and tetragonal crystals is the energy shift of several of the bands. The behavior of primary interest here is that of the most intense band in the spectrum, near 500 cm^{-1} , which is probably associated with a completely symmetric axial valence vibration of the Cu(1)-O(1)-Cu(2) bond.⁴⁻⁶ A frequency shift of this band had been observed previously in the Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ceramics⁶ at certain values of x , and it had been explained at a qualitative level in terms of a decrease in the dimensions of the unit cell as the structure became saturated with oxygen. We measured the frequency of this mode for several tetragonal and orthorhombic crystals differing in lattice constants and thus in the value of x (Fig. 2). According to x-ray structural data, for both the tetragonal crystals and the orthorhombic crystals the parameter values in the basal plane are approximately the same at different values of x ; the only substantial change is in the lattice constant c . According to Ref. 3, the changes in the parameter c are determined essentially entirely by the change in the distance (r) between the copper atom Cu(2) of the CuO_2 layer and the oxygen O(1), which binds the CuO_2 layer with the Cu(1)-O(4) chain (i.e., $\Delta r \approx \Delta c/2$). In the case of a variation in only a single bond in the lattice, the frequency ω and the length of the changing bond should be related by

$$\omega r^n = A, \quad (1)$$

where the constant A and the exponent n depend on the interatomic potential. It can be seen from Fig. 2 that the frequencies for the tetragonal and orthorhombic crystals form two different sets, which can be described by relations (1) with approximately the same values of n but different values of the constant A . This result apparently

implies a change in the nature of the interaction between the copper and oxygen atoms (an abrupt change in the corresponding strength constant). This change may be related to a change in the state of the copper atoms at the transition from the tetragonal to the orthorhombic crystal.

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