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LETTER TO THE EDITOR

Normal state charge redistribution as determined by the Raman scattering from orthorhombic and tetragonal single crystals of $YBa_2Cu_3O_{7-\delta}$

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Abstract. A polarised Raman study of $YBa_2Cu_3O_{7-\delta}$ single crystals revealed significant changes of light scattering anisotropy with reducing oxygen content. Strongly (y, y) and (x, x) polarised scattering from free carriers and its coupling with the phonon system (Fano interference) are characteristic for the orthorhombic crystal ($\delta \simeq 0$). In contrast, in the tetragonal crystal ($\delta \simeq 0.8$) enhanced continuum scattering and asymmetry lines were observed only in the tetragonal (z, z) polarisation. These findings are attributed to the reduction of free carriers in the xy CuO_2 planes due to chains-to-planes charge redistribution initiated by the decreased oxygen concentration.

The electronic light scattering of superconducting $YBa_2Cu_3O_{7-\delta}$ single crystals manifests itself through an anisotropic background continuum which exhibits interference with the 118 and 335 cm^{-1} vibrational modes [1, 2]. The existence of electronic scattering in (x, x) and (y, y) polarisation geometries correlates with the fact that the charge carriers (holes) are distributed within the O2–Cu2–O3 planes [3]. The stronger scattering in (y, y) polarisation provides evidence that the Cu1–O4 chains along the b axis also influence the scattering process as well [1].

It has been recently suggested [4] on the basis of the step-like stoichiometric dependence of some bonding lengths and interatomic distances that the electronic charge transfer from chains to the planes plays a significant role in the suppression of superconductivity in oxygen deficient $RBa_2Cu_3O_{7-\delta}$ compounds ($0 < \delta < 1$). According to the picture described in [4], the removal of O4 atoms gives excess electrons which still stay on the Cu1–O4 chains at low δ. With increasing δ the capacity of Cu1–O4 chains to hold charge is exhausted and electron transfer from the chains to the planes begins. The net effect of this mechanism is a reduction of the hole concentration in the pyramidal planes. Another experimental proof for charge redistribution in the CuO_2 planes of $RBa_2Cu_3O_{7-\delta}$ (R = Er, Ho; $0 < \delta < 1$) has been obtained by means of neutron crystal-field spectroscopy [5].

The charge redistribution should affect both the phonon and electronic scattering. In particular, the asymmetry (the Fano line shape) of the Raman line at 339 cm^{-1} (B_{1g}) is lost in the tetragonal phase [6, 7] and it could be attributed to the strong reduction of the free carrier concentration in the Cu2–O2, 3 planes. It should be noted that no conclusions about the existence of a (z, z) polarised electronic continuum (arising from interband excitations [2]) could be drawn in this case as the B_{1g} phonon is not seen in

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(z, z) polarisation. Fano interference in (z, z) polarisation has been reported in [8] for the Raman line at 470 cm^{-1} (A_{1g}) in tetragonal $YBa_2Cu_3O_{7-\delta}$ under high density excitations and has been ascribed to photo-induced carriers.

In this work we present results of a study of the Raman spectra of single crystals of $YBa_2Cu_3O_{7-\delta}$ in both orthorhombic and tetragonal phases and demonstrate that drastic changes in the anisotropy of the electronic scattering and the phonon line intensities take place with reducing the oxygen content. This is in agreement with the concept of chains-to-planes charge redistribution and reveals new possibilities in the study of the electronic properties of high temperature superconductors.

The orthorhombic single crystals $YBa_2Cu_3O_{7-\delta}$ ($\delta \simeq 0$) were grown by a method similar to that in [9]. The critical temperature T_c was determined from the dependence of the complex AC magnetic susceptibility on temperature upon warming. The crystal used for the Raman measurements ($T_c = 89$ K) was a square-shaped thin platelet ($800 \times 800 \times 30\ \mu m^3$) presenting (001) faces twinned according to the (110) twin law [10]. The twinning was easily observed under a polarising microscope, the typical width of the untwinned regions being 10–20 μm. Larger untwinned regions (up to 100 μm) also existed. The angle between the twin borders and the crystal edges was 45°; thus the edge direction coincided with the a or b axis, the thin side surface of the crystal being (100) or (010), depending on the twin under consideration. Taking the signal from spots within the untwinned stripes on (001), (010) or (100) surfaces we were able to measure the Raman spectra in (x, x), (y, y), (x, y), $(x + y, x - y)$, (z, z) etc scattering configurations. The a and b crystalline axes were identified by the stronger scattering background in the (y, y) spectrum [1].

For the study of the tetragonal phase a piece with dimensions $800 \times 300 \times 30\ \mu m^3$ was cut from the original crystal and was annealed in vacuum for 6 h at 700 °C. After the thermal treatment the twinning disppeared and the Raman spectrum measured on a fresh cut surface coinciding with the (100) plane was the characteristic one for tetragonal phase. The oxygen deficiency δ was estimated from the empirical linear dependence $\delta \simeq (502 - \omega')/27$ [11], where ω' is the position of the phonon line near 500 cm^{-1}. It should be noted that δ varied within the range $0.5 \leqslant \delta \leqslant 0.9$ depending on the distance from the anealed surface.

The Raman spectra were measured at room temperature using a Microdil 28 (Dilor) optical multichannel spectrometer equipped with a microscope (objective ×100). Improved software for data acquisition and processing [12] was used as a very effective means of detecting extremely weak signals. The laser beam was focused on a spot of 1 to 2 μm^2 and the laser power ($\lambda_L = 514.5$ nm) was kept below 3 mW. The plasma lines were rejected by means of a filter–monochromator combined with an interference filter.

Figure 1 shows the polarised Raman spectra of the original orthorhombic single crystal. The (x, x) and (y, y) spectra are almost identical to those of [1, 13]. The lines at 112.5 cm^{-1} and 337 cm^{-1} exhibit asymmetric Fano line shapes in (y, y) and to a lesser extent in (x, x) polarisation. Note that the line at 147 cm^{-1} assigned to the Cu2 breathing mode is very weak and seems to have opposite asymmetry to the former lines. The continuum scattering is stronger in (y, y) polarisation, where a line at 232 cm^{-1} is observed as well. In (z, z) polarisation the well pronounced low frequency lines emerge at 117.5 cm^{-1} and 149 cm^{-1} and have symmetrical profiles as clearly seen from figure 1(*a*).

The spectral weight of the electronic scattering (background) varies for different polarisation geometries, as is clearly displayed in figure 1, being strong in (y, y), but weaker or absent in (x, x) and (z, z). On the other hand, the observed Fano interference

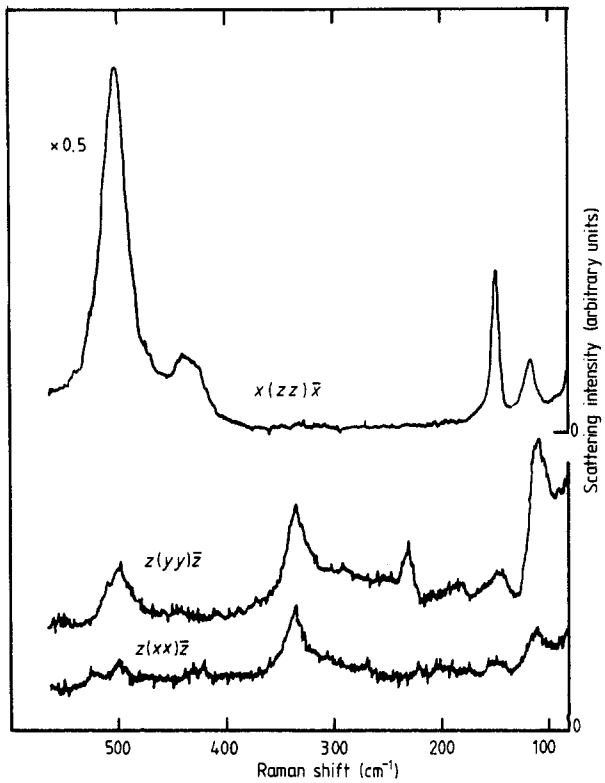

Figure 1. Polarised Raman spectra of orthorhombic single-crystal $YBa_2Cu_3O_{7-\delta}$ ($\delta \simeq 0$) at room temperature. Note that the upper spectrum is twice reduced. The (z, z) and (y, y) and (x, x) spectra are taken within the single twin strip. The laser power ($\lambda_L = 514.5$ nm) was 3 mW.

of phonon lines and the electronic continuum is a probe for the electronic scattering strength as well. Since the Raman active modes in $YBa_2Cu_3O_{7-\delta}$ are non-polar, the symmetric profile of the phonon lines in (z, z) polarisation for the orthorhombic phase gives a unique experimental method for comparing the Raman features of bare phonons and phonons coupled with the electronic continuum. The Fano line shape can be described [14] by the expression

$$I(\omega) = I_0(q + \varepsilon)^2/(1 + \varepsilon^2) \qquad \varepsilon = (\omega - \omega_0)/\Gamma \tag{1}$$

where I_0 is a scaling factor, ε is the reduced frequency, Γ is the width of the line and q is the Breit–Wigner–Fano coupling coefficient which accounts for the asymmetry of the observed line shape. From (1) it follows that for $\varepsilon = -q$, the phonon line has an antiresonance character. A negative value of q gives the antiresonance (or steeper decrease) at higher frequency than the central one at ω_0, while the positive sign of q determines an opposite asymmetry. Thus the lines at 112 cm^{-1} and 337 cm^{-1} are characterised by $q < 0$ while for the line at 147 cm^{-1}, $q > 0$ holds. The parameter q can be expressed [14] as

$$q \simeq T_p/VT_e \tag{2}$$

where V is the interband matrix element of the electron–phonon interaction between

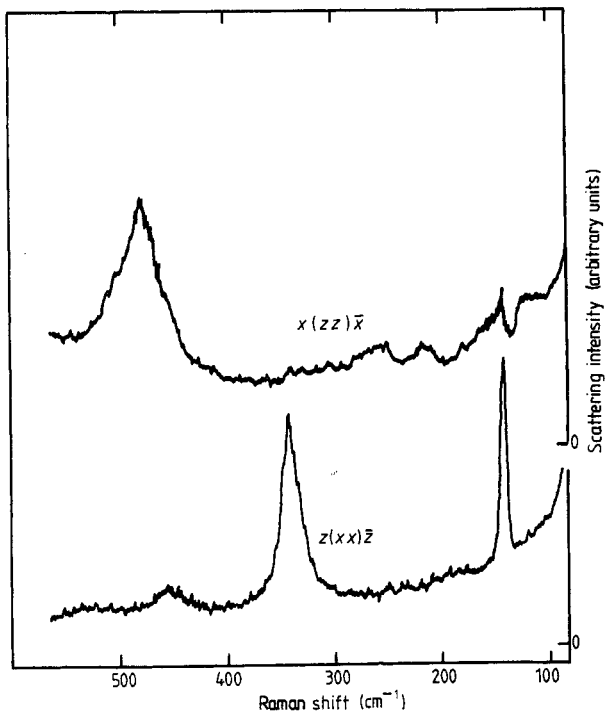

Figure 2. Polarised Raman spectra of tetragonal $YBa_2Cu_3O_{7-\delta}$ ($\delta \simeq 0.8$) at room temperature. The sample was obtained from the original orthorhombic crystal after annealing at 700 °C in vacuum for 6 h. The experimental conditions are the same as for the spectra of figure 1.

the states that contribute to the interference, and T_p and T_e are the scattering amplitudes for the decoupled phonon and electronic continuum respectively. The scattering amplitudes are proportional to the Raman polarisability (components of the Raman tensor). Taking into account that the sign of VT_e is conserved for the whole Raman spectrum, from (2) one can conclude that the Raman polarisability of the phonon at 147 cm^{-1} has an opposite sign to those for the phonons at 112 cm^{-1} and 337 cm^{-1}.

The above experimental findings are consistent with the existence in the orthorhombic phase of free carriers (holes) in the pyramidal planes (xy 'metallic' planes). Namely: (i) the effect of Fano interference are observed in (x, x) and (y, y) but not in (z, z) polarisation; and (ii) the phonon scattering intensities are reduced for incident polarisation along the x and y directions due to the lower penetration depth for the incident radiation.

With increasing oxygen deficiency δ (going from an orthorhombic to a tetragonal phase) the excess charge escapes, which in turn should affect both the interatomic distances and the polarisability. The latter implies that both the phonon frequencies and phonon intensities should be changed in the case of charge redistribution.

Figure 2 shows the polarised Raman spectra of the crystal converted to the tetragonal phase ($\delta \simeq 0.8$) after annealing in vacuum. The orthorhombic-to-tetragonal phase transition changes the Raman spectra significantly. In (x, x) polarisation the Ba line at 112.5 cm^{-1} disappears, whereas the Cu2 (140 cm^{-1}, A_{1g}) and the O2,3 out-of-phase

(341 cm^{-1}, B_{1g}) modes are strongly enhanced and exhibit a symmetrical line shape. The line at 450 cm^{-1} (which appears at 440 cm^{-1}, (z, z) polarised in the orthorhombic phase) is also seen in the (x, x) polarisation.

In the tetragonal (z, z) polarisation the continuum scattering is definitely present and the line shapes of the low frequency phonon modes are strongly modified. This concerns mainly the line near 140 cm^{-1} which decreases in intensity and becomes strongly asymmetric with a steeper decrease towards lower wave numbers, i.e. again characterised by $q > 0$ (figure 2). It is worth noting that the parameter q for the Cu2 phonon line does not change its sign with the orthorhombic-to-tetragonal phase transition. Since the removed O4 atoms are far enough from the Cu2–O2,3 atoms, no change of the sign of the Raman polarisability for the Cu2 phonon is expected. Thus from (2) it follows that the sign of the electronic continuum Raman polarisability does not change through the phase transition either.

In summary, it is plausible to accept that the changes of the Raman spectra in the orthorhombic-to-tetragonal phase transition are evidence for charge redistribution. In contrast to the orthorhombic phase, in the tetragonal (x, x) polarisation the electronic continuum is reduced and all phonon lines exhibit symmetrical line shapes. The enhancement of the 141 cm^{-1} and 341 cm^{-1} lines finds a natural explanation taking into account that the concentration of free carriers in the xy plane is strongly reduced. Electronic scattering and asymmetric lines are observed, however, in the tetragonal (z, z) polarisation configuration. In particular, the Cu(2) mode is of low intensity and strongly asymmetric line shape, similarly to what is found in the case of orthorhombic (y, y) polarisation.

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References

[1] Slakey F, Cooper S L, Klein M V, Rice J P and Ginsberg D M 1989 *Phys. Rev.* B **39** 2781–3
[2] Thomsen C and Cardona M 1989 *Physical Properties of High-Temperature Superconductors* ed D M Ginsberg (Singapore: World Scientific)
[3] Tarascon J-M, Barboux P, Miceli P, Greene L H, Hull G W, Eibschutz M and Sunshine S 1988 *Phys. Rev.* B **37** 7458
[4] Cava R J, Batlogg B, Rabe K M, Rietman E A, Gallagher P K and Rupp L W Jr 1988 *Physica* C **156** 523–7
[5] Furrer A and Allenspach P 1989 *J. Phys.: Condens. Matter* **1** 3715–20
[6] Cardona M 1989 *Proc. Ultrasonics International 89* (Guildford: Butterworth) at press
[7] Hadjiev V G, Iliev M N and Vassilev P G 1988 *Physica* C **153–155** 290–1
[8] Goncharov A F, Denisov V N, Mavrin B N and Podobedov V B 1988 *Zh. Eksp. Teor. Fiz.* **94** 321–7
[9] Schneemeyer L F, Waszczak J V, Siegrist T, van Dover R B, Rupp L W, Batlogg B, Cava R G and Murphy D V 1987 *Nature* **328** 601
[10] Hodeau J L, Caillout C, Capponi J J and Marezio M 1987 *Solid State Commun.* **64** 1349
[11] Feile P 1989 *Physica* C **159** 1–32
[12] Kalev L D 1989 *Diploma Thesis* Sofia University
[13] Thomsen C, Cardona M, Gegenheimer B, Liu R and Simon A 1988 *Phys. Rev.* B **37** 9860–3
[14] Abstreiter G, Cardona M and Pinczuk A 1984 *Light Scattering in Solids* vol 4, ed M Cardona and G Güntherodt (Berlin: Springer)