Nature of resonant behavior of Raman scattering by phonons in $YBa_2Cu_3O_{7-x}$

O. V. Misochko and E. Ya. Sherman

Institute of Solid State Physics, Academy of Sciences of the USSR;
L. D. Landau Institute of Theoretical Physics, Academy of Sciences of the USSR
(Submitted 30 July 1990)
Zh. Eksp. Teor. Fiz. **99**, 330–335 (January 1991)

The resonant behavior of the intensity of the Raman scattering of light by completely symmetric phonons in $YBa_2Cu_3O_{7-x}$ has been studied for various polarizations of the incident and scattered light. The scattering of phonons at 500 and 435 cm^{-1} occurs in a two-band fashion and is determined by the diagonal matrix elements of the electron-phonon interaction. The initial and final electron states which basically determine the Raman polarizability are identified. The shape of the resonance curve is explained on this basis.

Research on the resonance properties of the Raman scattering of light by completely symmetric phonon modes in $YBa_2Cu_3O_{7-x}$ ($x<0.1$) has revealed[1,2] that the frequency dependence of the intensity of the scattering in the zz polarization, $I_{zz}(\omega)$, is essentially identical for the phonons at 435 and 500 cm^{-1}. This aspect of the resonant dependence was explained in Ref. 3 under the assumption that a displacement of the bridge oxygen ion O1 is important in the 435-cm^{-1} mode, in which in-phase z displacements of oxygen ions of the CuO_2 plane are dominant.[4] A second distinguishing feature of the resonance curves of $I_{zz}(\omega)$, which has yet to be adequately interpreted, is the presence of two maxima, a first one at 2.5 eV (Ref. 1) or 2.35 eV (Ref. 2) and a second at >2.7 eV (Refs. 1 and 2). Since discrete lines of gas lasers were used in the experiments, and the maximum energy of the exciting photon did not exceed 2.7 eV, it was not possible to accurately determine the position of the high-frequency maximum.

In the present paper we are reporting a study of the reason for the appearance of two maxima on the resonance curve of the intensity of the scattering by completely symmetric phonons, $I_{zz}(\omega)$. We will discuss certain differences in the shape of the excitation spectra observed in Refs. 1 and 2. For a more thorough analysis, we have carried out some experiments to supplement those of Ref. 1. These new experiments made it possible to slightly expand the range of excitation energies and to construct resonance curves for scattering by completely symmetric phonons in the basal plane. The experimental apparatus and procedure are described in detail in Ref. 1.

Figure 1 shows the resulting resonance curves for the zz polarization, while Fig. 2 shows them for the case in which the electric vector lies in the basal plane. In contrast with Refs. 1 and 2, we used values of the integral scattering intensity normalized to the integral intensity of the scattering by the 240-cm^{-1} phonon in the BaF_2 crystal.

To describe the Raman scattering, we work from the model proposed in Ref. 5 to explain the large polarization ratio $I_{zz}/I_{xx} \gg 1$ for the mode of the bridge oxygen, O1, in $YBa_2Cu_3O_{7-x}$. The explanation for this ratio is that σ_h is chosen as the initial electronic state of the system. This state is an odd combination of p_z orbitals of bridge oxygen (O1) ions (Fig. 3). This combination forms a slightly dispersive band, since it does not hybridize with the Cu1 $d_{y^2-z^2}$, $d_{3z^2-r^2}$ orbitals (because of the different parity). With the other Cu1 orbitals, it forms π bonds. Here and below, we are using a coordinate system in which the y axis is directed along the Cu1–O4 chains. The matrix element $\hat{z}$, which is dominated by transitions from the initial state to the $d_{y^2-z^2}$, $d_{3z^2-r^2}$ orbitals of Cu1, is large, since it contains a σ overlap of the initial and final states. The matrix elements $\hat{x}$ and $\hat{y}$ are small, since the overlap is of the π type in their case.

To estimate the Raman scattering intensity, we take the approach pointed out in Ref. 6. The scattering of the intensity in the $\alpha\alpha$ polarization is given by

$$I_{\alpha\alpha} \propto \omega^4 f(\delta) \sum \langle Q_\Omega^2 \rangle \left| \frac{\partial}{\partial Q} P_{\alpha\alpha} \right|^2, \qquad (1)$$

where ω and Ω are the photon and phonon frequencies, respectively, $f(\delta)$ is some function of the penetration depth δ, Q is the normal coordinate of the phonon, and $P_{\alpha\alpha}$ is the polarizability tensor. The ω^4 dependence can be omitted from an analysis of the experimental data because of the specified normalization of the intensity.

We assume that $P_{\alpha\alpha}$ and the penetration depth δ are determined by all possible transitions, and we assume that the scattering in the zz polarization is dominated by a displacement of the O1 bridge oxygen ions. According to the experimental data of Ref. 7, the depth δ depends only weakly on ω in this frequency region. We will ignore that dependence, assuming that it is not responsible for the shape of the resonance curve. We link the shape of the resonance scattering profile with the properties of the electronic structure of $YBa_2Cu_3O_{7-x}$. In the analysis we start from the results of one-electron calculations of the band structure,[8] according to which the current carriers—holes—fill part of the Brillouin zone with a vertex at the point Y ($k_y = \pm\pi$; we express the wave vector k in reciprocal-lattice constants, and we assume $k \| y$). The derivative of the polarizability tensor with respect to the displacement of the O1 ion consists of terms of two types. The first type is related to a dependence of the matrix elements on the O1 displacements, while the second is related to a corresponding dependence of the band energies. The second terms differ from the first in that they are of a more resonant nature, since they contain an additional power of the energy denominator.

Since experiments reveal a strong dependence of the scattering intensity on the energy of the exciting photon, and since the shape of the resonance curve differs from that of the absorption-coefficient spectrum,[7] one might suggest that

 0038-5646/91/010185-04$03.00

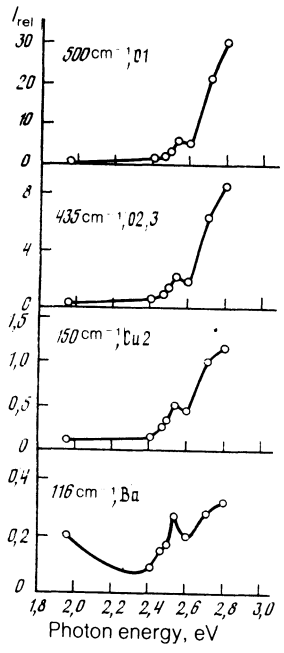

FIG. 1. Resonance curve of the integral intensity of light scattering by completely symmetric phonons in $YBa_2Cu_3O_{7-x}$ for the zz polarization. The curve is normalized to the integral intensity of the 240-cm^{-1} phonon in the BaF_2 crystal. The phonon frequency and the ion which dominates the normal coordinate of the corresponding phonon are shown with each curve.

the second of these contributions is predominant. This interpretation would mean that the scattering in the zz polarization for the 500-cm^{-1} mode occurs primarily in a two-band manner and is determined by the diagonal terms of the electron-phonon interaction. We can distinguish a resonant contribution to the polarizability tensor, which is the strongest function of the displacements of the O1 ion. In our two-band approximation, it is given by

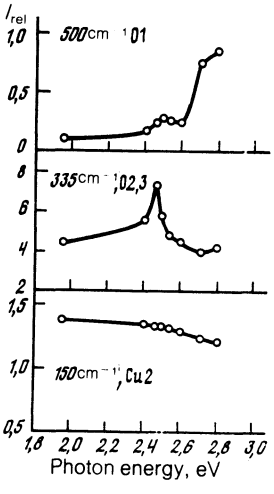

FIG. 2. Resonance curves of the integral intensity of light scattering by completely symmetric phonons in twinned $YBa_2Cu_3O_{7-x}$, for scattering in the basal plane. The curves are normalized to the integral intensity of the 240-cm^{-1} phonon in the BaF_2 crystal. The phonon frequency and the ion which dominates the normal coordinate of the corresponding phonon are shown with each curve.

$$P_{zz} \propto \int dk\, |M_z(k)|^2/(\omega_{if}(k)-\omega+i/\tau). \qquad (2)$$

Here $\omega_{if}(k)$ is the difference between the energies of the states (the final state f and the initial state i) which we have selected, and ω is the energy of the photon involved in the scattering. The interband matrix element M_z here depends on the wave vector k by virtue of the k dependence of the wave functions, but we will ignore that dependence in the present paper. We add an imaginary frequency i/τ in order to deal with the finite width of the intermediate state in the energy denominator (we assume $\Omega\tau \ll 1$).

Since the polarizability tensor is formed by transitions between occupied and vacant states, the integration in (2) goes over that part of the Brillouin zone which satisfies the condition $E_f(k) > E_F$, where $E_f(k)$ is the energy of the carriers in the upper band (with a large contribution to the density of states from the Cu1 $d_{y^2-z^2}$ and O4 p_y orbitals). This upper band is intersected by the Fermi level. Consequently, the dependence $\partial P_{zz}(\omega)/\partial Q$ should have singularities at $\omega \approx E_f(k_F) - E_i(k_F)$ (case 1) or $\omega \approx E_f(k=\pi) - E_i(k=\pi)$ (case 2). With the first of these singularities we link the first of the maxima observed experimentally on the $I_{zz}(\omega)$ curve, and with the second we link the sharp increase in the intensity at energies above 2.5 eV. Introducing the deviation from resonance $\Delta = |E_f(k) - E_i(k) - \omega|$ in case 1, which corresponds to a resonance on the Fermi surface for the zz polarization, we find

$$I \propto \begin{cases} 1/(v_F\Delta)^2, & \tau\Delta \gg 1, \\ (\tau/v_F)^2, & \tau\Delta \ll 1. \end{cases} \qquad (3)$$

Here v_F is the Fermi velocity. For case 2, which corresponds to a resonance at the top of the band, we have, correspondingly,

$$I \propto \begin{cases} m/\Delta^3, & \tau\Delta \gg 1, \\ m\tau^3, & \tau\Delta \ll 1. \end{cases} \qquad (4)$$

Here m is the effective carrier mass in the band. The resonance in the second case should thus be stronger than that in the first, because of the higher power of Δ in the denominator. The difference between the resonance energies in this case is E_F, and the steepness of the maxima depends strongly on the Fermi velocity v_F. This fact may be pertinent to the difference between the shapes of the resonance curves found in different experiments. In Ref. 2, for example, the first

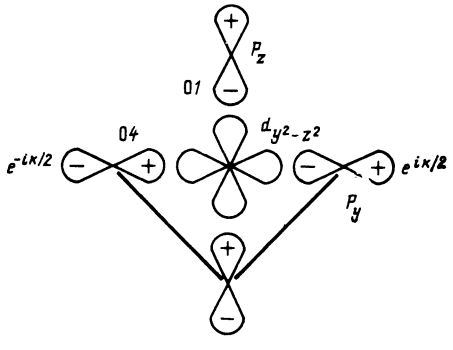

FIG. 3. Positions of orbitals in the Cu1–O4–O1 complex.

maximum on the resonance curve was more rounded and occurred at an excitation energy lower than in our own experiments (Fig. 1). The explanation may lie in a difference in the oxygen contents in the test samples and in a shift of the Fermi level with the extent of doping. As the Fermi level rises, the velocity v_F decreases, and the resonance peak should become steeper. If nonlinear processes[9] are involved in the scattering, the position of the Fermi level may also depend on the power density of the exciting light; this situation should affect the shape of the resonance curve.

The observed similarity of the frequency dependence at excitation energies > 2.3 eV for (on the one hand) the high-frequency phonons at 500 and 435 cm^{-1} and (on the other) that for the low-frequency phonon at 150 cm^{-1}, which is dominated by a displacement of the Cu2 ion, can be attributed to the participation of the O1 ion in this vibrational mode. The small contribution of the displacement of this ion to the normal vector of the 150-cm^{-1} mode is amplified substantially by the polarizability of the Cu1–O1 bond, which is large in this frequency region.

We turn now to the scattering by the 500-cm^{-1} phonon in the case in which the vector of the exciting and scattered light fields lies in the *ab* basal plane. Since there are no experimental data on the resonant dependence of the scattering of light for single-domain (untwinned) $YBa_2Cu_3O_{7-x}$ crystals at this point, we restrict the discussion to the case in which the electric vector of the optical field is directed along the chains, under the assumption that this is the dominant part of the scattering. Evidence in favor of this assumption comes from the fact that the experimental Raman spectra which we found for the basal plane of a twinned $YBa_2Cu_3O_{7-x}$ crystal in the case in which the electric vector of the exciting light is in the basal plane contains the 585-cm^{-1} mode. This mode corresponds to vibrations of chain oxygen and is manifested in the Raman spectrum because of a defectiveness of the chains only in the *yy* polarization.[4]

In contrast with the *zz* polarization, in which it is simple to see the predominant contribution to the scattering, different transitions contribute in the case of the *yy* polarization (we wish to stress that the mechanisms for the scattering by phonons with frequencies of 435 and 500 cm^{-1} are different). A displacement of O1, for example, perturbs the energy bands and the wave functions of the Cu1–O4 chain, in which the matrix element $\hat{y}$ is large. This contribution is apparently not resonant in the frequency region of interest. If transitions to the O4 p_y orbital play an important role in scattering in the *xy* basal plane, the scattering efficiency in the *yy* polarization should be higher than that in the *xx* polarization. It is possible that this effect was observed in Ref. 10.

The fact that the intensity of the scattering by this phonon in the basic polarization exhibits features similar to those in the *yy* polarization (Figs. 1 and 2) suggests that transitions between bands with energies close to those which we have been discussing are also contributing substantially to I_{ab}. As the initial state we adopt σ_h: an even combination of O1 p_z orbitals with an energy close to the E_i value which we selected previously. The final state is the same as in the discussion of $I_{zz}(\omega)$. Transitions between orbitals of O4 and O1 ions dominate I_{yy} in this case; these transitions are described by π matrix elements. Since the transitions go between the orbitals of ions belonging to different unit cells, which are coupled by factors e^{ik}, the quantity $M_y \propto \cos(k/2)$ vanishes at the boundary of the Brillouin zone. In this case we have $I_{yy}(\tau\Delta) \propto I_{zz} \cos^4(k_F/2)(M_y/M_z)^4$ for the resonance on the Fermi surface, where M_y are the matrix elements taken between the wave functions of the O1 and O4 ions, and M_z are matrix elements taken between the wave functions of the O1 and Cu1 ions. For a resonance at the top of the band we find

$$I_{yy} \propto \begin{cases} m/\Delta, & \tau\Delta \gg 1, \\ m\tau, & \tau\Delta \ll 1. \end{cases} \qquad (5)$$

Because of the factor $\cos(k/2)$, the second resonance peak in the *yy* polarization is thus less sharp than for the transitions discussed for the *zz* polarization. The asymmetry of the first peak for this polarization (the faster decay at large ω) which was observed in Ref. 2 can be explained on the basis that with increasing excitation frequency the resonance is reached at larger values of k and thus smaller values of $\cos(k/2)$.

For the phonon at 335 cm^{-1}, which corresponds to out-of-phase motions of oxygen ions in the CuO_2 plane,[5] the resonance curve is of a very different nature. It has a single maximum, near 2.45 eV (Fig. 2). This result is evidence that the scattering by this phonon is dominated by other energy bands, which apparently form on orbitals of ions of the CuO_2 plane. Another distinctive feature is the excitation profile for the phonon at 116 cm^{-1}, which is dominated by a displacement of a Ba ion.

We believe that it would be very worthwhile to study the shape of the resonance curves as a function of the oxygen deficiency in the superconducting phase and the effect of hydrostatic compression in order to reach an understanding of the mechanisms for the inelastic scattering of light and to provide information on the band structure of the high T_c superconductors. Hydrostatic compression experiments would offer a way to continuously and controllably change the energy parameters of this system.

In summary, it has been shown in this study that the shape of the resonance curve of the intensity of Raman scattering by completely symmetric phonons in $YBa_2Cu_3O_{7-x}$ can be explained on the basis that the scattering occurs in a two-band fashion. The first maximum on the resonance profile in this case is associated with transitions to the Fermi surface, and the second with transitions to the top of the band.

We wish to thank V. B. Timofeev for interest in this study and useful discussions. We also thank A. V. Lomsadze for assistance in analyzing the experimental data.

(*Note added in proof 11 October 1990*). After this paper had already been prepared for publication, we learned of Ref. 11, which also reported a study of the relationship between resonant scattering and the properties of the electronic subsystem. The results of Ref. 11 agree qualitatively with our own. It is difficult to make a more accurate comparison at the moment because of the particular way in which the experimental data were analyzed in Ref. 11. One of the present authors (O. V. M.) wishes to thank E. T. Heyen and C. Thomsen for a discussion of questions taken up in Ref. 11.

[1] O. V. Misochko, Fiz. Tverd. Tela (Leningrad) **31** (11), 280 (1989) [Sov. Phys. Solid State **31**, 1998 (1989)].
[2] E. T. Heyen, R. Liu, C. Thomsen, and M. Cardona in *Phonons-89* (ed. S. Hunklinger, W. Ludwig, and G. Weiss), World Scientific, 1990, p. 113.
[3] O. V. Misochko, E. I. Rashba, E. Ya. Sherman, and V. B. Timofeev in *Progress in High Temperature Superconductivity*, Vol. 21 (ed. N. N. Bogolubov, V. L. Aksenov, and N. M. Plakida), World Scientific, 1989, p. 438; O. V. Misochko, E. I. Rashba, E. Ya. Sherman, and V. B. Timofeev, Phys. Rep. 1990. Agranovich Festschrift volume.
[4] V. D. Kulakovskiĭ, O. V. Misochko, and V. B. Timofeev, Fiz. Tverd. Tela (Leningrad) **31**, 220 (1989) [Sov. Phys. Solid State **31**, 1599 (1989)].
[5] É. I. Rashba and E. Ya. Sherman, Sverkhprovodimost' (KIAE) **3**, 60 (1989) [*sic*]; É. I. Rashba and E. Ya. Sherman, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 404 (1988) [JETP Lett. **47**, 482 (1988)].
[6] D. L. Mills, A. A. Maradudin, and E. Burstein, Ann. Phys. (NY) **56**, 504 (1970).
[7] M. Carriga, J. Humliček, J. Barth *et al.*, J. Opt. Soc. Am. B **6**, 470 (1989).
[8] J. Yu, S. Massida, and A. J. Freeman, Phys. Lett. A **122**, 203 (1987).
[9] V. N. Denisov, B. N. Mavrin, V. B. Podobedov *et al.*, Phys. Lett. A **130**, 411 (1988).
[10] C. Thomsen, M. Cardona, B. Gegenheimer *et al.*, Phys. Rev. B **37**, 9860 (1988).
[11] E. T. Heyen, S. N. Rashkeev, I. I. Mazin *et al.*, Preprint, Max Planck Institut, 1990.

Translated by D. Parsons