Micro-Raman Spectra of YBaCuO Superconductors

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A systematic study of the Raman spectra of Y-Ba-Cu-O superconducting materials under different experimental conditions clarifies the controversial results given in the literature. Under the determined conditions and thanks to the micro-Raman technique, reproducible polarized Raman spectra can be obtained and a coherent assignment can be suggested for $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$. For $YBa_2Cu_3(O/F)_7$, the introduction of fluorine atoms was found to be localized in pyramidal CuO units rather than in CuO chains.

I. INTRODUCTION

Since the discovery of Y-Ba-Cu-O materials exhibiting superconductivity at nearly 93 K, febrile activities have been manifested in many fields. We attend to a burst of research works circulating in the form of preprints which are as much an authority as any printed papers in well established journals.

Chu's materials Y-Ba-Cu-O[1] have been easily reproduced and their macro--physical properties have been reconfirmed and extended[2]. But things are going perhaps too fast. This high competition for publishing is certainly a good thing; nevertheless, we must be careful.

Many papers are concerned with Raman spectroscopy but generally the reported spectra differ from one author to another[3-17]. As Raman spectroscopy is well known to be a very accurate technique which allows investigating down to the molecular and sub-molecular scales[18-22], one can ask what is going wrong.

In this paper, we try to find an explanation for this apparent inconsistency by studying, under variable experimental conditions, the Raman spectra of $YBa_2Cu_3O_{7-\delta}$, $YBa_2Cu_3O_{7-\delta}F_{0.1}$ and $EuBa_2Cu_3O_{7-\delta}$ using micro-Raman spectro-

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scopy, this technique being able to give the Raman spectra of materials of micrometer size[23,24].

$MBa_2Cu_3O_{7-\delta}$ (M = Y, Eu; $\delta = 0.2$) were prepared from appropriate amounts of barium carbonate, rare-earth oxide (Y_2O_3 or Eu_2O_3) and copper oxide. The finely ground mixture was heated for 20 hours in air at 950 °C, then quenched and re-ground. Pellets of 8 mm diam. were pressed and sintered at 950 °C for 2 hours and finally heated at 450 °C for two days.

A phase containing a small amount of fluorine was also prepared in the same way starting from the following mixture: 1.95 $BaCO_3$, 0.05 BaF_2, 1.5 Y_2O_3 and 3 CuO. As barium fluoride is very stable, it can be assumed that there is no hydro-lysis and that the composition is close to $YBa_2Cu_3O_{7-\delta}F_{0.1}$.

X-ray diffraction powder analysis was carried out on a diffractometer. D. C. resistivity measurements versus temperature were performed using the standard four probe method. The Raman spectra were recorded at room temperature on a micro-Raman spectrometer DILOR/OMARS using an ion argon laser source Spectra--Physics emitting at 514.5 nm, and a diode-array multichannel detector.

III. RESULTS AND DISCUSSION

$MBa_2Cu_3O_{7-\delta}$ and the related compounds exhibit »normal« macrophysical properties.

A — X-ray Diffraction Analysis

The X-ray diffraction analysis shows quite similar patterns to those previously reported and characteristic of the orthorhombic symmetry with the following cell parameters:

Compound	a (Å)	b (Å)	c (Å)	V_m (Å³)
$YBa_2Cu_3O_{7-\delta}$	3.83	3.88	11.71	174
$YBa_2Cu_3O_{7-\delta}F_{0.1}$	3.82	3.88	11.66	173
$EuBa_2Cu_3O_{7-\delta}$	3.86	3.87	11.71	175

Replacement of yttrium by europium slightly increases the unit cell volume while a decrease is observed for the fluorinated compound, as expected from the difference in ionic radius sizes[25].

B — Resistivity Measurements

Typical resistivity measurements for YBaCuO and YBaCuOF are shown in Figure 1. The superconducting transition temperatures are, respectively, 90.6 K and 89.3 K (zero-resistance T_c) in very good agreement with previous results[2].

The introduction of a small amount of F ions does not affect significantly the T_c value but increases somewhat the resistivity of the sample above T_c. This can be explained by the higher electronegativity of fluorine as compared to oxygen, which increases the electronic localization. Higher concentrations of fluorine lead to multiphase materials which become insulators. In the course of this work, Ovshinsky et al. reported Y-Ba-Cu-O-F materials with
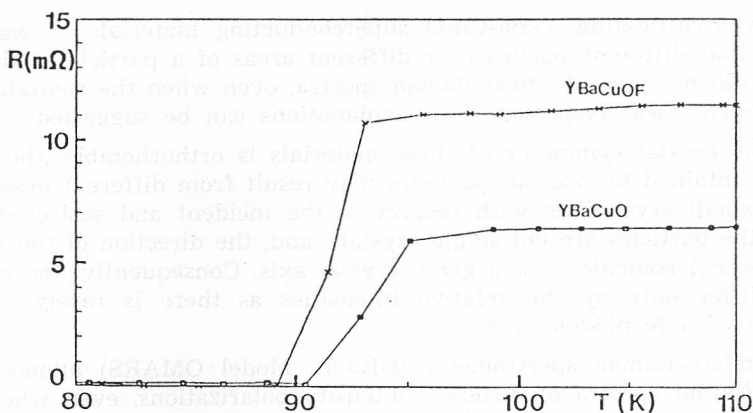
Figure 1. Resistance vs. temperature measured at a constant current of 10 mA for $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}F_{0.1}$.

large amounts of fluorine, showing very high superconducting temperatures[26]; these results do not seem to be reproducible.

Eu-Ba-Cu-O compound shows a superconducting state under 90 K, again in agreement with previous results[27].

C — Raman Spectroscopy

It should be noted, as we have already mentioned, that all the spectra previously reported are different although they are concerned with supposedly identical materials, this identity being actually supported by the fact that the macro-physical properties, i. e. resistance vs. temperature, magnetic properties, etc. are quite similar.

1 — Influence of Laser Source Power

Our samples have been illuminated with different laser source powers for obtaining Raman spectra. It was observed that the obtained Raman spectra depend strongly on the source power used. This means that the structure of these superconducting materials is very sensitive to the laser beam and may drastically change. This can be due to a local increase of temperature or to photo-induced chemical changes. To obtain reproducible Raman spectra, the illuminating laser reaching the sample must be always kept lower than 2 mW.

2 — Hetero-domains

Thanks to the micro-Raman technique, a spatial selectivity is possible. Instead of sending the laser beam directly onto the sample as in normal Raman investigations, the incident beam is directed through an optical microscope before reaching a limited area of the sample surface and then, the back-scattered beam can be collected into the monochromator of a classical Raman spectrometer. In this way, Raman spectra of sample areas as small as 1 μm^2 can be obtained; the size of these areas is only limited by the wavelength of lasers commonly used (0.3—0.8 μm).

When investigating Y-Ba-Cu-O superconducting materials, it was often observed that different particles, or different areas of a particle of the same material, did not give identical Raman spectra, even when the reproducibility of experiments was respected. Two explanations can be suggested.

As the crystal symmetry of these materials is orthorhombic, the Raman spectrum obtained for various particles may result from different orientations of these small crystallites with respect to the incident and scattered lights. Usually, the particles are not single crystals, and, the direction of the incident beam does not coincide with a given crystal axis. Consequently, the obtained spectra differ only by the relative intensities as there is rarely complete extinction of a forbidden mode.

The micro-Raman spectrometer (DILOR, Model OMARS) allows one to record different spectra of different intensity polarizations, even when scanning at different areas on the same surface of the sample. These results are in agreement with recent electron microscopy investigations[28,29], showing that a common feature of the orthorhombic Y-Ba-Cu-O phases is the existence of twin domains.

As the spatial resolution used was 0.4 μm, the size of these hetero domains can be evaluated as 0.16 μm² and larger.

3 — Heterogeneity

For some samples, the spectra appear too different from one to the other to be considered as issued from the same chemical entity.

As the Raman spectrum is directly connected to the local structure of the illuminated area or volume, it should be admitted that some of the micro-Raman spectra do come from different »chemical species«. We must admit the existence of heterogeneity in many samples.

This heterogeneity could come from the existence of defects involving oxygen over- or sub-stoechiometry in the superconducting materials.

All these reasons explain the previous controversial results.

When avoiding all these unconveniences, and thanks to the micro-Raman technique, the Raman spectra of micro-single crystals of superconducting materials can be obtained.

4 — Micro-Raman Spectra of Micro-Single Crystals

Small particles of Y-Ba-Cu-O, Eu-Ba-Cu-O and Y-Ba-Cu-O-F were first selected under an optical microscope to present planar surfaces.

The regularity was then checked by Raman spectroscopy: various spots on the same surface might give the same Raman spectrum with the same relative intensity for all bands.

— As the orientation of the crystal is not known, the first configuration may be fixed by the total extinction of at least one Raman band; the spectrum is then recorded. The other configuration is obtained by rotation in relation to the previous one. When changing the particle, research on Raman intensity extinction of other band(s) will lead to other and remaining configurations.
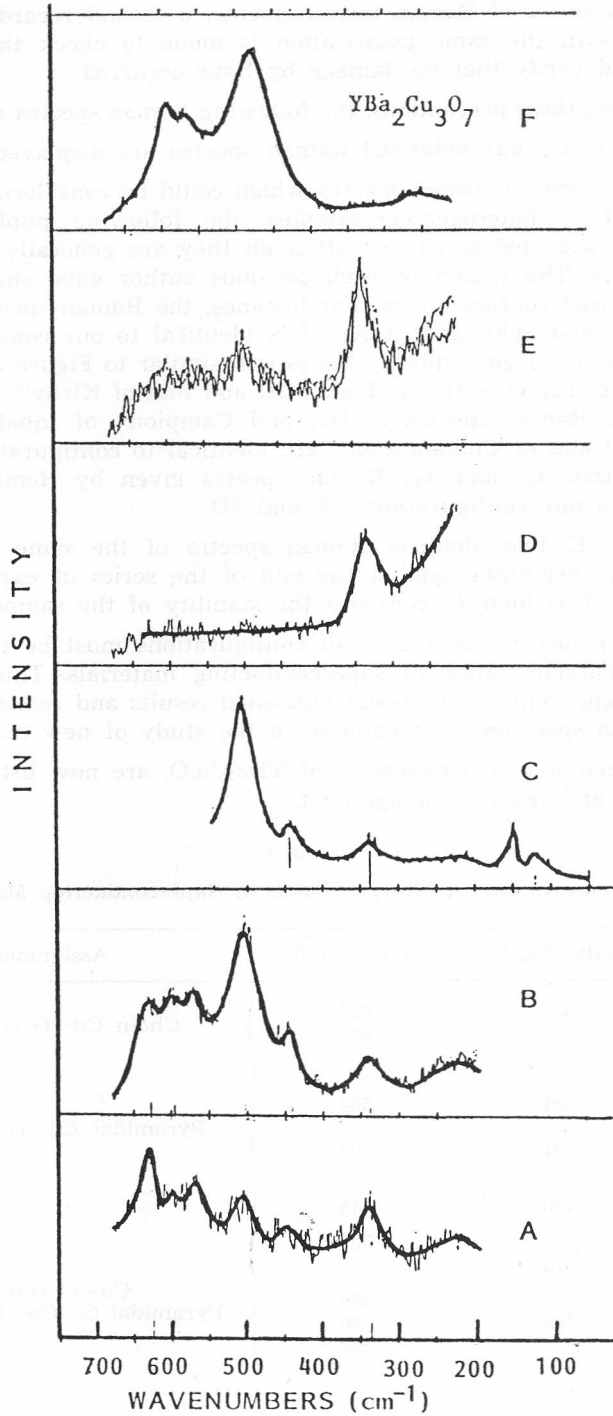
Figure 2. Polarized Raman Spectra from different configurations of single crystals of YBa$_2$Cu$_3$O$_7$.

— After a series of Raman measurements, a second record on the same repered spot with the same polarization is made to check the stability of the sample and verify that no damage by laser occurred.

When taking these precautions, the following Raman spectra were obtained.

For $YBa_2Cu_3O_{6.8}$, our polarized Raman spectra are displayed in Figure 2.

Except for some published spectra which could be considered as resulting from damaged or heterogenous samples, the following published Raman spectra can be accepted as correct although they are generally different one from the others. The reason is: each previous author gave only one or un-complete polarized configurations. For instance, the Raman spectrum of Mac-Farlane, Rosen and Seki[8] and of Krol[13] is identical to our configuration 2C,; that of Liu[11] is not of good quality but is still similar to Figure 2C, while that of Yamanaka[5] coincides with our Figure 2D and that of Kirby[15] is the same as 2B. Again, the Raman spectra of Dai and Campion[6], of Iqbal[7], of Rosen[10], of Kourouklis[14] and of Chrzanowski[16] are identical to configuration 2A, while the two polarized α_{ZZ} and α_{XY} Raman spectra given by Hemley and Mao[4] are identical to our configurations 2F and 2D.

In Figure 2E, two identical Raman spectra of the same configuration, recorded at the beginning and at the end of the series of experiments, are super-imposed. This identity confirms the stability of the sample.

Thus, the polarized spectra of all configurations must be taken into ac-count for a characterization of superconducting materials. This result helps to clarify the apparent controversial published results and restores confidence into the Raman spectroscopy technique in the study of new materials.

The obtained Raman frequencies of $YBa_2Cu_3O_7$ are now listed in Table I with a partial and tentative assignment.

TABLE I

Frequencies (in cm^{-1}) of Raman Bands of Superconducting Materials

$YBa_2Cu_3O_7$	$EuBa_2Cu_3O_7$	$YBa_2Cu_3(O/F)_7$	Assignments
632	635	635	Chain Cu—O stretchings
		625	
592			
	581	584	Pyramidal Cu—O stretchings
513			
501	501	502	
492			
	450	445	
337		337	
	313		
		298	Cu—O bendings
220	220	230	Pyramidal O—Cu—F stretchings
		210	
150			
118			

Figure 3. Polarized Raman spectra from different configurations of single crystals of
EuBa$_2$Cu$_3$O$_7$.

For EuBa$_2$Cu$_3$O$_{7-\delta}$, different polarized Raman spectra are obtained by the micro-Raman technique, and given in Figure 3.

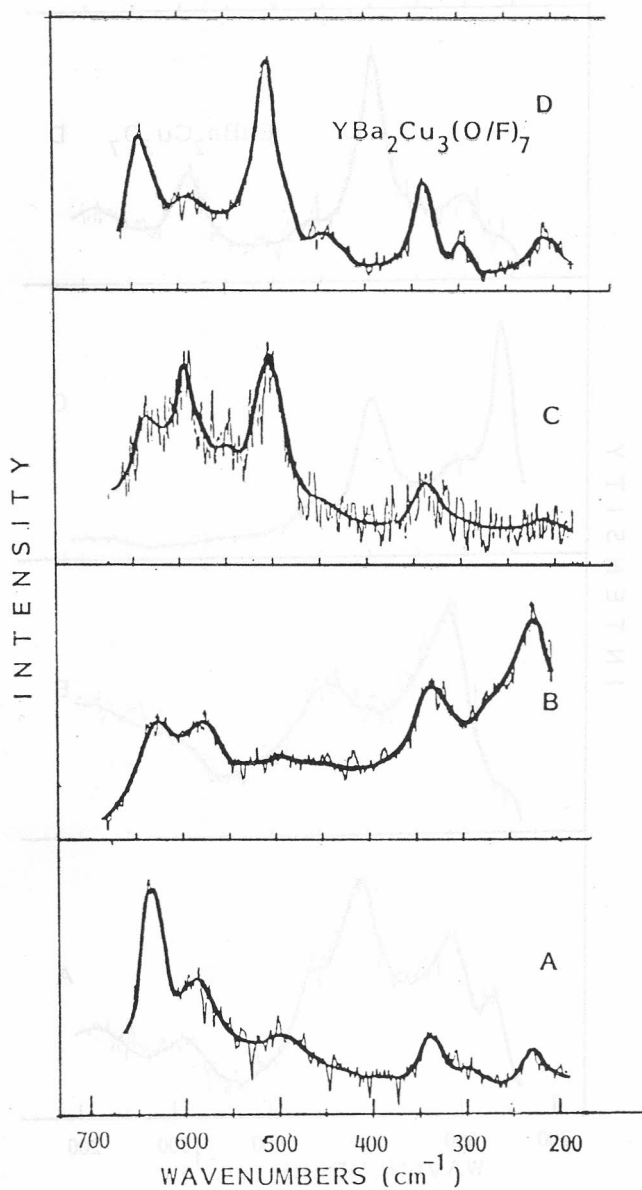No strong effect was observed by comparison to the Raman spectra of YBa$_2$Cu$_3$O$_7$. This is coherent of the assignment (Table I) that the observed

Figure 4. Polarized Raman spectra from different configurations of single crystals of $YBa_2Cu_3O_7F_{0.1}$.

bands are mostly due to Cu-O vibrations, as there is no oxygen in the Y or Eu planes.

Note that the Raman spectrum given by Batlogg and Cava[3] and by Liu[11] is identical to our configuration 3C; that of Cardona[12] could represent an intermediary orientation between 3C and 3D.

For $YBa_2Cu_3O_{7-\delta}F_{0.1}$, the introduction of some fluorine atoms seems to affect strongly the relative intensity of the Raman bands. A new band appears at 298 cm^{-1}. This could indicate that the fluorine atoms occur in the pyramidal CuO units rather than in CuO chains, as the latter vibrate at higher frequencies.

IV. CONCLUSION

Under well defined experimental conditions micro-Raman polarization spectra can be recorded for Y-Ba-Cu-O superconducting materials.

This systematical study makes it possible to explain the different Raman spectra presented by previous workers, to eliminate some others and to propose a coherent assignment.

Note added in proof. — Recently, having a homogeneous single crystal of $YBa_2Cu_3O_{6.5}$ with big size enough to allow the recording of the six Raman scattering configurations corresponding to an orthorhombic structure, Pmmm. We can thus identify spectra F, E, D and C in Figure 2. respectively to configurations $X(ZZ)\overline{X}$, $Y(XX)\overline{Y}$, $X(YY)\overline{X}$ and $Y(ZX)\overline{Y}$, while spectra B and A are due to twinned solid and can be considered as linear combinations of the previous spectra. A new band around 50 cm^{-1} in configurations $X(YY)\overline{X}$ and $Z(XY)\overline{Z}$ (Figure 5) is also observed.

By using the exciting line 488 nm, bands at 593 and 570 cm^{-1} in polarization ZZ and at 592 and 635 cm^{-1} in polarization XX and YY are strongly enhanced (Figure 6). This resonance Raman effect also suggests the presence of O_2^-, as its stretching vibration is expected in this frequency range.

Finally, we can assign the bands at 594, 548, 474—503 cm^{-1} (the frequency of this band depends on the amount of oxygen in the material), 154 and 117 cm^{-1} can be assigned to A_g phonon modes while the bands at 635, 586, 457, 342, 145 and 50 cm^{-1} to phonon of B_g symmetries.

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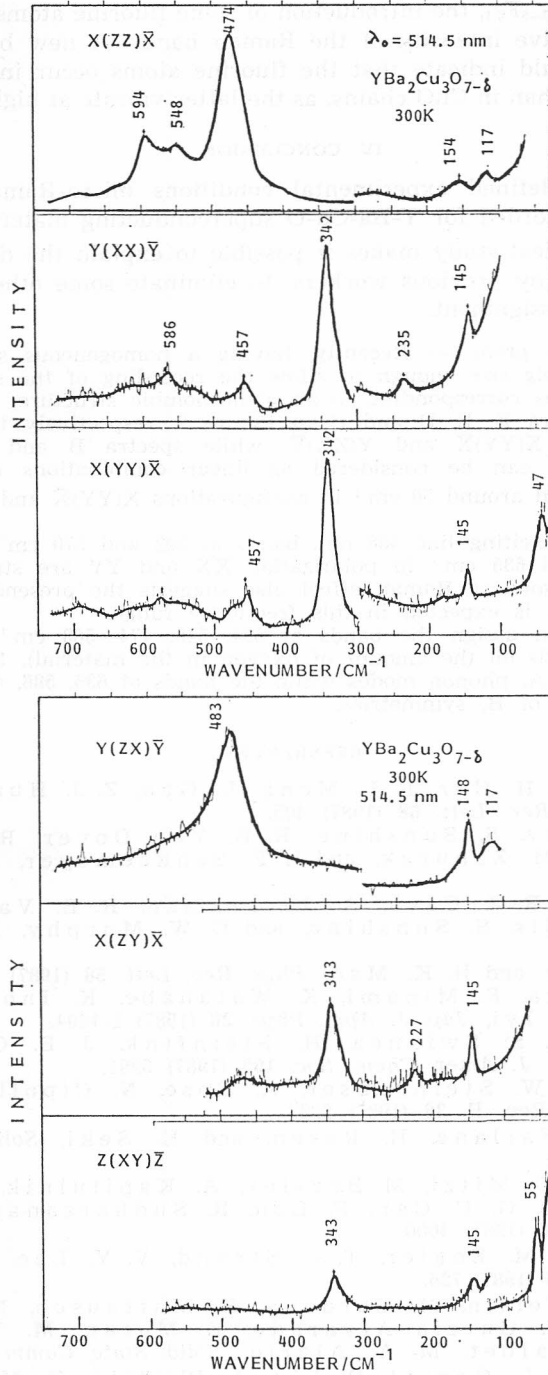
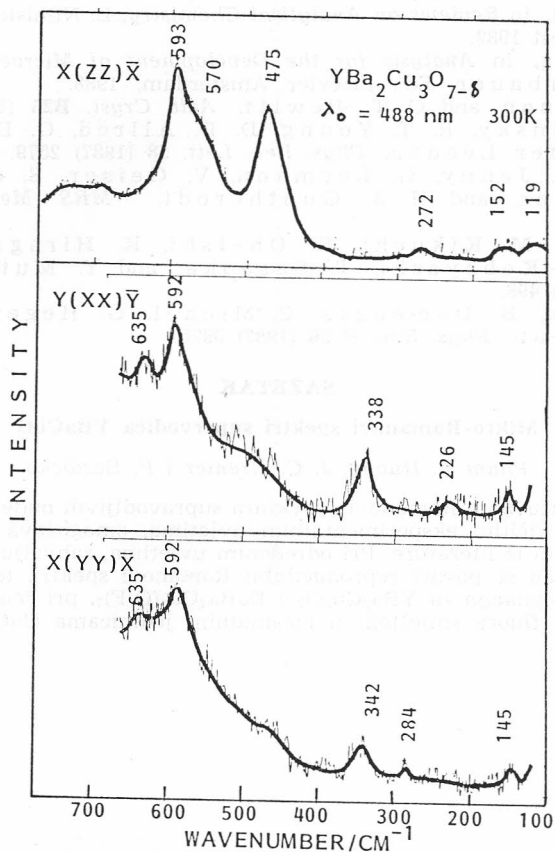Figure 5. Raman spectra of a single crystal of $YBa_2Cu_3O_{6.5}$ excited with 514.5 nm laser.

Figure 6. Raman spectra of a single crystal of $YBa_2Cu_3O_{6.5}$ excited with 488.0 nm laser.

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SAŽETAK

Mikro-Ramanovi spektri supervodiča YBaCuO

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Sustavno proučavanje Ramanovih spektara supravodljivih materijala Y-Ba-Cu-O, snimljenih pri različitim eksperimentalnim uvjetima, omogućava objašnjenje kontroverznih rezultata iz literature. Pri određenim uvjetima, zahvaljujući mikro-Ramanovoj tehnici, mogu se postići reproducibilni Ramanovi spektri, te se može predložiti koherentna asignacija za $YBa_2Cu_3O_7$ i $EuBa_2Cu_3(O/F)_7$, pri čemu je utvrđeno da su uvedeni atomi fluora smješteni u piramidnim jedinicama CuO, prije nego li u lancima CuO.