

Raman scattering from the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ superconductor

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The Raman spectrum from 10 to 550 cm^{-1} has been obtained from the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ superconductor. Modes similar to those exhibited by $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ are found, as expected from similarities in the crystal structures of the two materials. In addition, several strong low-frequency modes are present, suggestive of a material with loosely coupled substructures consistent with the structural x-ray analysis of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$. Meissner analysis shows that the sample used exhibits bulk superconductivity.

Recently Tarascon *et al.*¹ have described the crystal structure of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ superconductor which has $T_c = 85\text{ K}$. While the space group¹ of this material differs²⁻⁵ from that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, the Raman-active plane is common to both; thus, the spectra of the two superconductors can be expected to have strong similarities. This will indeed prove to be the case.

The apparatus used has been described in detail elsewhere⁶ and consists of a Raman microprobe apparatus with a spot size of $\sim 1\text{ }\mu\text{m}$. A backscattering geometry is used in all experiments such that the exciting electric vector E_{in} is in the plane of the sample. This exciting radiation is provided by the 4880-\AA line of the Ar^+ laser. All data were taken at room temperature.

Micalike crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ for these studies were grown using a flux composed of bismuth and copper oxides in excess of the stoichiometric requirements.⁷ A piece was picked off which weighed $70\text{ }\mu\text{g}$ with an estimated 30% error. Figure 1 shows as evidence of bulk superconductivity the Meissner curve for this sample, which was obtained in a field of 10 G. The percent superconduc-

tivity is not quoted because sample geometry does not warrant calculation of the appropriate demagnetizing factor. T_c is seen to be 80 K; the broad transition indicates some nonuniformity in the material.

Figure 2 shows the spectrum obtained from this sample from 10 to 550 cm^{-1} . Although the polarization of the electric vector of both the exciting and scattered radiation was varied, no effects on the spectrum were observed. This indicates that there was no long-range single-crystal order within the $1\text{-}\mu\text{m}$ spot size. All spots observed gave the same line spectra; however, signal-to-noise ratio varied as much as a factor of 10 from point to point which we attribute to areas of greater surface roughness.

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, the Y, Cu(1), and O(4) atoms cannot participate in Raman modes^{2-5,8} (identification of atom positions as in Ref. 2). Out-of-phase bond bending²⁻⁵ of O(2)-O(3) gives rise to the 340 cm^{-1} mode; in-phase bond bending of these same oxygens²⁻⁵ accounts for the mode at 447 cm^{-1} . Axial stretching of O(1) leads to the 500 cm^{-1} mode;²⁻⁵ similarly axial stretching of

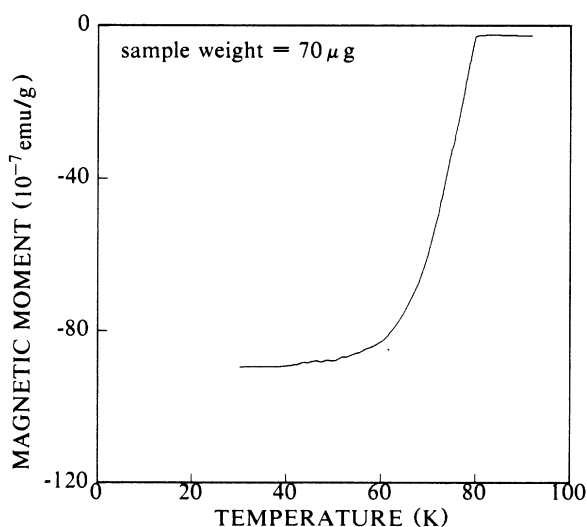


FIG. 1. Magnetization vs temperature for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ sample used for Raman data. The curve represents cooling in field of 10 G (Meissner).

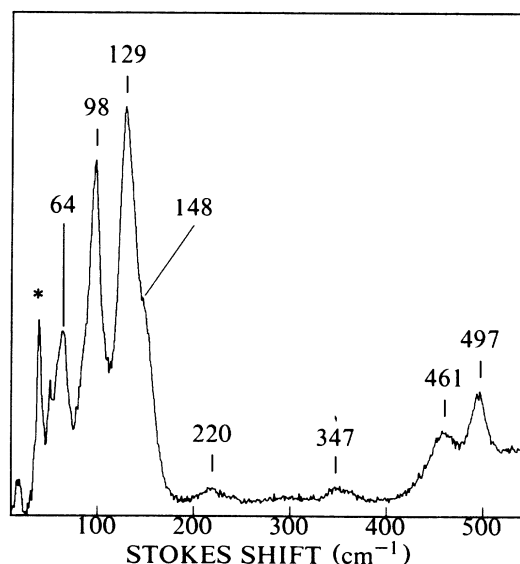


FIG. 2. Raman scattering from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$. Asterisk indicates plasma line. Background has been subtracted.

Cu(2) gives the 220 cm^{-1} mode.²⁻⁵ Finally, the 150 cm^{-1} mode derives from symmetric stretching of the Ba planes.²⁻⁵ It is obvious from Fig. 2 that each of the above mentioned $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ modes has a counterpart in the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ superconductor. This is to be expected, since the substructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ has in-plane Raman-active Cu and O atoms with similar environment to those active in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. The Ba plane is replaced by a Sr plane, which is also Raman active, as determined from group theory used in conjunction with the crystallographic information.

The space group¹ for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ substructure is $I4/mmm (D_{4h}^2)$. On the basis of the Wyckoff notation for equivalent sites,¹ we find⁸ that Ca has point-group symmetry D_{4h} , and therefore is not involved in any Raman modes. O(1) has symmetry C_{2v} and can have Raman modes $A_{1g}(R_{xx} + R_{yy}, R_{zz})$, $E_g(R_{xz}, R_{yz})$, and $B_{1g}(R_{xx} - R_{yy})$. The remaining atoms [Sr, Bi, Cu, O(2), O(3)] each have symmetry C_{4v} , which gives the A_{1g} and E_g Raman-active modes. If the modes of Fig. 2 which are

at 148, 220, 347, 461, and 500 cm^{-1} are analogous to those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, they can be expected to have A_{1g} symmetry.²⁻⁵

The strong low-frequency modes at 64, 98, and 129 cm^{-1} are unique to the spectrum of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$. It is interesting to note that Fig. 2 resembles spectra of polytype structures⁹ where unit-cell substructures are loosely coupled together in layers. The weaker high-frequency modes discussed above come from within the unit cell, while these large low-frequency modes arise from motion between layers. Such a picture is consistent with the fact that, within $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$, slabs are displaced from one another along the c axis by a distance (Ref. 1) $(\frac{1}{2}a, \frac{1}{2}b)$; this structure gives the sample its mica-like character as found in graphite or layered materials. The low-frequency modes might also be due to scattering from long-range fluctuations observed perpendicular to the c axis in the bismuth oxygen plane. Clarification of mode assignments will be made with data from more uniform crystals combined with lattice-dynamic calculations.

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