Temperature dependence of the Raman scattering spectra of superconducting $YBa_2Cu_3O_{7-\delta}$ single crystals

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The temperature dependence of the frequencies and half-widths of the Raman-scattering lines of active phonons in $YBa_2Cu_3O_{7-\delta}$ single crystals with various oxygen concentrations has been studied. A relationship has been established between the softening of the frequency of the 335-cm^{-1} mode, on the one hand, and the superconducting characteristics and the ordering of oxygen, on the other.

Several recent studies have taken up the temperature dependence of the Raman-scattering spectra of the new superconductors.[1–4] One of the most interesting results is the anomalous temperature dependence which has been observed[1] for the frequency of the valence-deformation mode at ~ 335-cm^{-1} in ceramic $YBa_2Cu_3O_{7-\delta}$ samples. As the temperature was reduced from room temperature to $T \cong T_c$, the frequency of this mode was observed to increase, while a further lowering of the temperature to 10 K resulted in a softening of the frequency. Similar results were found in Ref. 4 for a single crystal. Further research[2,3] has revealed that there is no softening of the mode at 335 cm^{-1} in nonsuperconducting samples of the tetragonal modification of $YBa_2Cu_3O_6$.

In this letter we report detailed studies of the temperature dependence of the frequencies and half-widths of the Raman-scattering lines of active phonons in $YBa_2Cu_3O_{7-\delta}$ single crystals[5–7] over the temperature range 2–300 K. The crystal samples were of orthorhombic D_2^1h (P_{mmm}) symmetry and were rectangular plates with a well-developed **ab** basal plane, with characteristic dimensions of $2\times 3\times 0.2$ mm. All the crystals contained large numbers of twins with a ⟨110⟩ twinning axis.

The Raman spectra were recorded during excitation by the 488-nm line of an Ar^+ laser, with a spectrometer with a microscope attachment. The diameter of the excitation spot was 5–10 μm. It was found that all of the $YBa_2Cu_3O_{7-\delta}$ single crystals studied are inhomogeneous to some extent or other in terms of the oxygen concentration. This inhomogeneity was seen in the circumstance that the frequencies of the various phonon modes in the Raman spectrum of the inhomogeneous samples depended on the particular place on the surface of the crystal where it was excited; these frequencies could vary by several reciprocal centimeters. The typical dimensions of the inhomogeneities were on the order of tens of microns, so a correct measurement of the temperature dependence of the oscillation frequency required a careful control of the excitation position. For this purpose we used a microscope attachment, which made it possible to excite the same region of a crystal, within ~ 10 μm, in different measurements.

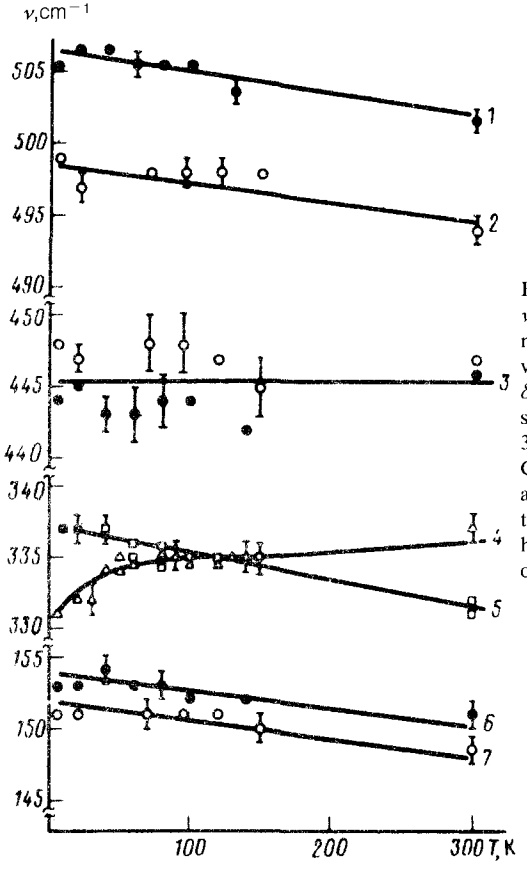

FIG. 1. Temperature dependence of the frequency $\nu(T)$ of the Raman scattering of the active phonons in $YBa_2Cu_3O_{7-\delta}$ crystals in regions with various oxygen concentrations. Open circles: $\delta \approx 0.25$. Filled circles: $\delta \approx 0.1$. 1, 2—Completely symmetric A_g vibration of the O4 oxygen atoms; 3—in-phase vibrations of the oxygen atoms in the Cu-O2-O3 plane; 6, 7—vibrations of copper atoms; 4, 5—out-of-phase vibrations of oxygen of the Cu-O2-O3 plane for samples which are (4) homogeneous and (5) inhomogeneous in terms of oxygen concentration (see the text proper).

During excitation of the end fact of the single crystals, we studied the *zz*-polarization Raman spectra at various temperatures. From these measurements we found the temperature dependence of the frequency ν and the half-width $\Delta\nu$ of the lines of various modes of A_g symmetry of the $YBa_2Cu_3O_{7-\delta}$ crystals (Fig. 1). Results were obtained for regions with various oxygen concentrations, $\delta \approx 0.25$ (the open circles in Fig. 1) and $\delta \approx 0.1$ (the filled circles). The values of δ were estimated, in accordance with the data of Ref. 8, from the frequency of the completely symmetric valence vibration of the O4 oxygen atoms at room temperature: $\nu \approx 494$ cm^{-1} and $\nu \approx 498$ cm^{-1}, respectively. From the results (Fig. 1) we see that all the vibrations of A_g symmetry which are observed in the *zz* spectra harden with decreasing temperature, down to $T = 2$ K, regardless of the observation point. However, the changes in the half-widths of the valence vibrations of oxygen are different in nature for regions with a greater or lesser oxygen deficiency: a sharp decay at low temperatures in the former case and a flat dependence $\Delta\nu(T)$ (an independence) at $T \leqslant T_c$ in the latter case (lines 1 and 2 in Fig. 2). Furthermore, the intensity of the low-frequency, completely symmetric vibrations of the copper atoms ($\nu \approx 150$ cm^{-1}) and the barium atoms ($\nu \approx 115$

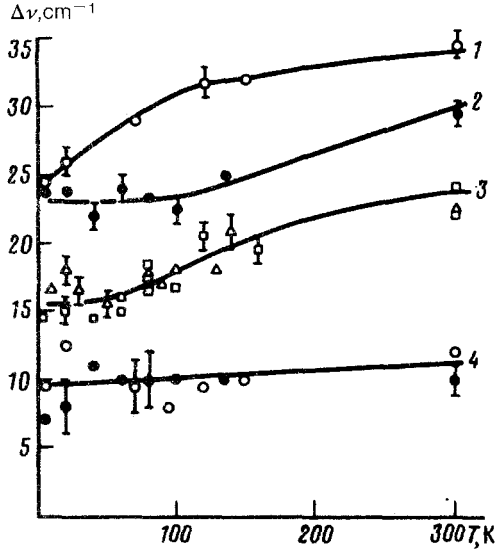

FIG. 2. Temperature dependence $\Delta\nu(T)$ of the half-widths of the Raman scattering lines in $YBa_2Cu_3O_{7-\delta}$ crystals. 1, 2—The mode at 500 cm^{-1}; 3—335 cm^{-1}, for (Δ) a homogeneous sample and (□) an inhomogeneous sample; 4—~150 cm^{-1}; ○—$\delta\approx 0.25$; ●—$\delta\approx 0.1$.

cm^{-1}) decreases with decreasing temperature more rapidly than the quantity $n(\nu)+1$ decreases [$n(\nu)$ are the occupation numbers of the corresponding phonons]. At $T\leqslant 5$ K, for example, the line of the A_g vibrations of Ba is essentially not detected.

The temperature dependence of the frequency of the phonons with $\nu\approx 335$ cm^{-1} turned out to be more complex, and it differed from sample to sample. This vibration is associated with an out-of-phase motion of the oxygen atoms of the superconducting plane.[6,9] In the tetragonal phase of the $YBa_2Cu_3O_6$ single crystals, it has a symmetry B_{1g}. If there is a slight orthorhombic distortion of the lattice, the 335-cm^{-1} mode converts into a vibration with a polarizability tensor which has the properties $\alpha_{xx}\approx -\alpha_{yy}$ and $\alpha_{xx}, \alpha_{yy}\gg\alpha_{zz}$. As a result, this vibration is observed during excitation of the **ab** plane of the single crystal in the *xx* and *yy* polarizations. The intensity of the 335-cm^{-1} band is some 10–15 times lower than that of the most intense mode ($\nu\approx 500$ cm^{-1}) in the *zz* spectra.

Figure 3 shows Raman spectra of $(xx+yy)$ polarizations of two different $YBa_2Cu_3O_{7-\delta}$ samples, recorded during excitation of the basal plane of the single crystals at $T=5$ K. The lower spectrum corresponds to a crystal which was inhomogeneous in terms of oxygen concentration, with $0.1\leqslant\delta\leqslant 0.25$; the upper spectrum was found for the most nearly homogeneous of the samples studied, with $\delta\approx 0$ (the frequency of the A_g valence vibrations of the oxygen atoms at room temperature was $\nu\approx 501$ cm^{-1}). In the latter case, the frequency of the Raman scattering of the active phonons remained constant within ~1 cm^{-1} when we studied various parts of the sample.The superconducting transition temperature T_c found from the magnetic susceptibility was 94 K, with a transition width $\Delta T=1$ K for a homogeneous sample, with respective figures of 90 K and $\Delta T=5$ K for a sample inhomogeneous in terms of oxygen (see the inset in Fig. 3). Furthermore, the presence of the fairly intense high-

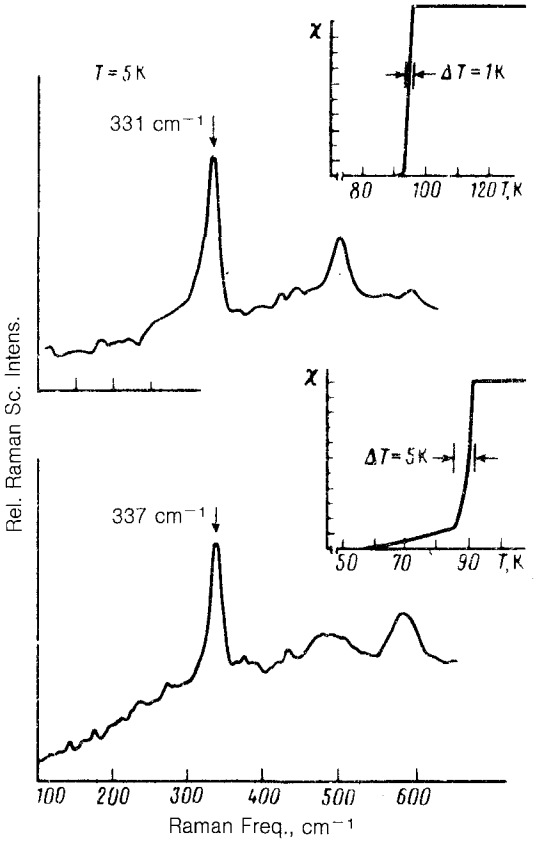

FIG. 3. Raman-scattering spectra of $YBa_2Cu_3O_{7-\delta}$ crystals during excitation of the **ab** basal plane. Upper spectrum—Homogeneous sample in terms of oxygen concentration, with $\delta \approx 0$; lower spectrum—inhomogeneous sample, with $0.1 \leqslant \delta \leqslant 0.25$ (see the text proper). The insets show the magnetic susceptibilities of the samples versus the temperature near the superconducting transition.

frequency band at ~ 590 cm^{-1} in the Raman spectrum of the inhomogeneous samples seems to be evidence of a large number of defects in this crystal.[5]

As the temperature was lowered to $T = 5$ K in a sample inhomogeneous in terms of oxygen concentration, we observed a monotonic increase in the frequency of the 335-cm^{-1} mode (line 5 in Fig. 1a). In a homogeneous crystal, in contrast, we also observed a monotonic change in the frequency of the mode, but in the opposite direction; the rate of change of the frequency with the temperature increased significantly below T_c (line 4 in Fig. 1a). This study thus confirms that there is a softening of the 335-cm^{-1} phonon in certain $YBa_2Cu_3O_{7-\delta}$ samples, but the actual $\nu(T)$ dependence differs from that observed in Refs. 1, 2, and 4.

The difference between the dependences $\nu(T)$ for two crystals seems to be evidence that the observed softening of the frequency of the 335-cm^{-1} phonon is associated with better superconducting characteristics (see the inset in Fig. 3) and a better ordering in terms of oxygen of the homogeneous sample. This conclusion is consistent with the data of Ref. 3, found for ceramic $MBa_2Cu_3O_{7-\delta}$ samples (M represents mixed rare-earth elements).

The curves of the half-width of the 335-cm^{-1} mode for the various samples are essentially identical (Fig. 1b): The half-width increases monotonically and smoothly with increasing temperature. It should be noted, however, that in the case of the softening of the frequency of the 335-cm^{-1} phonon the Raman line of this vibration is asymmetric, with a sharper high-frequency edge. This result may be evidence of features in the interaction of the 335-cm^{-1} vibration with electronic excitations of the crystal.

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