

## Raman effect in Bi-Sr-Ca-Cu-O superconducting crystals

I. V. Aleksandrov, A. B. Bykov, A. F. Goncharov, V. N. Denisov,  
B. N. Mavrin, O. K. Mel'nikov, V. B. Podobedov, and N. I. Romanova  
*Institute of Spectroscopy, Academy of Sciences of the USSR*

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The polarized Raman scattering spectra of crystals of the Bi-Sr-Ca-Cu-O system have been studied. A preliminary identification of the bands is offered. The most intense bands (at 65, 460, and 634-655  $\text{cm}^{-1}$ ) are associated with Bi-O vibrations.

We have studied the polarized Raman spectra of single crystals in the Bi-Sr-Ca-Cu-O system. In contrast with most previous work,<sup>1-7</sup> we were able to measure the Raman spectra from both the basal and lateral planes of the crystals, so we were able to study the Raman effect in the *zz* polarization and to identify the observed bands.

TABLE I.

Composition	Designation	Growth method	$c$ , Å	$T_c$ , K
$\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_{6+\delta}$	BSCCO-1	Spontaneous crystallization	24.3	< 4.2
$\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_3\text{Cu}_2\text{O}_{8+\delta}$	BSCCO-2 a	Zone melting	31.0	36 - 61
$\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_3\text{Cu}_2\text{O}_{8+\delta}$	BSCCO-2 b	Zone melting	30.9	68 - 90

The crystals which we studied are described in Table I.

The parameters of the unit cell were measured, and the superconducting properties were studied, by methods similar to those in Ref. 8.

The crystal samples were small plates with dimensions of  $2 \times 1 \times 0.005$  mm, with a  $c$  axis oriented perpendicular to the plane. Some of the BSCCO-2b samples reached dimensions of  $6 \times 2 \times 0.5$  mm.

The Raman spectra were excited by the line at 514.5 nm from an argon laser in a reflection geometry and analyzed with a triple multichannel spectrometer<sup>9</sup> over the

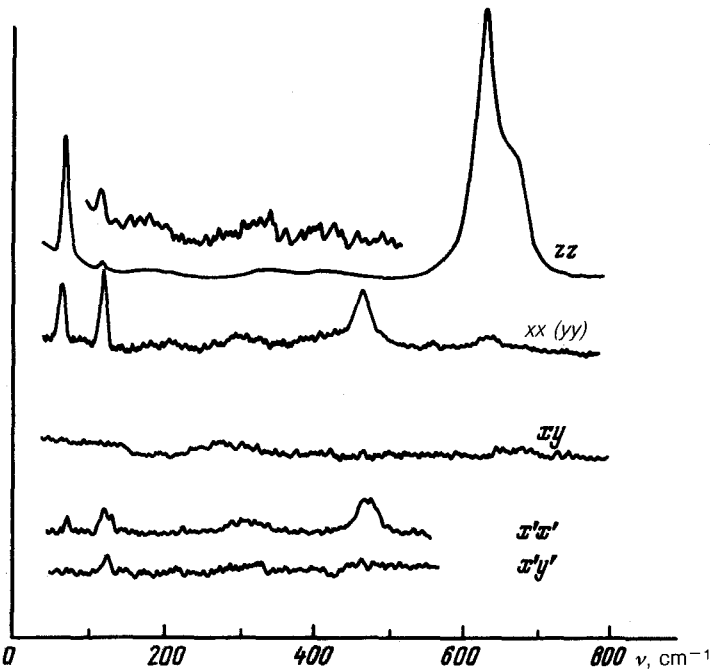


FIG. 1. Polarized Raman spectra of a BSCCO-2b crystal at room temperature. The  $x'$  and  $y'$  axes are rotated  $45^\circ$  around the  $c$  axis from the  $x, y$  axes.

range 20–800  $\text{cm}^{-1}$ . For our study of the polarized Raman spectra we used freshly cleaved basal planes, while the lateral planes were produced through a dry polishing of the samples.

Figure 1 shows polarized spectra of BSCCO-2b. In the  $zz$  geometry we see intense bands at 65 and 634  $\text{cm}^{-1}$  (with a knee at 655  $\text{cm}^{-1}$ ) and some very faint bands at 120, 175, 320, and 400  $\text{cm}^{-1}$ . By analogy with the spectrum of YBCO, we should link the band at 634  $\text{cm}^{-1}$  with an axial vibration of the bridge oxygen, O3, which binds Cu and Bi atoms. The low-frequency band at 65  $\text{cm}^{-1}$ , which has no analog in YBCO, should be associated with vibrations of heavy Bi atoms. In the  $xx$  geometry we see bands at 65, 122, 200, 300, 460, and 634  $\text{cm}^{-1}$ , which can be associated with axial vibrations of Bi, Sr, Cu, O1, O2, and O3 atoms, respectively (see Ref. 10 regarding the designations of the O atoms). It follows from this figure and from the selection rules for orthorhombic crystals that the bands observed in the  $zz$  geometry and  $xx$  geometry should be associated with completely symmetric vibrations of  $A_g$ . Because of the large width of the lines and/or the dependence of their shape and position on the particular point which was probed, we have not yet been able to determine whether the lines in these two configurations are identical. However, if they are, the observed spectra are in excellent agreement with the structural data.<sup>10</sup> Other wise, there is a doubling of the primitive cell in the  $ab$  plane.

The spectra of the BSCCO-1 and BSCCO-2a crystals measured from the basal planes are generally similar. However, the spectra of BSCCO-1 do not have the band at 280  $\text{cm}^{-1}$  in the  $xy$  geometry (Fig. 1). This band is associated with out-of-phase vibrations of O1 atoms from the  $\text{CuO}_2$  planes.<sup>5</sup> Furthermore, the BSCCO-1 spectra contain a single band at 655  $\text{cm}^{-1}$  instead of the composite 634–655- $\text{cm}^{-1}$  band.

Note that the Bi–O vibrations (65, 460, and 634–655  $\text{cm}^{-1}$ ) are quite intense in comparison with most of the other modes; note also their polarization properties ( $\alpha_{xx} \gg \alpha_{zz}$  for the band 460  $\text{cm}^{-1}$  and  $\alpha_{xx} \ll \alpha_{zz}$  for the band at 634–655  $\text{cm}^{-1}$ ), which suggest to us that the Bi–O bonds are essentially localized.

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