

Raman scattering of light used as a method of analyzing the oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films

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Raman scattering is shown to yield information on the orientation of crystallographic axes, labile oxygen concentration, and degree and nature of the disorder of oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films. A correlation is established between the temperature of the transition to the superconducting state, T_{c0} , and the width of the line at $\nu_{-1} = 500 \text{ cm}^{-1}$.

In the present letter we report the results of an experimental study of thin (0.8–1.2 μm) single-crystal films of a high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which was synthesized by a method involving magnetron sputtering of ceramic targets in a mixture of argon and oxygen. The films were deposited on polished SrTiO_3 and ZrO_2 plates which were heated to 500–700 °C. The Raman light scattering was excited by a Ar^+ laser ($\lambda_0 = 514.5 \text{ nm}$, power level 30 W) and detected by a DFS-24 spectrometer.

The experimental results for six films with different orientations of the crystallographic axes and different transition temperatures are shown in Figs. 1 and 2. The labeling of the curves is the same as that of the samples. The scattering geometry is shown in the inset in Fig. 2. To describe it, we used the laboratory coordinate system x, y, z . The a, b , and c crystallographic axes and the a' and b' axes are rotated through an angle of 45° with respect to the a and b axes. The normal to the surface of the sample is denoted by n .

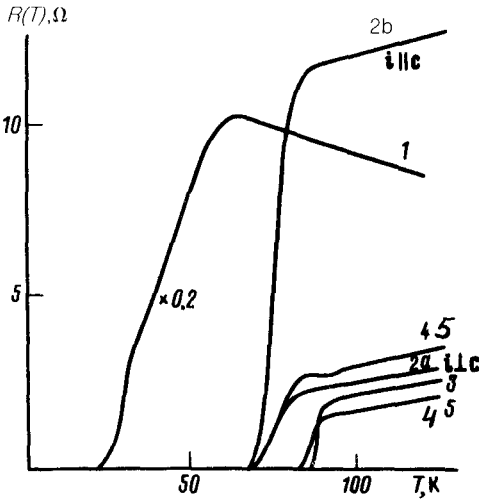


FIG. 1. Temperature dependence of the resistance $R(T)$ of the oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$ films on various substances. 1— SrTiO_3 (110), $T_{c0} = 22$ K; 2a, 2b— SrTiO_3 (110), $T_{c0} = 68$ K; 3— SrTiO_3 (100), $T_{c0} = 88$ K; 4— SrTiO_3 (100), $T_{c0} = 83$ K; 5— ZrO_2 (100), $T_{c0} = 68$ K.

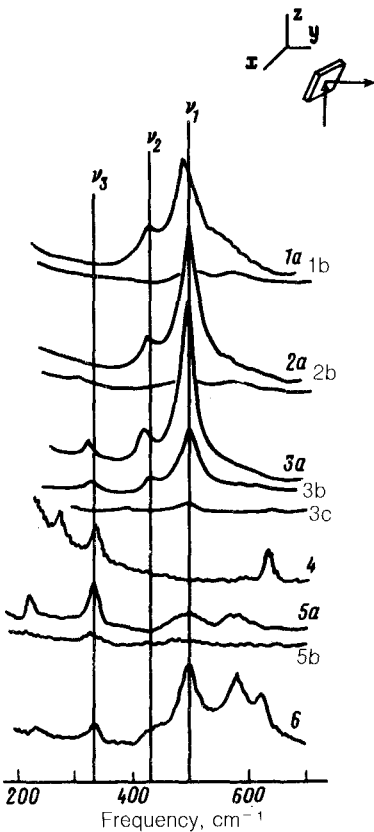


FIG. 2. Polarized Raman-scattering spectra of the oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-s}$ films. The labels on the curves are the numbers of the samples described in the text proper. Spectra 1, a and b; 2, a and b; and 3a were measured in the xx polarization; the remaining spectra were measured in the xz polarization. The orientation of the a , b , and c axes in the laboratory frame of reference corresponds to: 1a, 2a— $x||c$; 1b, 2b— $x\perp c$; 3a, 3c— $x||c, b$; 3b— x makes a 45° angle with the c and b axes; 4a, 5a— $x||a'$; 5b— $x||a$.

Studies of ceramics¹⁻⁵ and single crystals⁶⁻⁸ and analysis of the Raman-scattering intensities⁹ have made it possible to reliably determine the frequencies and the polarization of the three vibrations of the oxygen sublattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. One of the vibrations, ν_1 , corresponds to a completely symmetric, valent vibration of the group $\text{O}(4)\text{-Cu}(1)\text{-O}(4)$.²⁾ The frequency ν_1 varies from 505 cm^{-1} to 470 cm^{-1} when δ varies from 0 to 1 (Refs. 2-4 and 8), and the polarization is determined by the Raman scattering tensor with the components $\alpha_{cc} \gg \alpha_{aa}, \alpha_{bb}$. The off-the-plane vibrations of the oxygen in the CuO_2 layers are represented by the $\nu_2 = 430\text{-cm}^{-1}$ line [the in-phase $\text{O}(2)$ and $\text{O}(3)$ vibrations, the Raman-scattering tensor $\alpha_{cc} \gg \alpha_{aa}, \alpha_{bb}$] and by the $\nu_3 = 335\text{-cm}^{-1}$ line [the out-of-phase $\text{O}(2)$ and $\text{O}(3)$ vibrations, the Raman-scattering tensor $\alpha_{aa} \approx -\alpha_{bb}$ or $\alpha_{a'b'} \gg \alpha_{a'a'}$ on the a' and b' axes]. These data alone can be used to interpret the Raman-scattering spectra obtained by us and to identify the hidden anisotropy of the films even when an analysis of these films using crossed polarizers shows them to be optically isotropic.

In films 1 and 2 grown on SrTiO_3 (110) the c axis lies in the plane $c \perp n$. The optical and electrical properties of these films have a macroscopic anisotropy. The Raman scattering of light in these films is completely polarized and is similar to that of a bulk single crystal. Intense ν_1 and ν_2 lines are observed in the cc polarization. As a result of a 90° rotation of the film around n , the spectrum retains only the weak $\approx 500\text{-cm}^{-1}$ and $\approx 580\text{-cm}^{-1}$ bands. The absence of the ν_3 line in this case means that this spectrum corresponds to the $a'a'$ polarization and hence the a axis in film 1 and the b axis in film 2 lie at a 45° angle with respect to the surface.

Films 3 and 4 were grown on SrTiO_3 (100), where films with $a \parallel n$ or $c \parallel n$ are obtained, depending on the conditions under which the films are grown.¹⁰

The Raman scattering spectrum of film 3 exhibits intense ν_1 and ν_2 lines, in addition to the ν_3 line. The intensity of Raman scattering measured in the xx polarization does not depend on the orientation of the sample and the intensity of Raman scattering measured in the xz polarization depends strongly on the orientation of the sample. The intensity of Raman scattering in the xz polarization is minimal when the crystallographic axes of the substrate are parallel to x . Consequently, film 3 consists of microscopic regions with mutually perpendicular positions of the axes, $b \perp n$ and $c \perp n$, consistent with Ref. 10.

Since the ν_1 and ν_2 lines are absent in the Raman scattering spectrum of film 4, the c axis in this film is parallel to n . In addition to the $\nu_3 = 335\text{-cm}^{-1}$ line, the spectrum exhibits the 296 and 635-cm^{-1} lines. The intensity of the Raman scattering spectrum depends only slightly on the orientation, possibly because of the elastic strain due to the considerable difference in the lattice constants of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ along the a axis and SrTiO_3 (100) (Ref. 10).

The Raman scattering of light from film 5 grown on ZrO_2 (100) is similar to the Raman scattering of light from the ab plane of a bulk single crystal. In the $a'b'$ polarization, aside from the $\nu_3 = 335\text{-cm}^{-1}$ line, we see faint bands at ≈ 500 and 580 cm^{-1} and an intense line at 230 cm^{-1} , whose rf frequency wing merges with the ν_3 line. As we go to the ab polarization, the intensity of the Raman scattering decreases almost to zero, indicating a high degree of orientation of the film.

The intensity of Raman scattering in film 6 grown on SrTiO₃ (111) does not depend on its orientation. The ratio of the intensities of the $\nu_1 = 500\text{-cm}^{-1}$ and $\nu_3 = 332\text{-cm}^{-1}$ lines suggests that the c axis is directed at an angle to the surface. In addition to the principal lines, we see the ≈ 600 and $\approx 630\text{-cm}^{-1}$ lines, whose relative intensities change from one sample to another.

We would like to call attention to the correlation between the width of the ν_1 line and the transition temperature T_{c0} . In film 1 ($T_{c0} = 22$ K) this line has the lowest frequency $\nu_1 = 492\text{ cm}^{-1}$, which implies that there is a deficiency of labile O(1) oxygen, a drawn-out rf wing, and the largest width 60 cm^{-1} , suggesting that the O(4) sublattice is disordered. In film 2 ($T_{c0} = 68$ K) and film 3 ($T_{c0} = 88$ K) this line has a higher frequency ($\nu_1 = 500\text{ cm}^{-1}$) and a smaller width (40 and 32 cm^{-1} , respectively). In film 6 ($T_{c0} = 88$ K) the linewidth of ν_1 is no greater than 40 cm^{-1} . The exact width of the ν_1 line is difficult to determine because of the complex nature of the spectrum.

Analysis of the results which we have obtained allows us to make the following assumptions concerning the nature of the three Raman-scattering bands whose frequencies and intensities depend strongly on the fabrication technology of the sample and on their heat treatment. The Raman scattering of light at frequencies $230\text{--}330\text{ cm}^{-1}$ is probably caused by the off-the-plane vibrations of O(2) and O(3) which are localized at the defects situated near the CuO₂ planes. The band at $580\text{--}600\text{ cm}^{-1}$ can be attributed to the stretching vibrations of the oxygen-deficient O(4)–Cu(1)–O(4) groups (those lacking a single oxygen atom). The band at $630\text{--}640\text{ cm}^{-1}$ is attributable to the stretching vibrations of the Cu(1)–O(1) bond, which manifest themselves in the Raman scattering of light, for example, as a result of “breaks” in the chain.

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²The symbols for the positions of atoms adopted in Refs. 1–7 are used.

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