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RAMAN EXPERIMENTS ON YBaCuO-SUPERCONDUCTORS*

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YBaCuO-superconductors (sintered ceramics, sputtered films and single crystallites) prepared by different laboratories have been investigated by Raman spectroscopy. In addition we have performed experiments to characterize the superconducting properties of these samples. A comparison of both methods enables us to determine those characteristic lines which represent zone center optical phonons of the superconducting phase. We also present the results of lattice dynamics calculations which reproduce the Raman lines, and give the normal coordinates for these phonons.

1. INTRODUCTION

A comparison of published Raman spectra (1,2) on the YBaCuO superconductors shows common features, but also differences in details, although the superconducting properties are reported to be nearly the same. Our Raman experiments on various samples (sintered ceramics, sputtered films and a single crystal) in connection with magnetization measurements should give information about the vibrational excitations in the superconducting YBaCuO-phase. Additional lattice dynamics calculations give ideas about internal displacements for the different phonons.

2. EXPERIMENTS

The sintered samples were produced by standard techniques in several laboratories (3) and reached macroscopic critical current densities $j_c \simeq 250\ A/cm^2$ (4). The superconducting films, sputtered onto various substrates (ZrO_2, Al_2O_3, $SrTiO_3$) reached $j_c \simeq 10^5\ A/cm^2$ (5). Our single crystal, a platelet ($0.5x0.5x0.05\ mm^3$) grown by a flux method (6), was not superconducting at 77 K, which indicates some oxygen deficiency.

The Raman spectra were obtained by a conventional set-up, details being described in Ref. (2). A large laser focus ($0.05x1\ mm^2$) and low laser power (40 mW) were used to reduce heating of the scattering volume. The spectra from ceramic pellets were taken both for as-prepared samples and for surfaces carefully ground by fine emery paper. The films had a relatively smooth surface and correspondingly low elastic background scattering. Spectra of the single crystal could only be obtained from the surface perpendicular to the c-axes, because it was pressed into an indium holder to ensure good thermal contact.

In order to characterize the superconducting properties of our samples we have performed conductivity and magnetisation measurements and - for ceramic pellets - have also investigated macroscopic persistent currents in rings prepared from these pellets (4). In one of our good samples, a ring current ($j= 200\ A/cm^2$) was observed to stay constant within our resolution of 1% over more than 10 days.

3. RESULTS

Raman spectra of different samples are collected in Fig. 1. The most pronounced peaks are those at 334 and 500 cm^{-1} which appear in all of the polycrystalline samples (sintered ceramic (a) and sputtered film (b)). In addition peaks at 145, 434, and 600 cm^{-1} are observed especially for the sputtered film (b). The spectra of a film on a $SrTiO_3$ substrate (c) and of the single crystal (d) differ from the spectra (a),(b) because there the only pronounced line is the one at 334 cm^{-1}. Between 400 and 600 cm^{-1} only a broad intensity distribution is seen in the film. The single crystal displays more structure especially at 640 cm^{-1}. Also the line at 145 cm^{-1} can be seen, superimposed on the elastic background scattering at low Raman shift. The spectra from a sintered pellet before and after removal of a thin surface layer are shown in spectra (e) and (f), respectively. A line at 640 cm^{-1}, in addition to the lines observed in the other polycrystalline samples, is seen at the untreated surface; it vanishes after grinding. The lines around 800 cm^{-1} are due to traces from the emery paper.

4. DISCUSSION

In polycrystalline materials many lines are observed. This is so because the selection rules for Raman processes are less restricted in polycrystalline material than in single

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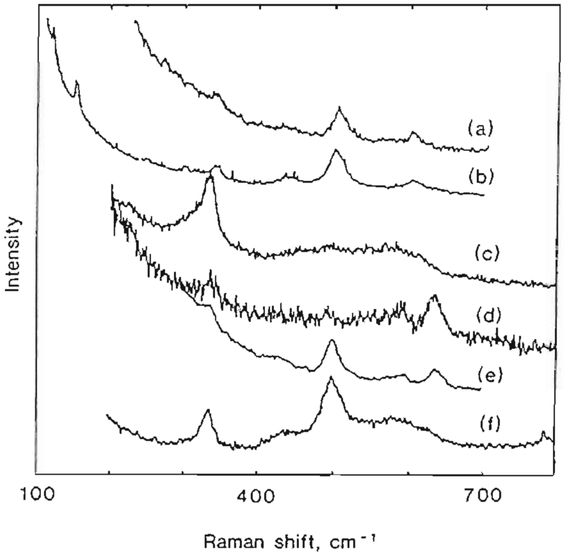

FIGURE 1
Raman spectra of different YBaCuO samples, (a) polycrystalline ceramic, (b) polycrystalline film, (c) oriented film on $SrTiO_3$, and (d) single crystal. Spectra (e) and (f) show the results for a ceramic sample before and after removing a surface layer, respectively.

crystals or oriented films. We conclude that the lines at 145 and 334 cm^{-1} are modes of $Ag(\alpha_{xx})$ symmetry. The other modes observed in polycrystalline samples may be of $Ag(\alpha_{zz})$, B_{2g} or B_{3g} symmetry. The line at 640 cm^{-1} seen in the spectrum of the single crystal is probably due to the $BaCuO_2$ flux. Its appearance in the spectra from the surface of polycrystalline samples may indicate some corrosion (2), because it dissappeared after grinding. A comparison of persistent current data for the ring before and after grinding gave no indication that the surface layer showing the 640 cm^{-1} line yields enhanced superconductivity.

5. THEORY

The lattice dynamic calculations are based on a Born-von Karman model. Starting values for the force constants are taken from Ref. 7, corrected to account for the different bond lengths. The force constants have been slightly modified to fit the energy of most of the observed phonons. The results for the Raman active phonons are summarized in Table 1. The calculated normal coordinates (nc) show that for all A_g phonons the motion of the ions is along the c-axis. The phonon at 139 cm^{-1} describes the motion of Ba-ions, for the nc at 220 cm^{-1} the Cu2 ions move, the nc at 496 and 507 cm^{-1} reveal 02/03 ion motions, in phase and out of phase, respectively. The nc calculated at 602 cm^{-1} displays an 01 vibration between the Cu1/Cu2 ions. The B_{3g} mode at 424 cm^{-1} gives an antisymmetric motion of the 01 ions along the x-axis. These calculated modes give a possible interpretation of the experimental lines, although there are discrepancies in the energy and the selection rules of some modes. A complete discussion of these results will be given in Ref. 8.

TABLE 1
Comparision of calculated phonon lines and experimental results. The energies are given in cm^{-1}. The symmetry of the normal coordinates are indicated above the rows.

Exp	A_g	B_{2g}	B_{3g}
		92	93
145	139	167	169
	221		
335		353	
435			424
500	497/507	508	512
600	602	693	698

6. SUMMARY

We have shown the Raman results of various samples. Additional measurements of the superconducting properties of the samples helped to identify the lines which most probably display phonons of the superconducting phase. The lattice dynamical calculations can describe the experimental results. The discrepancies between theory and experiment may display the simplifications of the model.

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