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TEMPERATURE DEPENDENCE OF THE RAMAN SPECTRUM OF THE HIGH T_c SUPERCONDUCTOR $YBa_2Cu_3O_7$

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The Raman spectrum of polycrystalline sintered $YBa_2Cu_3O_7$ has been measured at several temperatures between 10K and 300K. Ten Raman active phonon modes are observed with frequencies of 153, 217, 291, 309, 335, 441, 493, 506, 601 and 640 cm^{-1}. The 335 cm^{-1} mode shows anomalous behavior: Above T_c it increases in frequency on cooling but below T_c its frequency shift changes sign as the mode begins to soften. The fact that most of the mode frequencies we observe do not coincide with the measured infrared frequencies supports the assignment of the symmetry of the crystal to a centrosymmetric space group.

Introduction - Intense interest in oxygen deficient perovskite superconductors has been generated by the discovery of superconductivity at >30K in the La-Ba-Cu-O system by Bednorz et al.[1,2] and above 90K in the Y-Ba-Cu-O system by Wu et al.[3] and Zhao et al.[4] The role of phonons and electron-phonon coupling in the mechanism of superconductivity is a central issue. Proposals have been made[5,6] that structural instabilities associated with the superconducting transition might be expected in this class of materials. Raman scattering is a sensitive probe of such anomalies and the Raman spectra of superconducting $(La_{1-x}Sr_x)CuO_4$ have been reported.[7] We have undertaken a study of the temperature dependence of the Raman spectrum of the Y-Ba-Cu-O system above and below the superconducting transition temperature T_c = 92K. We find a weak anomaly in the the temperature dependent frequency shift of the 335 cm^{-1} mode.

Experimental - The material used in this study had the nominal stoichiometry corresponding to $YBa_2Cu_3O_7$ which was identified to be the superconducting phase in the Y-Ba-Cu-O system.[8-10] It was prepared by the technique described by Engler et al.[11] The sample used here had been annealed in air and slowly cooled from 900°C to 200°C over five hours. Resistivity measurements showed the onset of the superconducting transition at 94K and vanishing resistance at 92.5K.

Rosen et al.[12] recently reported the room temperature Raman spectrum of $YBa_2Cu_3O_7$ containing significant amounts of other phases such as $BaCuO_2$ and Y_2BaCuO_5. They showed that Raman scattering is a sensitive probe of impurity phases and they identified the spectra of these phases. Using their results we are able to say that our samples contained the essentially pure superconducting phase $YBa_2Cu_3O_7$. The possibility of a small residual impurity, $BaCuO_2$ is mentioned below.

Raman measurements were carried out using a standard Jobin-Yvon double monochromator as described previously.[12] The temperature dependent spectra were obtained using a stationary sample mounted in an Oxford Instruments flow cryostat. The sample was surrounded by approximately 1 atm. of helium exchange gas and irradiated with 100 mW 5145 Ar^+ laser beam focused by a cylindrical lens to give a line image on the sample with a maximum power density of 50 W/cm^2. The temperature was measured by a Ge sensor mounted in the cooling chamber and also checked by an iron constantan thermocouple mounted directly on the sample. The temperature of the laser excited volume was estimated by measuring the anti-Stokes/Stokes intensity ratio for the 504 cm^{-1} and 337 cm^{-1} lines at room temperature. This was consistent with the laser heating being much less than 10K. Similar conclusions were reached by a consideration of the heat flow problem.[13]

Results and Discussion - Figure 1 shows the Raman spectra obtained at five temperatures (10K, 60K, 90K, 115K and 295K) with 4 cm^{-1} resolution and a total time per scan of about 15 hours. Ten Raman active modes were observed with frequencies given in Figure 1. The weak line at 640 cm^{-1} may be due to small amounts of $BaCuO_2$ since it coincides with the strongest line of that phase. The 601 cm^{-1} line matches that of the strong scatterer Y_2BaCuO_5, however, the spectrum does not contain the 380 cm^{-1}

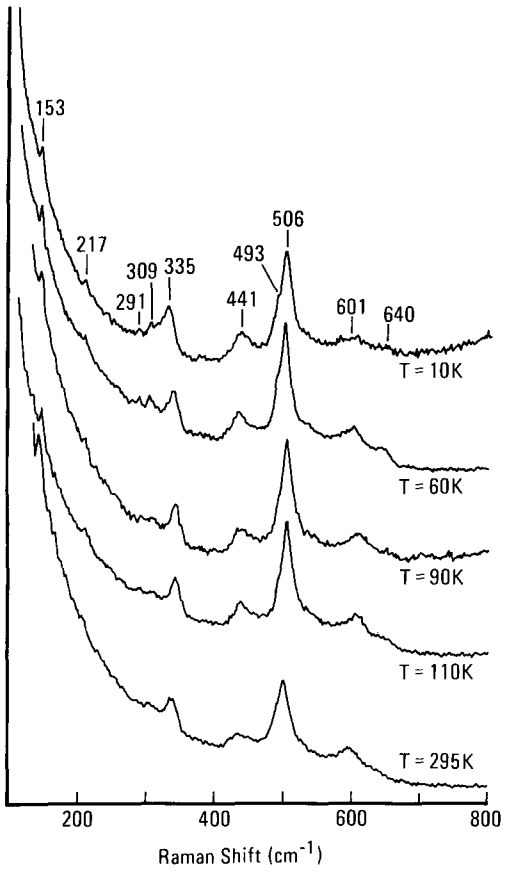

Figure 1. Temperature dependence of the Raman spectrum of sintered pellets of $YBa_2Cu_3O_7$. The superconducting transition temperature is 92K. Spectral resolution is 4 cm-1 and the run time per trace was 15 hrs.

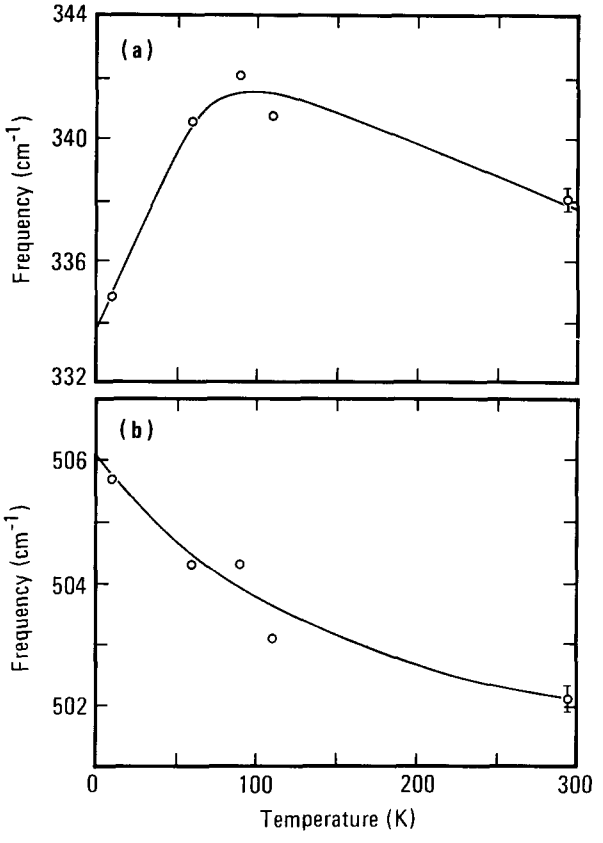

Figure 2. (a) Temperature dependence of the frequency of the 337 cm^{-1} mode showing the anomalous softening below T_c and (b) the 504 cm^{-1} mode, in contrast, shows a normal monotonic frequency increase on cooling. The curves are drawn for visual aid only.

mode of Y_2BaCuO_5 so this phase is thought to be absent.

Perhaps the most interesting feature of the Raman spectra presented in Figure 1 is the anomalous temperature dependence of the 337 cm^{-1} line which exhibits a normal increase in frequency on cooling from room temperature to the superconducting transition temperature T_c~90K. Below T_c, however, the temperature dependent shift changes sign and the mode softens, falling 7 cm^{-1} by 10K (Figure 2a). While this is a relatively small anomaly, it is clearly associated with the superconducting transition temperature. In addition, it may signal larger changes at other k values or phonon frequencies. In contrast, the 504 cm^{-1} mode exhibits a normal monotonic frequency increase of 5 cm^{-1} on cooling to 10K (Figure 2b). It is also interesting to note that infrared measurements[14] show a shift to lower frequencies by 4 cm^{-1} for the 279 cm^{-1} and 310 cm^{-1} IR active modes on cooling below T_c.

A detailed assignment of the motion associated with each Raman active mode would require a full lattice dynamics calculation, which is not yet available. However, we have carried out a symmetry analysis of the vibrational modes, based on the structure of the unit cell shown in Figure 3. It has been proposed in a number of X-ray[15] and neutron diffraction[16,17] studies that the unit cell is orthorhombic with centrosymmetric space group Pmmm. It is now generally agreed that the oxygen vacancies are essentially ordered: No oxygens occur in the plane of the yttrium atom and the Cu(1) atoms are connected in ribbons within which O(1)–Cu(1)–O(1) chains occur. Perpendicular to this direction, Cu(1) has two oxygen vacancies, which results in an orthorhombic rather than tetragonal structure. The exact oxygen stoichiometry of this material depends somewhat on cooling rates and ambient atmosphere so that, more commonly, there are 7 – x oxygen atoms per cell with x ~ 0.1. One

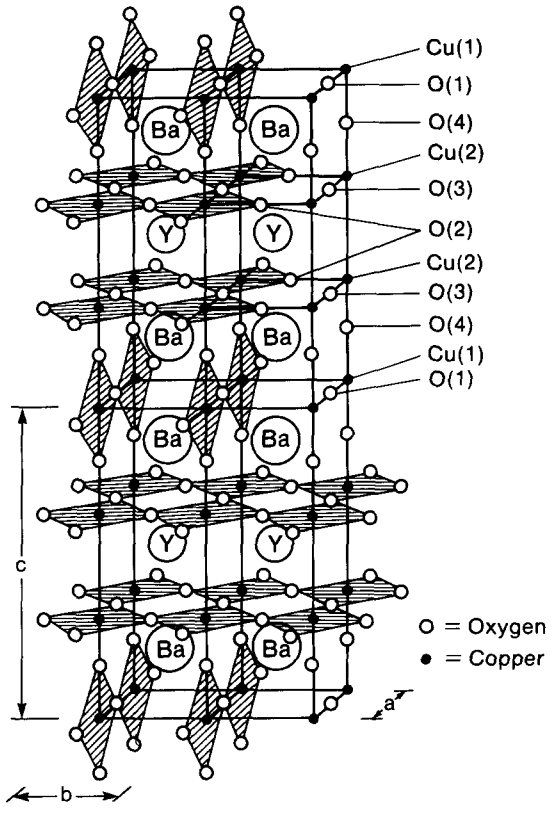

Figure 3. Unit cell of $YBa_2Cu_3O_7$ showing the positions of the atoms. The orthorhombic cell, containing one formula unit has dimensions a = 3.8863(1)Å, b = 3.8231(1)Å, c = 11.6809 (2)Å.[14]

feature of the structure, in addition to the oxygen deficiency, is that O(1) exhibits a large vibrational amplitude.[16,17] Four unit cells are shown in Figure 3 highlighting copper oxygen planes and ribbons which are thought to play a major role in the superconductivity.

There are a total of 39 vibrational modes, 15 of which are Raman active with symmetries at k = 0 of $5A_g + 5B_{1g} + 4B_{2g} + B_{3g}$. The representations of $mmm(D_{2h})$ are given here in the Bethe notation.[18] The 21 infrared active modes are $7(B_{1u} + B_{2u} + B_{3u})$ and there are three acoustic modes. The symmetries of the modes associated with the motion of particular atoms is given in Table 1. The most interesting result is that the motion of Cu(1) and O(1) do not contribute to Raman active modes, but they are infrared active. The O(4) motion in the "flat" part of the Cu(1) ribbons may contribute to a Raman active mode however.

Table 1. Classification of modes associated with displacements of atoms at specific sites in $YBa_2Cu_3O_7$. (See Figure 3 for atomic positions.) Total of 39 modes: 15 Raman active, 21 infrared active, 3 accoustic

atoms	mode classification
Y	$B_{1g} + B_{2g} + B_{3g}$
Ba	$A_g + B_{1g} + B_{2g} + B_{1u} + B_{2u} + B_{3u}$
Cu(1)	$B_{1g} + B_{2g} + B_{3g}$
Cu(2),O(4)	$2(A_g + B_{1g} + B_{2g} + B_{1u} + B_{2u} + B_{3u})$
O(1)	$B_{1g} + B_{2g} + B_{3g}$
O(2)	$A_g + B_{1g} + B_{2g} + B_{1u} + B_{2u} + B_{3u}$
O(3)	$A_g + B_{1g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$

The infrared reflectivity of $YBa_2Cu_3O_7$ has been measured[13] and a number of infrared active modes identified with frequencies of 151, 191, 279, 310, 548 and 609 cm^{-1} at 105K. With two exceptions (151 and 310 cm^{-1}), there is no correspondence between the Raman and IR frequencies, supporting the assignment of a centrosymmetric structure. However TEM studies of similar material[19] has shown the presence of smaller amounts of material with the noncentrosymmetric Pmm2 structure. It is possible that the lines which coincide in the Raman and IR spectra are due to this phase.

In conclusion, we have measured the temperature dependence of the Raman spectrum of essentially pure, single-phase, high T_c superconducting $YBa_2Cu_3O_7$. While no dramatic structural changes are observed, consistent with previous neutron diffraction work,[16,17] a very interesting anomaly is observed in the temperature dependent frequency shift of the 335 cm^{-1} mode in the vicinity of T_c. This may suggest the possibility of larger changes in the phonon spectrum occurring at non-zero wavevectors.

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