

# Instability of the crystal lattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in the temperature region 240–200 K inferred from the data on Raman scattering of light

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A part of the lattice of a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  high-temperature superconductor was found to be unstable in the orthorhombic phase at temperatures in the range 240–200 K. At these temperatures a new band at  $640\text{ cm}^{-1}$  can be seen in the Raman-scattering spectrum and there is an anomalous shift of the bands at 147, 340, 432, and  $501\text{ cm}^{-1}$ . The formation of metastable  $\text{CuO}_6$  complexes accounts for the lattice instability.

A group of copper-oxide compounds with a high-temperature superconductivity is characterized by an unusual lability of the crystal structure in terms of the oxygen content and those positions which it occupies. Relatively small changes in the oxygen deficiency ( $0 \leq x \leq 1$ ) change the crystal structure of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from the tetragonal structure ( $D_{4h}^{17}$ ) to an orthorhombic structure ( $D_{2h}^1$ ) when the vacant lattice sites in the Cu(1) planes become filled.<sup>1)</sup> The transition temperature is extremely sensitive to the oxygen deficiency<sup>1,2</sup> and hence to the change in the architecture of the oxygen positions and their vacancies. Using Raman spectra, we have detected a new region of the lattice instability in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in the temperature region 240–200 K, which is characterized by the formation of complexes with an oscillation frequency of  $640\text{ cm}^{-1}$ .

The  $\text{Y}_1\text{Ba}_2\text{Cu}_{7-x}$  samples were synthesized by a standard method from  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  powders. Cold-pressed tablets were heated at  $T = 90\text{--}950^\circ\text{C}$  in an

oxygen stream for approximately 10 hours. They were then thoroughly ground and again pressed. The samples obtained after three heating cycles have a resistivity of 1–2 m $\Omega$  at room temperature and go superconducting at  $T_c = 90\text{--}91$  K ( $\Delta T_c = 1.5$  K). Taking into account that  $T_c$  depends on the oxygen content,<sup>2</sup> our samples had  $x \lesssim 0.1$ .

The Raman-scattering spectra were excited by Ar<sup>+</sup> laser lines. The laser light was focused into a spot 60  $\mu\text{m}$  in diameter and its power level was held within 50 mW. The Raman-scattering spectra were recorded in the “backward-scattering” geometry using a OMARS-89 Raman spectrometer with detection on an optical rule. The samples were immersed in helium vapor in the cryostat and the temperature was recorded at

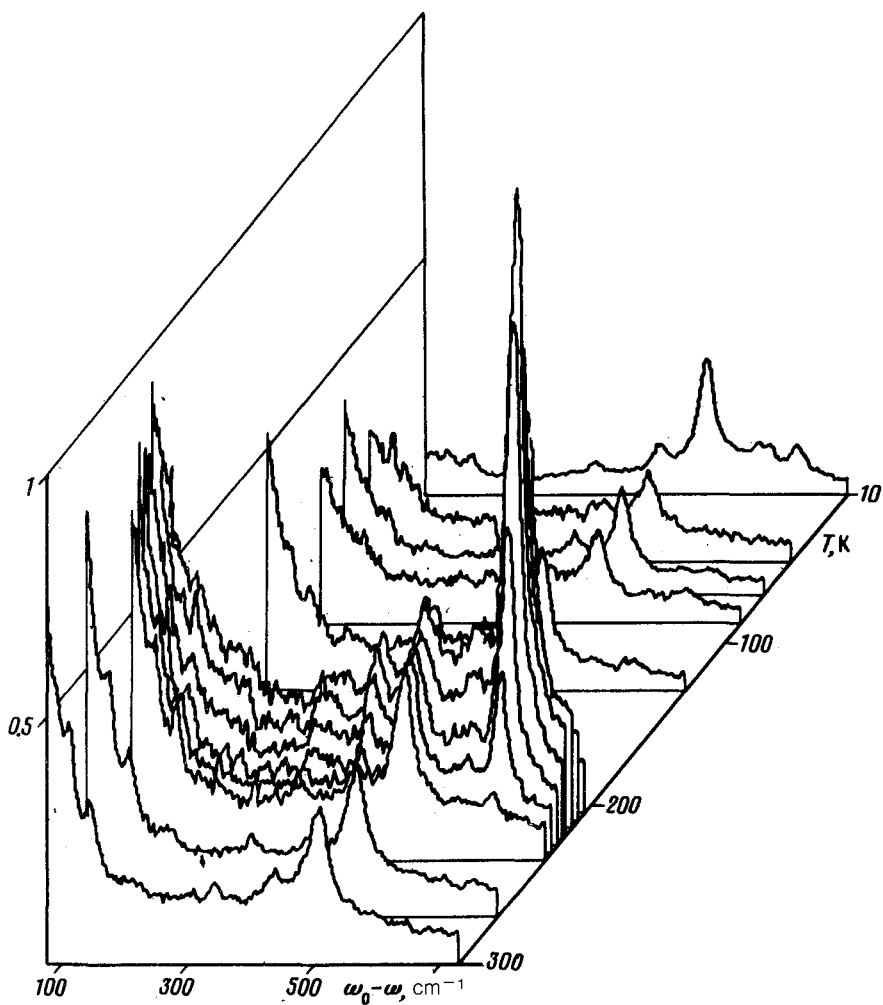


FIG. 1. The Raman-scattering spectra of the polycrystalline orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in the temperature region 300–8 K.

the sample holder. All spectra were measured from a freshly cleaved surface of the tablet which had a polycrystalline structure.

At 300 K (Fig. 1) the Raman-scattering spectrum is in good agreement with the spectra for the orthorhombic phase presented in Refs. 3–5. This spectrum contains bands with the frequencies 116, 147, 340, 432, and 501  $\text{cm}^{-1}$ . In the case of certain samples, measurements of the uncleaved surface showed that Raman-scattering spectrum also contains the 635- and 580- $\text{cm}^{-1}$  bands which vanish after heating the sample in oxygen. On the basis of the Raman-scattering spectrum at 300 K we conclude that our samples have an orthorhombic structure and a strong proclivity for the single phase.

Figure 1 shows the evolution of the Raman-scattering spectrum as the temperature is lowered. The largest changes occur in a narrow temperature region 240–200 K, where the 640- $\text{cm}^{-1}$  band intensifies sharply and then again disappears almost completely. A weaker band (at 593  $\text{cm}^{-1}$ ) also appears, whereas the intensity of the bands characterizing the spectrum at 300 K decreases slightly. At 190 K the spectrum recovers the original structure almost completely. This structure, affected only slightly by the high-temperature superconducting transition, remains virtually the same down to 8 K. Figure 2 shows the change with the temperature in the area under the bands at 500  $\text{cm}^{-1}$  and 640  $\text{cm}^{-1}$ . We see that the intensity of the new band peaks at 220 K. The increase in the 640- $\text{cm}^{-1}$  band is accompanied by a decrease in the intensity of the 500- $\text{cm}^{-1}$  band, whose minimum occurs at  $T = 216$  K. The intensity of this band also changes suddenly at 125 K.

Figure 3 shows the temperature shifts of the principal vibrational bands of the orthorhombic phase. All these bands reveal an anomalous behavior. A lowering of the

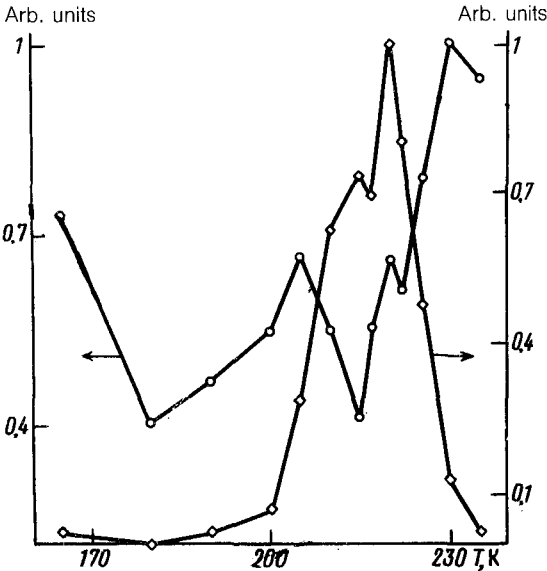


FIG. 2. Variation of the integrated intensity  $I$  of the 500- $\text{cm}^{-1}$  band (curve 1) and the 640- $\text{cm}^{-1}$  band (curve 2) as a function of temperature in the Raman-scattering spectra, based on the data of Fig. 1.

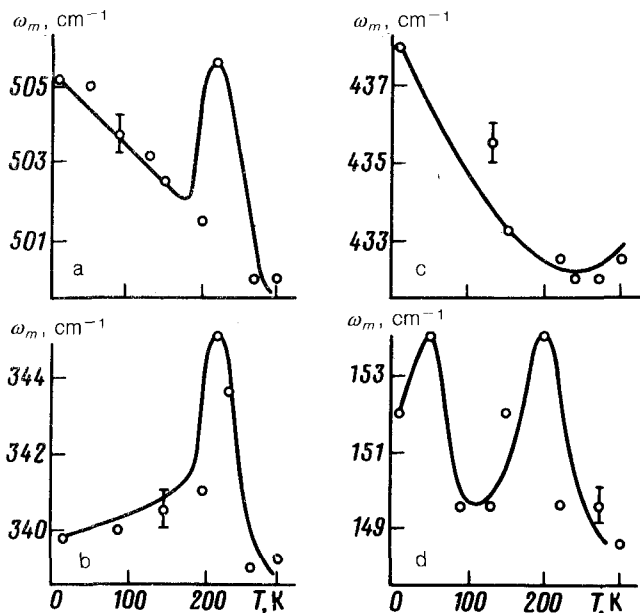


FIG. 3. Temperature dependence of the position of the vibrational bands  $\omega_m$  in the Raman-scattering spectrum. a—The 500-cm<sup>-1</sup> band; b—340-cm<sup>-1</sup> band; c—430-cm<sup>-1</sup> band; d—150-cm<sup>-1</sup> band.

temperature from 300 K to 8 K results in a nearly linear shift  $\Delta\omega$  of the 500-cm<sup>-1</sup> band with the temperature toward higher frequencies. A frequency discontinuity  $\Delta\omega = 5 \text{ cm}^{-1}$ , which occurs at temperatures at which the Raman-scattering spectrum reveals intensification of new bands, is “superimposed” on this band shift. Aside from the anomalous region, the shift of the 500 cm<sup>-1</sup> band agrees well with the results reported in Refs. 5 and 6. The shift of the 340-cm<sup>-1</sup> band also has a maximum at 220 K and the shift of the 432-cm<sup>-1</sup> band has a minimum at 250 K, i.e., it shows that this vibration “softens” in the anomalous temperature region. Finally, the 150-cm<sup>-1</sup> band reveals a complex behavior with two maxima and a minimum at 120 K; i.e., this is the only vibration which “senses” the high-temperature superconducting transition.

The anomalous shifts in the frequencies of the crystal vibrations which we have observed and the intensification of new bands suggest that the lattice is unstable in the temperature region 240–200 K. The instability of the crystal structure is accompanied by the formation of complexes which are responsible for the 640-cm<sup>-1</sup> vibration. It also causes the lattice constants to change. A decrease of the lattice constant  $c$  is attributable to the increase of the 500-cm<sup>-1</sup> oscillation frequency and a decrease of the lattice constant  $b$  results from the increase of the 340-cm<sup>-1</sup> oscillation frequency. X-ray-diffraction studies<sup>7</sup> showed that the lattice constants  $b$  and  $c$  decrease in the orthorhombic phase at temperatures near 200 K. An internal-friction maximum and an ultrasound-damping maximum were observed<sup>7</sup> at 220 K. These data show that there is an internal motion of the hopping diffusion type in the lattice in the temperature

region 240–200 K, which corresponds very closely to the instability region determined from the Raman-scattering spectra.

Before considering the complex responsible for the 640-cm<sup>-1</sup> vibration, we should point out that vibrations of similar frequencies are contained in the Raman-scattering spectrum of BaCuO<sub>2</sub> at 635 cm<sup>-1</sup> (Ref. 8) and in the Raman-scattering spectrum of La<sub>2</sub>CuO<sub>4</sub> at 664 cm<sup>-1</sup> (Ref. 9). In these spectra these vibrations are linked with the planar vibrations of CuO<sub>4</sub> in the oxygen octahedra. The appearance of 640-cm<sup>-1</sup> band as a result of instability of the orthorhombic lattice of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> can be attributed to the formation of octahedral CuO<sub>6</sub> complexes around Cu in position (1) when two oxygen vacancies are filled in the direction of the *a* axis. A complex of this sort may exist a rather short time. The filling of vacancies with oxygen along the *a* axis may be considered as an intermediate step between the lattice state with broken O(1)–Cu(1)–O(1) chains and disordered arrangement of “departed” oxygens at *T* > 240 K and the state of the ordered chains at temperatures below 200 K. The formation of metastable CuO<sub>6</sub> complexes is consistent with the NMR data,<sup>10</sup> where copper nuclei in the six-coordinate surroundings were observed in the spectrum at *T* > 200 K.

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<sup>1)</sup>The positions of the atoms in the unit cell taken from Refs. 4 and 5 are used.

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