

# Effect of oxygen concentration on the Raman spectra of $\text{YBa}_2\text{Cu}_3\text{O}_x$

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An anisotropic scattering has been observed in the basal plane of an orthorhombic crystal for vibrations associated with a filling of copper-oxygen chains. These vibrations exhibit an anomalous concentration, resonant, and temperature behavior.

The differences which exist among the Raman spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Refs. 1–4) can be attributed to different oxygen concentrations in the samples. Furthermore, the absence of polarization data, or gaps in the data which have been reported, leave uncertainties regarding the identification of the vibrations. In this letter we report measurements of the Raman spectra in polycrystalline materials with a controlled oxygen concentration and also in tetragonal and orthorhombic single crystals. We have studied the symmetry of the excitations in the phonon and electron parts of the spectrum.

The method used to synthesize the ceramics and the single crystals is described in Refs. 5 and 6. The crystals which were grown, with  $T_c \sim 60\text{--}70\text{ K}$  ( $c = 11.705\text{ \AA}$ ), were rectangular wafers with dimensions of  $1 \times 1 \times 0.03\text{ mm}$ , with edges running parallel to the  $a$  and  $b$  axes. Tetragonal crystals ( $c = 11.80\text{ \AA}$ ) were synthesized by annealing in vacuum. For the measurements we used mechanically polished surfaces of the single crystals and also natural facets and cleaved surfaces of the single crystals with grazing incidence ( $\sim 70^\circ$ ) of the beam from a 100-mW argon laser. The spectra were recorded on a DFS-24 spectrometer fitted with a photon counting system.

In the spectra of the ceramic we can distinguish a group of four lines (141–153, 339, 454–439, and 470–508  $\text{cm}^{-1}$ ), which are observed in all nine of the compositions studied ( $x = 6.05\text{--}6.94$ ). As  $x$  is increased, the frequencies of the lines at 141 and 470  $\text{cm}^{-1}$  are observed to increase, while the band at 454  $\text{cm}^{-1}$  softens. In addition, there is a significant decrease in the intensity of the lines at 141 and 339  $\text{cm}^{-1}$ . For the second group, the lines typically appear in a limited region of compositions for the orthorhombic phase. For example, the line at 115  $\text{cm}^{-1}$  is found in the spectra only at  $x \geq 6.61$ ; its intensity increases with increasing  $x$ . The rather narrow band ( $\sim 10\text{--}12\text{ cm}^{-1}$ ) at the frequency 230  $\text{cm}^{-1}$  is clearly observed in the interval  $6.61 \leq x \leq 6.79$ ; at  $x = 6.88$  its intensity has fallen off substantially, and it is not seen in the spectrum at  $x = 6.94$ . In this composition we see only a slight structural feature at 212  $\text{cm}^{-1}$ . In roughly the same region, the intensities of the bands at 585 and 630  $\text{cm}^{-1}$  increase.

The scattering spectra of polarized light in the single crystals provide evidence that all of the observed lines correspond to  $A_{1g}$  and  $B_{1g}$  vibrations for the tetragonal phase ( $A_g$  for the orthorhombic phase). The  $ZZ$  component of the crystals annealed in vacuum ( $x \sim 6.2$ ) contains lines 470 and 590  $\text{cm}^{-1}$ ; in the superconducting crystals

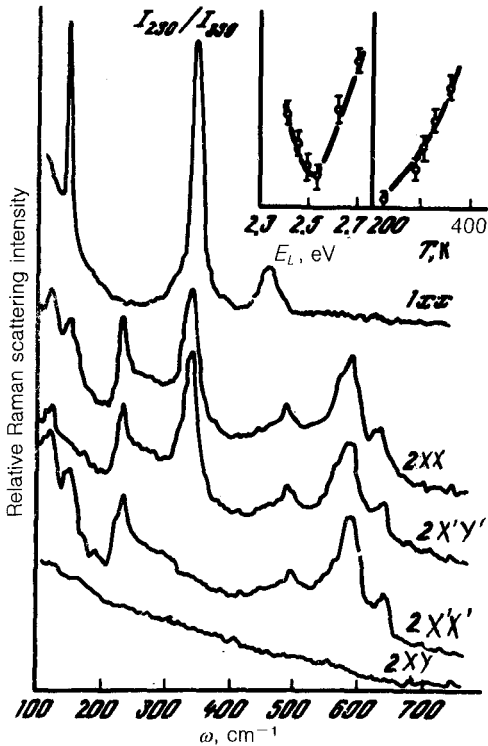


FIG. 1. Polarized Raman spectra of (1) tetragonal and (2) twinned orthorhombic crystals at 300 K. The inset shows the reduced scattering cross section for the line at  $230\text{ cm}^{-1}$  versus the excitation energy and the temperature.

( $x \sim 6.7$ ), these lines are accompanied by bands which appear at  $147$  and  $445\text{ cm}^{-1}$ . We observed no significant intensity from  $B_{2g}$  or  $B_{3g}$  ( $E_g$ ) vibrations. The  $XX$  and  $YY$  spectra measured in the basal plane contain lines at  $141$ ,  $339$ , and  $454\text{ cm}^{-1}$  for the tetragonal crystal and a substantially larger number of lines for the orthorhombic crystal (Fig. 1). Despite the fact that it is not possible to distinguish the  $XX$  and  $YY$  spectra in most of the orthorhombic crystals, because of the small-scale twinning structure, the lines at  $147$  and  $339\text{ cm}^{-1}$  definitely have an isotropic scattering tensor in the basal plane. The last band, of symmetry  $B_{1g}$ , in the tetragonal phase preserves the relation  $\alpha_{XX} \approx -\alpha_{YY}$  in the orthorhombic phase also. This conclusion is implied by measurements of the polarization of light at an angle of  $45^\circ$  ( $X' = 110$ ) with respect to the crystallographic axes. The additional lines characteristic of the orthorhombic phase are characterized by a highly anisotropic scattering in the basal plane. This conclusion also follows from direct measurements with a single-domain single crystal.<sup>7</sup> In the course of observations under a polarizing microscope, we observed a large domain,  $0.5 \times 0.5\text{ mm}$  in size, with an anisotropic reflection in the  $ab$  plane in one of the single crystals. The  $a$  and  $b$  axes in this domain were identified in accordance with Ref. 8. Measurements of the Raman spectra of this domain confirmed the conclusion that there is a pronounced anisotropy in the scattering tensor, with  $\alpha_{YY} \gg \alpha_{XX}$  for the lines at  $115$ ,  $230$ ,  $495$ ,  $585$  and  $630\text{ cm}^{-1}$  (Fig. 2a). In contrast with the data of Ref. 7,

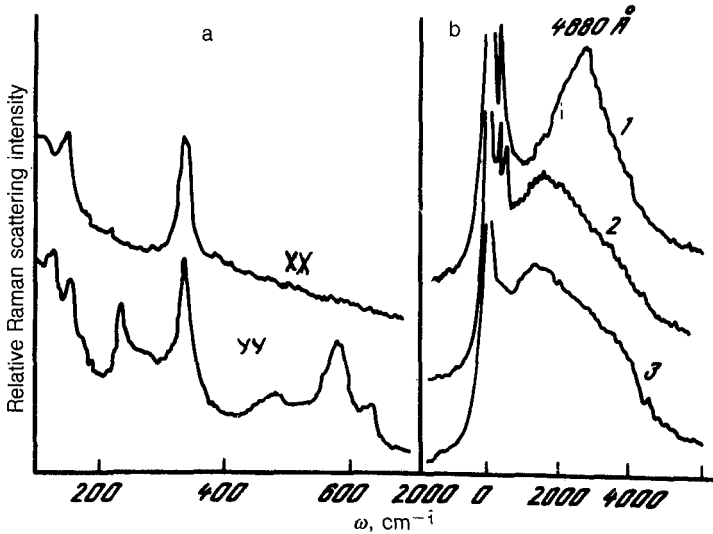


FIG. 2. a—Polarized Raman spectrum in a single-domain orthorhombic crystal ( $X \parallel a, Y \parallel b$ ); b—Raman spectra of (1) a tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_x$  crystal, (2) in orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_x$  crystal, and (3) a Re single crystal in the electron-scattering region.

we observed a clearly defined line at  $630 \text{ cm}^{-1}$  with this anisotropy; we also observed a sharper anisotropy for the lines at  $115$  and  $495 \text{ cm}^{-1}$ .

This result points clearly to a relationship between the anisotropic lines and  $\text{Cu}(1)\text{--O}(4)$  chains. The intensity of two of these lines, at  $115$  and  $495 \text{ cm}^{-1}$ , increases with increasing filling of the chains with oxygen atoms; this result is evidence that these vibrations are coupled with the chains. It is natural to link these bands with the  $A_g$  modes of Ba and O(1). The isotropic nature of the scattering for the lines at  $147$  and  $339 \text{ cm}^{-1}$  is yet further confirmation that these bands are associated with vibrations of atoms in more-remote  $\text{CuO}_2$  layers. The assignment of the line at  $141\text{--}153 \text{ cm}^{-1}$  to displacements of  $\text{Cu}(2)$  atoms agrees with the increase in its frequency as the length of the  $\text{Cu}(2)\text{--}(1)$  bond decreases with increasing  $x$ . We also note the decrease in the intensity of the  $XX$  and  $YY$  components of this vibration, by nearly an order of magnitude, accompanied by the simultaneous, appearance of a  $XX$  component in the orthorhombic phase, which may imply a strengthening of the coupling between the planes and the chains. Yet another vibration, common to the two phases ( $454\text{--}439 \text{ cm}^{-1}$ ), is apparently due to in-phase displacements of O(2, 3) atoms with some  $\text{Cu}(2)$  component; this conclusion would explain its appearance in the orthorhombic phase in the  $ZZ$  spectrum.<sup>9</sup>

In addition to the five lines of  $A_g$  symmetry allowed by the selection rules, we thus observe some additional bands in the orthorhombic phase with an anisotropic scattering tensor. The intensity of these bands is high in the comparatively narrow interval  $x = 6.6\text{--}6.8$ . The appearance of these bands may be attributed to either a violation of the selection rules in a defective structure or the appearance of superstruc-

tures during the ordering of oxygen vacancies. In the latter case, vibrations at the former boundary of the Brillouin zone may become active, as may vibrations of Cu(1) and O(4) atoms which are forbidden in the spectra at  $x = 6$  and  $x = 7$ . The line at  $230 \text{ cm}^{-1}$  is distinguished from all other lines by its unusual dependence on the excitation energy and also an anomalous temperature dependence (see the inset in Fig. 1). The antiresonance near 2.5 eV may be caused by an interference of contributions from intraband and interband scattering mechanisms, if there is a structural feature in the electron spectrum near the Fermi level. A behavior of this sort indicates a relationship between this vibration and the atoms of the chains which are responsible for the formation of the structure in the electron spectrum.

In the spectral region to  $5000 \text{ cm}^{-1}$  we observe in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  a broad scattering band of electronic origin,<sup>10,11</sup> whose shape is shown in Fig. 2b. These spectra were obtained from the same single crystals and at the same time as the measurements of the phonon spectra (Fig. 1), which allow a clear distinction between tetragonal and orthorhombic crystals. The electron spectrum in the former has a well-defined maximum at  $2600 \text{ cm}^{-1}$ , while in the orthorhombic phase it is substantially broadened and shifted down the frequency scale, possibly because of an effect of free carriers. The spectra change only slightly during cooling to 100 K. In both phases this band is observed in the  $XX$ ,  $X'X'$ , and  $X'Y'$  polarizations, while it is absent in the  $XY$  polarization. Although the nature of the electronic transitions near 0.3 eV is not clear at present, we would like to point out that a similar scattering is observed in rhenium (Fig. 2b) and other superconducting transition metals with an hcp structure. Since we know that these metals are not antiferromagnets, this circumstance casts doubt on the relationship between the scattering in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and spin fluctuations.<sup>11</sup>

<sup>1</sup>R. J. Hemley and N. K. Mao, *Phys. Rev. Lett.* **58**, 2340 (1987).

<sup>2</sup>M. Stavola *et al.*, *Phys. Rev.* **B36**, 850 (1987).

<sup>3</sup>A. Yamanaka *et al.*, *Jpn. J. Appl. Phys.* **26**, L1404 (1987).

<sup>4</sup>V. D. Kulakovskii *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **46**, 460 (1987) [*JETP Lett.* **46**, 580 (1987)].

<sup>5</sup>N. M. Chebotaev *et al.*, *Problems of High-Temperature Superconductivity. Information Materials, Part I, Sverdlovsk*, 1987, p. 103.

<sup>6</sup>A. A. Samokhvalov, N. M. Chebotaev, N. N. Loshkarev *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 338 (1988) [*JETP Lett.* **47**, 404 (1988)].

<sup>7</sup>C. Thomsen *et al.*, *Physica* **C153**, 1756 (1988).

<sup>8</sup>V. K. Vlasko-Vlasov, M. V. Indenbom, and Yu. A. Osip'yan, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 312 (1988) [*JETP Lett.* **47**, 375 (1988)].

<sup>9</sup>É. I. Rashba and E. Ya. Sherman, *Pis'ma Zh. Eksp. Teor. Fiz.* **47**, 404 (1988) [*JETP Lett.* **47**, 482 (1988)].

<sup>10</sup>Yu. S. Ponosov, *Fiz. Met. Metalloved.* **66**, 184 (1988).

<sup>11</sup>K. B. Lyons *et al.*, *Phys. Rev. Lett.* **60**, 732 (1988).

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