

# IR reflection and Raman spectra of Bi-Sr-Ca-Cu-O superconducting compounds

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The IR reflection and Raman spectra of Bi-Sr-Ca-Cu-O ceramic and single-crystal high-temperature superconductors have been measured. The polarizations of the vibrations corresponding to 460 to 630  $\text{cm}^{-1}$  have been determined. The frequencies of plasma vibrations are estimated. The width of the superconducting gap is also estimated:  $2\Delta = 250 \text{ cm}^{-1}$ .

In this letter we are reporting data on the IR reflection and Raman scattering spectra of ceramic samples and single crystals of the Bi-Sr-Ca-Cu-O system, in which a high-temperature superconductivity was recently discovered.<sup>1</sup>

The ceramic samples were synthesized through a solid-phase synthesis of a mixture of oxides (or nitrates) with the initial composition Bi:Sr:Ca:Cu = 2:2:1:2 at 850-870 °C in air. They exhibit a superconductivity with a transition temperature  $T_c = 88$  K in the presence of a high-temperature phase with  $T_c = 100$  K (Fig. 1). According to the results of an x-ray spectral microanalysis on a Camebax apparatus, the ceramic had the composition  $\text{Bi}_{2.4}\text{Sr}_2\text{Ca}_{1.6}\text{Cu}_2\text{O}_y$ . Single crystals in the form of thin wafers, with dimensions  $(2-4) \times (1-2) \times (0.02-0.06)$  mm, with  $c$  axis running perpendicular to the surface, were grown by slowly cooling a partially molten mixture of the initial components. The single crystals had the composition  $\text{Bi}_{2.1}\text{Sr}_{1.23}\text{Ca}_{0.23}\text{Cu}_1\text{O}_y$  and did not exhibit a superconductivity. For the optical measurements, the ceramic was polished.

The Raman spectra were excited with an argon laser ( $\lambda_0 = 514.5$  nm) and recorded with a DFS-24 spectrometer while the sample was at room temperature. The reflection spectra were measured over the frequency range 100-700  $\text{cm}^{-1}$  with an LAFS-1000 Fourier spectrometer and over the frequency range 300-4000  $\text{cm}^{-1}$  with a Specord M-80 spectrophotometer.

The Raman spectra of the ceramic (lines 1 and 2 in Fig. 1) are dominated in the region 200-700  $\text{cm}^{-1}$  by a single wide and asymmetric band which peaks near 630  $\text{cm}^{-1}$  and which has knees at 580 and 500  $\text{cm}^{-1}$ . Judging from its shape, this band is a superposition of several closely spaced lines, which may belong to different phases of the system under study. For some of the samples we also observed a faint band peaking at 460  $\text{cm}^{-1}$  (line 2). Similar spectra were recorded for ceramics in Refs. 2-4.

Polarized Raman spectra were recorded from the **ab** and **ac** (**bc**) planes of the single crystal. In the **cc** polarization (line 3) we observe only the intense line at 630

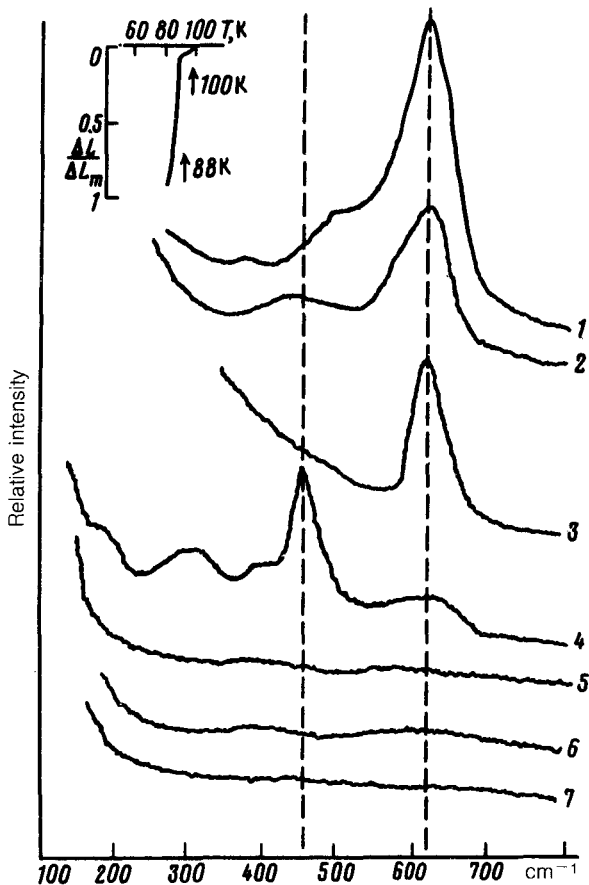


FIG. 1. 1, 2—Raman spectra of a ceramic sample; 3–7—polarized spectra of a single crystal of the Bi–Sr–Ca–Cu–O system. The scattering geometry is determined by the following tensor components: 3—*cc*; 4—*aa* (*bb*); 5—*ab*; 6—*a'b'*; 7—*ac*. The *a'* and *b'* axes are rotated 45° from the *a* and *b* axes. The inset shows the temperature dependence of the diamagnetic response of the ceramic.

$\text{cm}^{-1}$ . The Raman spectrum in the *aa* (*bb*) polarization, as in Ref. 5, contains, in addition to the sharp line at  $460 \text{ cm}^{-1}$ , some faint bands at 190, 320, and  $400 \text{ cm}^{-1}$  and another at  $630 \text{ cm}^{-1}$ , which apparently penetrates from the *cc* polarization.

Cardona *et al.*<sup>5</sup> attribute the  $630\text{-cm}^{-1}$  band to extraplanar vibrations of O(4) and O(5) atoms in BiO layers, and they attribute the  $460\text{-cm}^{-1}$  band to valence vibrations of an O(3) atom between BiO and  $\text{CuO}_2$  layers. According to our data, the  $460\text{-cm}^{-1}$  band corresponds to *aa* and *bb* components of the Raman scattering tensor, while the  $630\text{-cm}^{-1}$  band corresponds to the *cc* component. On this basis it would be preferable to assign the  $630\text{-cm}^{-1}$  band to valence vibrations of O(3), by analogy with the  $500\text{-cm}^{-1}$  band in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The high frequency of this vibration may be a consequence of an interaction with O(4) and O(5) atoms on a  $\text{Cu-O(3)-Bi-O(4.5)}$  line. The band at  $460 \text{ cm}^{-1}$ , on the other hand, may be due to extraplanar vibrations of oxygen in  $\text{CuO}_2$  or BiO planes.

Figure 2 shows IR reflection spectra of the single crystal and the ceramic. The reflection spectrum of the single crystal is described satisfactorily by a Drude curve

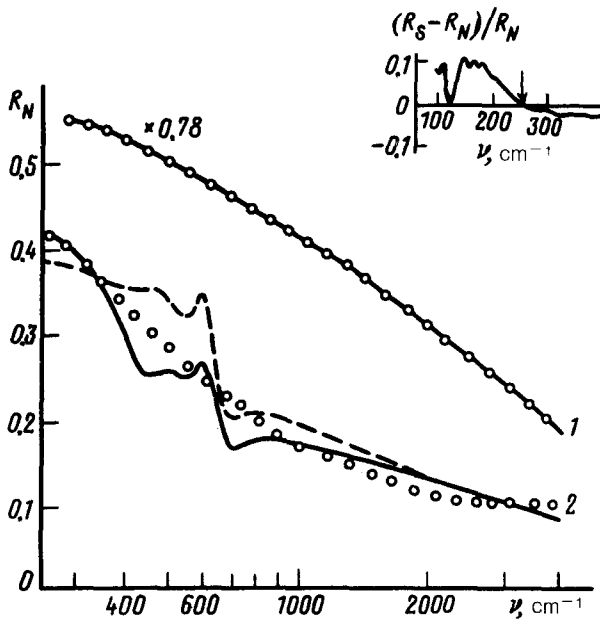


FIG. 2. IR reflection spectra of (1) a single crystal and (2) a ceramic. Solid line—experimental; circles and dashed line—calculated. The inset shows the spectrum of the relative change in the reflection at 78 K ( $R_S$ ) and 290 K ( $R_N$ ).

(the circles) with the parameter values  $\epsilon_\infty = 4$ ,  $\omega_p \approx 7000 \text{ cm}^{-1}$ , and  $\gamma_p \approx 9000 \text{ cm}^{-1}$ . On the other hand, the spectrum  $R(\omega)$  of the ceramic has a complex shape and contains phonon structure with maxima at  $\approx 450$  and  $\approx 600 \text{ cm}^{-1}$ . Since the ceramic is a mechanical mixture of highly anisotropic single crystals in various orientations, we calculated the reflection spectrum by averaging it over polarizations and over the angle between the  $c$  axis and the normal to the surface. We assumed that plasma vibrations are polarized in the  $ab$  plane, while there are no plasma vibrations along the  $c$  axis, although there are lattice vibrations. The dashed line in Fig. 2 shows the result of a calculation with  $\omega_p \approx 2500 \text{ cm}^{-1}$ ,  $\gamma_p \approx 4500 \text{ cm}^{-1}$ , and phonon frequencies of 490(510) and 590(630)  $\text{cm}^{-1}$  (the longitudinal phonon frequencies are given parentheses). The averaging method which we used is valid in the short-wave limit,  $\lambda < d$ , where  $\lambda$  is the wavelength of the light, and  $d$  is a typical grain size of the ceramic ( $d \approx 5\text{--}10 \mu\text{m}$ ). In the long-wave limit, a ceramic is isotropic and should be described by the Drude model. The circles in Fig. 2 show the corresponding calculated curve with  $\omega_p \approx 2000 \text{ cm}^{-1}$ , and  $\gamma_p \approx 4500 \text{ cm}^{-1}$ .

An estimate of the size of the superconducting gap,  $2\Delta$ , can be found from the spectrum of the relative change in the reflection in the superconducting state ( $R_S$ ) and in the normal state ( $R_N$ ), shown in the inset in Fig. 2. The characteristic frequency  $245 \text{ cm}^{-1}$ , at which the ratio  $(R_S - R_N)/R_N$  changes sign, is marked by the arrow. This is the approximate position of the gap.

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<sup>1</sup>H. Maeda, Y. Tanaka, M. Fukutomi *et al.*, Jpn. J. Appl. Phys. **27**, L209 (1988).

<sup>2</sup>T. A. Fimberg, É. R. Ioon, Ya. O. Past, and L. A. Rebane, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 33 (1988)

[JETP Lett. **48**, 34 (1988)].

<sup>3</sup>Z. V. Popovic, C. Thomsen, M. Gardona *et al.*, Solid State Commun. **66**, 965 (1988).

<sup>4</sup>M. I. Iliev and V. G. Hadjiev, Physica **C156**, 193 (1988).

<sup>5</sup>M. Cardona, C. Thomsen, R. Liu *et al.*, Solid State Commun. **66**, 1225 (1988).

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