

## Raman scattering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (theory)

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The Raman scattering spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are analyzed at a qualitative level. Arguments are presented to support the suggestion that bridges connecting planes and chains play a definite role in the formation of the predominant polarization of the oxygen  $A_g$  bands along the  $c$  axis.

The Raman scattering of light by crystals of the orthorhombic ( $D_{2h}^1$ ) and tetragonal ( $D_{4h}^1$ ) modifications of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has now been studied experimentally. Measurements carried out with ceramics<sup>1-3</sup> have yielded the frequencies of the oscillations and a tentative identification of these oscillations. Experiments with single crystals<sup>4-7</sup> have made it possible to study the polarization of the scattering and to construct an essentially complete classification of the oscillations. So far, there has been no theoretical work in this field. A quantitative theory of the Raman scattering should be based on numerical calculations, which are extremely laborious since the expression for the polarizability contains tens of electron bands as intermediate states. In such a theory, the physical mechanisms would unavoidably be masked. There is accordingly a need to analyze those qualitative aspects of the Raman spectra (e.g., their polarization), which should be generated by a pronounced anisotropy of the lattice but which do not follow from group-theory limitations. This is the purpose of the present letter. In particular, we reach the conclusion that the spectrum of the one-phonon ( $1ph$ )

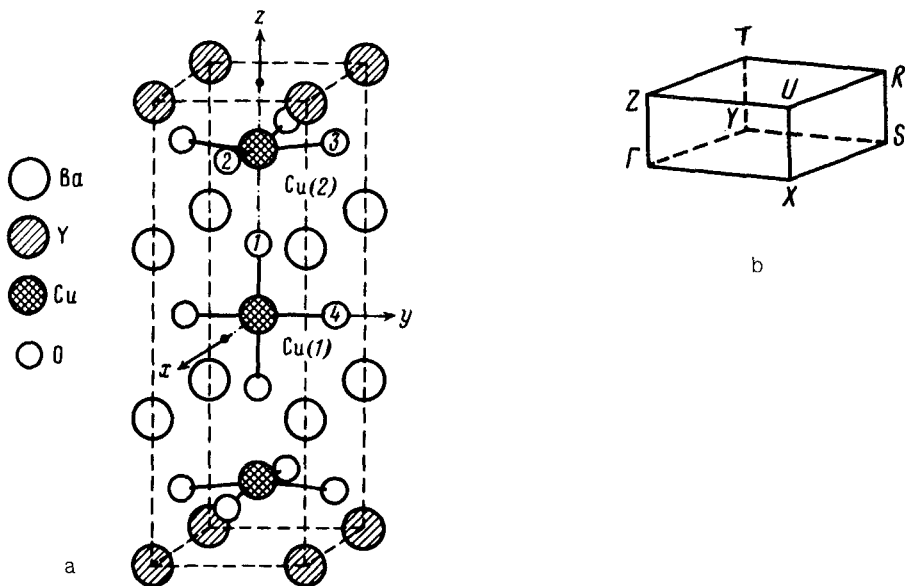


FIG. 1. a—Structure of the unit cell according to Refs. 8 and 9; b—shape of the Brillouin zone ( $\Gamma$  is the center of the zone) ( $z||c$ ).

Raman scattering has a large component corresponding to O1 bridge oxygen (Fig. 1a).

Let us examine the oscillations of O ions, which interact most strongly with the charge carriers. Oxygen belongs to nearly plane Cu(2)–O2–O3 layers with a slight ripple (“dimpled layers”) and Cu(1)–(O1)<sub>2</sub>–O4 chains with a planar-square coordination (in the bc plane). Results calculated on the band spectrum are given in Ref. 10 and, in particular detail, in Refs. 11 and 12. The latter studies were carried out for the structure in Fig. 1a. The valence states are formed through a hybridization of Cu–3*d* and O–2*p* orbitals. Near the spectral maximum (points S and R in Fig. 1b) there are three closely spaced bands: Two of them belong to planes, and one to chains. In the case  $\delta = 0$ , the tops of these bands are above the Fermi level  $E_F$  by an amount  $\approx 2$  eV. This separation decreases with increasing  $\delta$ . The spectrum of the planes corresponds to essentially no dispersion along  $z$ , while that of the chains corresponds to essentially no dispersion along  $z$  and  $x$ . It can be seen from the partial state densities that the energy spectra of the planes and chains are nearly independent. At  $E > E_F$ , they resonate with each other at the face SXUR. It follows from the splitting  $\sim 0.1$ – $0.2$  eV, caused by the interaction of planes (see Fig. 1 in Ref. 12), that the transfer integral for a “long” Cu(2)–O1 bond of a bridge is  $U \gtrsim 0.1$  eV. For short *p**d* $\sigma$  bonds, the transfer integral is  $U \sim 1$  eV.

Resonant processes make a significant contribution to the Raman scattering, as follows from the frequency dependence of the cross section  $\sigma(\omega)$  for some of the bands.<sup>7</sup> Among these processes are transitions between states  $i$  with  $E < E_F$  and  $m$  with  $E > E_F$  in valence bands. In view of the significant width of the levels, we use the very

simple expression

$$\sigma_{\alpha\beta}(\omega) \propto (\partial/\partial Q) |P_{\alpha\beta}(\omega)|^2, \quad (1)$$

where

$$P_{\alpha\beta}(\omega) = \sum_{im} \langle i | M_\alpha | m \rangle \langle m | M_\beta | i \rangle / (\omega_{mi}^2 - \omega^2) \quad (2)$$

is the electron polarizability tensor,  $Q$  is the normal coordinate of a phonon,  $\alpha$  and  $\beta$  are Cartesian coordinates, and  $\mathbf{M}$  is the dipole moment. We will consider separately the chain and plane components of  $\sigma(\omega)$ .

**1. Copper-oxygen chains.** Here we set  $\delta = 0$  (since the filling of O4 positions decreases at  $\delta > 0$ , and the chains are broken up). The symmetry  $D_{2h}$  allows oxygen vibrations  $A_g$ ,  $B_{2g}$ , and  $B_{3g}$ , which are associated with O1, in the Raman scattering. Experimentally, we find that the phonon  $A_g$  is dominant ( $\approx 500 \text{ cm}^{-1}$ ) in the  $zz$  polarization. The corresponding quantity  $Q_A$  is an out-of-phase displacement of two O1 ions. We restrict the discussion below to this vibration.

In the strong-coupling approximation, the matrix elements of the operator  $M_\alpha$  are nonzero only if an electron is transferred between O and Cu ions. In the case  $E \gtrsim E_F$  ( $m$  states), the  $d_{y^2-z^2}$  orbitals<sup>11</sup> and functions which are hybridized with them and which are even under reflection in the  $z=0$  plane by virtue of the exact  $\sigma_h$  symmetry are predominant. A large value of  $\langle i | M_\alpha | m \rangle$  may arise because of  $\sigma_h$ -odd O1- $p_z$  states. They do not hybridize with Cu if their energy lies near  $E_F$ . According to calculations, a contribution of this sort to the partial spectral density of O1, which corresponds to a dip in the partial density of Cu(1), actually exists (Fig. 4 in Ref. 11). It lies 1-2 eV below  $E_F$  (in approximately the same position as the maximum of the density of O levels found experimentally<sup>13</sup>). The matrix elements corresponding to resonant transitions between these  $i$  and  $m$  states are large, since they contain an overlap of the  $\sigma$  type between Cu(1)- $d_{y^2-z^2}$  and O1- $p_z$  functions. Their derivatives with respect to  $Q_A$  are also large. Consequently,  $P_{zz}(\omega, A_g)$  is large. In contrast,  $P_{xx}(\omega, A_g)$  and  $P_{yy}(\omega, A_g)$  are small because of the slight overlap of the Cu(1)- $d_{y^2-z^2}$  orbitals with O1- $p_x$  and O1- $p_y$ . The difference is intensified for cross sections  $\sigma \propto P^2$ .

**2. Copper-oxygen planes.** Analyzing planes is a more complicated matter. With  $\delta = 0$ , the symmetry of an individual plane is  $C_{2v}$ , but if we ignore (1) the dimples, (2) the axial field of Y and Ba, and (3) the effect of the Cu(2)-O1 bridges, we find that the symmetry is raised to  $D_{2h}$ . The  $1ph$  Raman scattering is forbidden in all polarizations. Consequently, it arises as a result of the presence of these perturbations (and also defects). The effect is to make it very difficult to identify the dominant mechanism for the Raman scattering. The problem is not simplified when the symmetry is raised to  $D_{4h}$ , as it can be in the case  $\delta = 1$ , and as it apparently also could be in the case  $\delta = 0$ , since the lattice constants satisfy  $b \approx a$ .

In the Raman spectrum we observe an intense band,  $B_{1g}$  ( $\approx 335 \text{ cm}^{-1}$ ), which is polarized in the  $x,y$  plane in  $D_{4h}$ , and a band  $A_g$  ( $\approx 435 \text{ cm}^{-1}$ ), with a predominant  $zz$  polarization (in  $D_{2h}$  and  $D_{4h}$ ). For the reason stated above, it is difficult to draw a

definite conclusion regarding the mechanism for the polarization of the  $A_g$  band. However, physical considerations do suggest an interesting possibility. A distinctive feature of this "oxygen"  $A_g$  vibration is that it also involves Cu(2) ions, which vibrate along  $z$  and which modulate the length of the Cu(2)–O1  $\sigma$  bond. The electron density at it is substantial. This conclusion follows from the significant value  $U \gtrsim 0.1$  eV under conditions which are close to a plane-chain resonance, with a pronounced mixing of  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  orbitals, according to Figs. 2 and 4 in Ref. 10. This conclusion also follows from the difference between the strength constants of the Cu(2)–O1 and Cu(1)–O1, which is only a factor of three.<sup>1</sup> In this approach, the large polarization ratio for the planar or chain  $A_g$  band is of common origin: It stems from the O1 bridge oxygen.

The high ratio of the intensities of  $B_{1g}$  and  $A_g$  in the  $Lz$  polarization can be related to the circumstance that the O2 and O3 ions are vibrating out of phase in  $B_{1g}$  [and Cu(2) is at rest], while they are vibrating in phase in  $A_g$ . In a vibration of this sort of the O ions in the double layer between Y and Ba, the change in the electron amplitudes at them,  $\Delta b$ , is larger in  $B_{1g}$  than in  $A_g$ . A rough estimate yields  $(\Delta b/Q)_B \sim 2(\Delta b/Q)_A$ . From the ratio of the masses of the normal modes we find  $Q_B \approx 2Q_A$ . According to (1) and (2), we then have

$$\sigma_{Lz}(B_{1g}) / \sigma_{Lz}(A_g) \sim (1/Q_B)(\Delta b)_B^2 / (1/Q_A)(\Delta b)_A^2 \sim 10. \quad (3)$$

Although this estimate is extremely crude, there is the hope that it correctly reflects the primary cause of the high intensity of the  $B_{1g}$  vibration.

**3. Two-phonon (2ph) spectra.** In the theory of the electron-phonon interaction in  $YBa_2Cu_3O_{7-\delta}$ , the special role played by phonons of the points  $S$  and  $R$ , in particular, the "breathing" mode, is usually emphasized. These phonons are manifested in the  $2ph$  Raman spectra, which, in contrast with the  $1ph$  spectra, are allowed even in the model of a planar Cu(2)–O2–O3 network. The theory of the  $2ph$  Raman spectra is thus in a sense simpler than the theory of the  $1ph$  Raman spectra. The higher harmonics or constituent frequencies of phonon points  $S$  and  $R$  are present in all polarizations, in particular,  $B_{1g}$ . Lyons *et al.*<sup>14</sup> have reported observing  $2ph$  Raman spectra, primarily in  $La_2CuO_4$ .

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