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Infrared-excited Raman scattering and photoluminescence of deep intragap states in semiconducting $YBa_2Cu_3O_{6+x}$

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The semiconducting parent compounds of the high-T_c superconducting system $YBa_2Cu_3O_{6+x}$, at low oxygen content ($0<x<0.25$) and different oxygen isotopes, have been investigated by means of infrared (IR) excited (1.16 eV) Raman scattering and photoluminescence (PL). The IR-excited Raman spectrum of the $YBa_2Cu_3O_6$ is dominated by a group of three bands in the spectral range of the apex oxygen O(4) A_g mode (475 cm^{-1} in the ^{16}O compound). The Raman spectrum changes dramatically upon oxygen doping with the appearance of a strong resonant band at 507 cm^{-1} accompanied by several overtones. By studying site-selective ^{18}O-isotope-substituted samples this band is assigned to A_g vibrations of apex O(4) atoms adjacent to the O(1) oxygen atoms occupying a chain site upon doping. The energy shift of this phonon and its associated overtones is caused by a strong lattice relaxation around the O(4)-Cu(1)-O(4) complex due to electronic charge-transfer processes involving O(4) sites. This behavior implies a strong coupling between O(4) vibration and charge-transfer excitations. PL, with a maximum at about 1.3 eV, has been observed in samples with very low oxygen concentrations. Peak energy and intensity are temperature and doping dependent. Both Raman and PL data are interpreted assuming the existence of a narrow band, associated with the O(4)-Cu(1)-O(4) complex (in $YBa_2Cu_3O_{6+x}$) which is located, for small x, within the CuO_2 plane charge-transfer gap.

I. INTRODUCTION

The study of resonant Raman scattering at different excitations frequencies allows clarification of important features of the electronic band structure and electron-phonon coupling in solids. Raman excitation profiles in $YBa_2Cu_3O_{6+x}$ were measured in the region of $1.8<\hbar\omega_L<2.7$ eV by Heyen *et al.*[1] Good agreement was found with Raman intensities calculated in the local-density approximation[2] for $x=1$, indicating that the electronic states of $YBa_2Cu_3O_7$ can be treated, at least in the high-frequency range, within the mean-field approach as for ordinary metals. However, electronic correlations are strong in the tetragonal semiconducting phase.[3] So far there is no reliable quantitative description of the metal-insulator transition in high-T_c oxides. Moreover, the origin of the insulating gap and the nature of the electronic states, filling the gap upon doping, are not clear. In this context, measurements of Raman spectra of the semiconducting phase, with laser excitation at photon energy lower than the charge-transfer gap (≈ 1.7 eV), can provide useful information. The first Raman spectra of $YBa_2Cu_3O_{6+x}$ ceramics ($x=0.15$, 0.3, and 0.85) exciting at 1.16 eV were reported in Ref. 4. The main spectral features were a strong band at 505 cm^{-1} with overtones at 1010 and 1515 cm^{-1} for $x=0.15$. This observation suggested the resonant nature of Raman scattering at 1.16 eV as well as a strong electron-phonon coupling.[4] In order to elucidate the nature of the electronic structure of $YBa_2Cu_3O_{6+x}$ at low oxygen doping we present in this paper new results of Raman scattering by exciting at 1.16 and 2.41 eV in $YBa_2Cu_3{}^{18}O_{6+x}$ and $YBa_2Cu_3{}^{16}O_{6+x}$ ceramics. Some preliminary results have been presented in Ref. 5. In the same framework we report also on near-infrared photoluminescence (PL). Both raman and PL data are accounted for by a model which assumes the existence of a narrow in-gap electronic band.

By site-selective oxygen-isotope substitution in the semiconducting $YBa_2Cu_3O_{6+x}$ we have unambiguously assigned the strong resonant Raman band at about 505 cm^{-1} to the A_g mode of the apex oxygen O(4) in the proximity of an occupied chain site. The appreciable shift of this mode, with respect to the unperturbed $YBa_2Cu_3O_6$, is a clear indication of the strong interaction of the apex oxygen atoms with electronic excitation. It is important to recall that several models that describe the coupling of correlated electrons to external degrees of freedom, such as the anharmonic vibration of the apex oxygen, have been proposed in order to explain the superconducting behavior of the high-T_c systems; for example, the model proposed by Bishop *et al.*[6] where the apex oxygen motion in a double-well potential coupled with a strong charge transfer is the source of superconductivity in the CuO_2 conducting plain. Moreover, it has been

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demonstrated that, within the Eliashberg theory, a double-well lattice anharmonicity can explain the anomalous oxygen isotope effect on T_c.[7]

Herein we would like to emphasize the importance of optical measurements in the semiconducting phase of high-T_c oxides, in particular, in the low doping regime, for the investigation of the interaction of individual carriers with lattice and magnetic excitations. In fact, one may expect that those interactions play a significant role in the superconducting properties of high-T_c materials.

II. EXPERIMENT

Ceramic samples of $YBa_2Cu_3O_{6+x}$ with different oxygen content and oxygen-isotope substitution are obtained by a three-step procedure monitored by a recording microbalance. A chemically homogeneous $YBa_2Cu_3{}^{16}O_n$ sample is prepared at 920 °C in flowing oxygen (100 cm^3/min) from high-purity Y_2O_3, CuO, and $BaCO_3$ powders. The product is pressed into pellets which are thereafter heated at 2 °C/min, annealed at 930 °C for 25 h, and cooled at 1.5 °C/min in flowing oxygen. The heating treatment is repeated with a shorter annealing time of about 10 h. Only those pellets which are free from hystersis of weight changes for the last circle were used. The final content of $n \approx 6.9$ is determined from the weight change of the synthesis and heating circles. The oxygen content is reduced afterwards to $n=6$ by heating at about 530 °C in vacuum. $YBa_2Cu_3{}^{16}O_6$ is annealed at about 530 °C in a static $^{18}O_2$ atmosphere at a prescribed initial pressure $P_i(^{18}O_2)$. After a sufficiently long annealing time (60 h) the composition $YBa_2Cu_3{}^{16}O_{n-z}{}^{18}O_z$ is obtained, where z is given by $z=(n-z)P_i(^{18}O_2)/P_f(^{16}O_2)$. The pressure $P_f(^{16}O_2)$ is determined by filling the closed apparatus with the same amount of oxygen which would be obtained by a complete O_2 evolution from $YBa_2Cu_3{}^{16}O_6$. This relation holds for pressures $P_i(^{18}O_2)$ greater than the decomposition pressure of $YBa_2Cu_3O_n$ above 350 °C. A coefficient $n=6+x$ with $0<x<1$ is obtained by annealing a $YBa_2Cu_3{}^{16}O_6$ sample at 530 °C in a static $^{16}O_2$ atmosphere at a pressure which results from the difference in the oxygen content assuming a complete evolutions from $YBa_2Cu_3{}^{16}O_6$ and $YBa_2Cu_3{}^{16}O_{6+x}$.

The difficulties in estimating accurately the oxygen content of the $YBa_2Cu_3O_{6+x}$ samples at very low doping levels and the impossibility of obtaining samples with exactly $x=0$ are well known. We conventionally label the oxygen content with $x=0$ and 0.05 to indicate two different levels of doping of our samples with very low oxygen content.

Infrared-excited Raman spectra have been performed in a backscattering configuration by means of an IFS 88 Bruker FT spectrometer equipped with the FT-Raman module at 4 cm^{-1} resolution. A diode-pumped c.w. Nd-YAG laser is used for excitation (1.16 eV). A cooled Ge detector allows us to collect the scattered radiation in a wide spectral range around the excitation energy (from 100 to 3300 cm^{-1} in the Stokes side and from 100 to 2100 cm^{-1} in the anti-Stokes side). To avoid heating and possible damaging effects due to absorption of the incident laser radiation laser power has been kept as low as possible (less than 25 mW within a spot of about 0.3 mm in diameter). The temperature estimated from the Stokes–anti-Stokes ratio of the main band at about 500 cm^{-1}, duly corrected for the response of the detector at both frequencies, was, in fact, about 300 K.

Raman spectra upon visible excitation have been recorded by means of a multichannel Raman spectrometer[8] in the grazing incidence geometry with 4 cm^{-1} resolution. The spectra have been obtained using a focused Ar^+-ion laser beam (2.41 eV) with 10 mW power in a spot size of 0.05×1 mm^2.

PL spectra in the range of 0.7–1.4 eV have been measured by a modified FT-Raman spectrometer exciting at 2.41 and 2.54 eV (Ar^+-ion laser). Samples have been kept at variable temperature (10–300 K) by using a continuous flow cryostat; the laser spot size was 2 mm in diameter and laser power was less than 5 mW. The PL measurements have been performed with a resolution of 8 cm^{-1}.

Because of the different penetration depths of the radiation in the visible and infrared regions the PL measurements are much more sensitive to surface conditions than the FT-Raman measurements. In fact, we have been able to observe PL only from freshly cleaved samples; after a few days the small surface contamination due to the interaction with oxygen in the atmosphere was sufficient to suppress PL.

III. RESULTS AND DISCUSSION

A. Raman scattering

The Raman-scattering spectrum of semiconducting $YBa_2Cu_3O_{6+x}$ dramatically depends on laser excitation energy. As an example IR (1.16 eV) and visible (2.41 eV) excited Raman spectra of $YBa_2Cu_3{}^{18}O_6$ are reported in Fig. 1. The IR-excited Raman spectrum [Fig. 1(a)] shows three strong bands at 387, 459, and 552 cm^{-1} which are absent in the visible excited spectrum [Fig. 1(b)]. At the same time the visible excited Raman spectrum is dominated by the 320 cm^{-1} band (340 cm^{-1} in $YBa_2Cu_3{}^{16}O_6$), which, on the other hand, is absent in the IR-excited Ra-

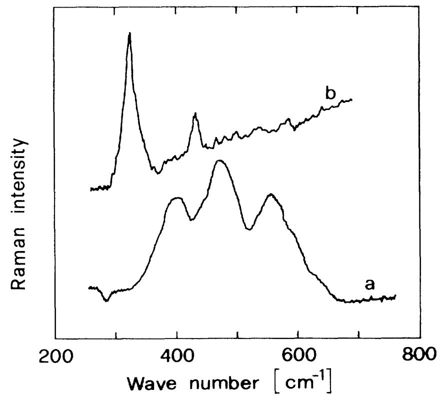

FIG. 1. Raman spectra of $YBa_2Cu_3{}^{18}O_{6.0}$ obtained (a) by exciting at 1.16 eV and (b) by exciting at 2.41 eV.

man spectrum. The latter band is usually present in Raman spectra of ceramics and crystals in the wide range of excitation energies from 1.8 to 2.7 eV.[1] Such behavior shows that the IR-excited Raman scattering is characterized by peculiar resonant conditions.

The oxygen doping dependence of the visible excited Raman scattering of $YBa_2Cu_3O_{6+x}$ is well known;[9] there is only a minor shift of the bands (less than 2 cm^{-1} at room temperature) and a small redistribution of their intensities by increasing the oxygen content from $x=0$ to 0.3. The same behavior has been confirmed by us in our samples. In contrast, the IR-excited Raman scattering exhibits spectral features which are strongly dependent on the oxygen content [see Figs. 2(a) and 2(b)]. The remarkable intensity of the bands observed in the IR-excited Raman spectrum, despite the adverse fourth-power dependence on frequency of the Raman cross section, indicates their resonance-enhanced nature. This observation suggests the presence of an electronic dipole transition deep inside the semiconducting charge-transfer gap. The origin of this transition will be discussed below (see Sec. III C).

A new resonant band appears at 477 cm^{-1} (in O^{18}-substituted samples) in the IR-excited Raman spectrum upon doping. For $x=0.2$ the peak at 477 cm^{-1} is the most intense [Fig. 2(b)], and its overtones are clearly observed. The inset of Fig. 2 shows the spectrum of $YBa_2Cu_3{}^{16}O_{6.05}$. All frequencies are shifted due to isotope substitution of oxygen. The peak at 507 cm^{-1} (477 cm^{-1} for ^{18}O) and its overtones are weaker.

The intensity of the 507 cm^{-1} band increases upon oxygen doping together with the associated overtones as shown in Fig. 3 for $YBa_2Cu_3{}^{16}O_{6.2}$. We conclude that the new doping induced band at 507 cm^{-1} (477 cm^{-1} in ^{18}O) is induced by the oxygen occupation of the O(1) chain sites in the basal plane (see Fig. 4).

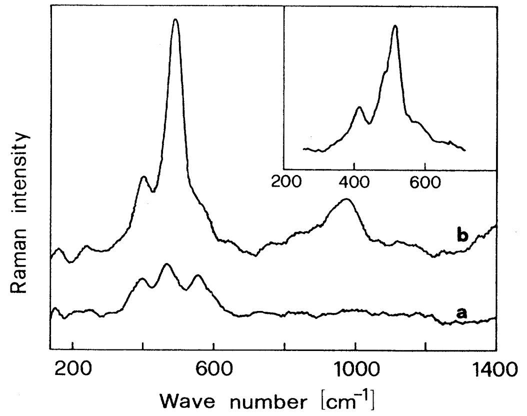

FIG. 2. FT-Raman spectra obtained by exciting at 1.16 eV of (a) $YBa_2Cu_3{}^{18}O_{6.0}$ and (b) $YBa_2Cu_3{}^{18}O_{6.2}$. The spectrum of $YBa_2Cu_3{}^{16}O_{6.05}$ is shown in the inset.

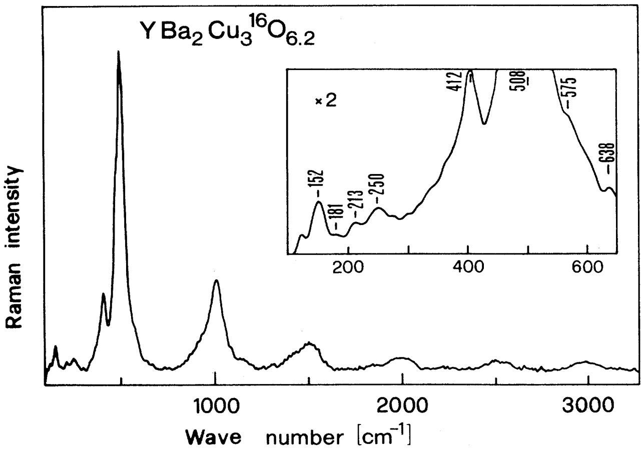

FIG. 3. FT-Raman spectrum exciting at 1.16 eV of $YBa_2Cu_3{}^{16}O_{6.2}$ (the spectrum is not corrected on detector response in order to emphasize the presence of overtones up to the sixth order). A blowup of the first-order phonon region is shown in the inset.

Upon further doping ($x>0.2$) the intensity of the whole IR-excited Raman spectrum decreases[4] suggesting less efficient resonance conditions due to a shift in energy of the resonant electron band. The frequency of the peak at 507 cm^{-1} is very close to the frequency of the A_g phonon mode of the O(4) atoms in the fully doped ($x=1$) system, and in a previous paper[4] it has been assigned to a vibration of the O(4) atoms in microscopic orthorhombic domains. In order to confirm this assignment we have performed site-selective isotope substitution of oxygen ^{16}O in $YBa_2Cu_3{}^{18}O_6$ by means of low-temperature annealing in air. The IR-excited Raman spectrum of pristine $YBa_2Cu_3{}^{18}O_6$ is shown in Fig. 5(a). Figure 5(b) shows the spectrum of the same sample after 30 min annealing at 200 °C in air. As expected, the spectrum changes with oxygen doping and a new peak at 477 cm^{-1} (ω_2^*) accompanied by a weak overtone ($2\omega_2^*$) appears. At this annealing temperature, oxygen ^{16}O (from the atmosphere) diffuses within the sample only in the basal plane but cannot jump in other oxygen sites occupied by ^{18}O atoms.[10] We notice that this new ω_2^* band at 477 cm^{-1} has the same frequency as the main band of the spectrum of the fully ^{18}O-substituted sample $YBa_2Cu_3{}^{18}O_{6+x}$ [Fig. 2(b)]. This confirms our assignment. In fact, chain sites are occupied after annealing by ^{16}O and therefore the doping induced band cannot be assigned to vibrations of oxygen atoms on chain sites because in this case we should have observed the band characteristic of ^{16}O which lies at 507

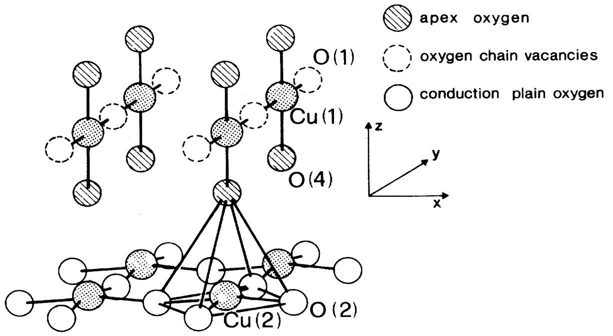

FIG. 4. Schematic representation of the crystal structure of conduction and basal planes in $YBa_2Cu_3O_{6+x}$.

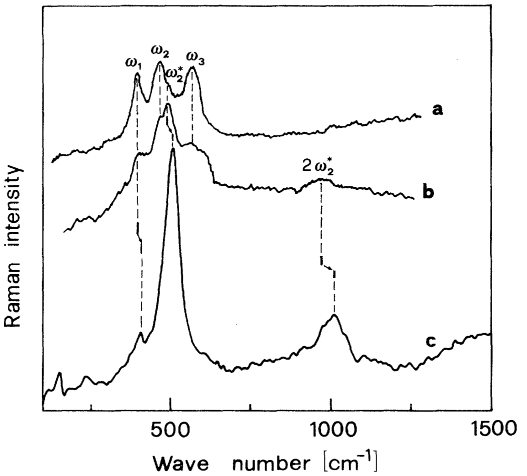

FIG. 5. FT-Raman spectra exciting at 1.16 eV of (a) $YBa_2Cu_3{}^{18}O_{6.0}$, (b) the same sample after 30-min annealing at 200 °C in air, and (c) the same sample after a second 60-min annealing at 300 °C in air.

cm^{-1}. A subsequent heat treatment of the sample is performed at 300 °C for 60 min. At this temperature O atoms in the O(1) sites may exchange with the ones in the near-neighbor apex O(4) sites. At the same time, as reported in Ref. 10, this temperature is not so high as to allow oxygen in CuO_2 planes to diffuse out. The IR-excited Raman spectrum shows a dramatic change [see Fig. 5(c)]. A shift towards higher frequencies of both the 385 (ω_1) and 477 cm^{-1} (ω_2^*) bands together with the ($2\omega_2^*$) overtone is clearly seen together with the increase in intensity of ω_2^* and $2\omega_2^*$. The similarities between the spectra of the annealed sample in Fig. 5(c) with the one of $YBa_2Cu_3{}^{16}O_{6.05}$ in the inset of Fig. 2 are clearly evident. The frequencies of the modes in both spectra do not exactly correspond because of an incomplete isotope substitution of ^{18}O on the apical site. The spectrum in Fig. 5(c) looks like the one of $YBa_2Cu_3{}^{18}O_{6.2}$ [see Fig. 2(b)] approximately shifted by 20 cm^{-1} to the higher energy. However, the band ω_3 observed in the pristine $YBa_2Cu_3{}^{18}O_6$ sample in Fig. 5(a) is absent in the spectrum of the same sample after the latter annealing [see Fig. 5(c)]; on the other hand, the band ω_3 is clearly seen as shoulder at 552 cm^{-1} in the spectrum of $YBa_2Cu_3{}^{18}O_{6.2}$ in Fig. 2(b). If this band is related to vibrations of oxygen atoms on apex sites, one should expect that the band at 575 cm^{-1}, which is seen in the spectrum of $YBa_2Cu_3{}^{16}O_{6.05}$ (see inset of Fig. 2), should be present also in the site-selective isotope substituted $YBa_2Cu_3{}^{16}O_x{}^{18}O_{6-y}$ in Fig. 5(c), at least as a shoulder. The absence of this feature at 575 cm^{-1} suggests its assignment to vibrations of oxygen atoms in CuO_2 layers which have not been isotope substituted during the annealing procedure. Thus, we conclude that all oxygen vibrational bands that appear in the IR-excited Raman spectra of $YBa_2Cu_3O_{6+x}$, with the exception of the highest-frequency 575 cm^{-1} peak (in ^{18}O samples), are assigned to phonons whose eigenvectors are mainly associated to apex oxygen atom displacements.

The resonance nature of the scattering suggests that the resonance electronic transition near 1 eV must involve $2p$-$3d$ electronic orbitals of the O(4)-Cu(1)-O(4) complex which, for $x=0$, seems to be weakly interacting with the CuO_2 planes due to the increased distance between planes and apex oxygen atoms. Our preliminary IR-excited Raman measurements on single crystals of $YBa_2Cu_3{}^{16}O_{6+x}$ ($x \approx 0$) show that the 412 and 507 cm^{-1} bands are observed only in the xx/yy polarization whereas the band at 475 cm^{-1} is seen in both xx/yy and zz geometries (the latter is always present in the Raman spectra excited by visible light and is more intense in zz geometry).

Site-selective oxygen-isotope substitution in the $YBa_2Cu_3O_{6+x}$ system therefore allows the bands observed in the IR-excited Raman spectra to be assigned. It is now widely recognized that the ω_2 band in the semiconducting samples ($x \approx 0$) is assigned to a totally symmetric (A_g) axial vibration of the apex oxygen.[1] We assign the ω_2^* band to an A_g vibration of apex oxygen atoms adjacent to occupied chain sites as discussed in more detail in Sec. III C.

The assignment of both the ω_1 and ω_3 bands is not so straightforward. These bands were not present in the visible excited Raman spectra. This means that these bands are very weak or not at all Raman active when out of resonance.

The best candidate for ω_1 (at 412 cm^{-1} in ^{16}O samples) is the Raman-forbidden IR E_u(LO) phonon calculated[11] at 414 cm^{-1} and found in reflectance measurements[12,13] near 420 cm^{-1}. According to calculations[11] this mode involves displacements of the apex oxygen atoms parallel to the CuO_2 planes. It is reasonable to assume that the LO component of the E_u mode becomes Raman active near resonance due to the Fröhlich electron-phonon mechanism[14] through the quadrupole therm. Other E_u(LO) modes, rather weak but reproducible, are also seen in the IR-excited Raman spectra. In the spectrum of $YBa_2Cu_3O_{6.2}$ shown in Fig. 3 (inset), at least three other peaks at 181, 250, and 638 cm^{-1} can be assigned to E_u(LO) modes which were observed, by infrared reflectance measurements,[12] at 199, 266, and 637 cm^{-1}, respectively. Confirmation of this assignment is given by the observation of the same four modes in $YBa_2Cu_3O_6$ when the red (1.82 eV) excitation light is used.[15]

We envisage at least two possible assignments for the ω_3 band at 575 cm^{-1}. The above-discussed isotope substitution shows that this band is related to the vibrations of oxygen atoms O(2) in the CuO_2 planes. Calculations[11] only predict one Raman-active mode close to 575 cm^{-1} in $YBa_2Cu_3O_6$ which is assigned to the E_g vibration at 577 cm^{-1} of the O(2) oxygen atoms. Another possibility for the assignment of the 575 cm^{-1} band is a defect-induced local vibration found in reflectance measurements (see Refs. 12 and 13), respectively, at 595 and 588 cm^{-1}. By comparing the calculated eigenvector of this mode (502 cm^{-1}) and the one of the E_u(LO) (414 cm^{-1}) vibration,[9] one can see that both have a similar mixed character. Therefore, its increased Raman intensity for

1.16 eV excitation may be caused by the admixture of the resonantly enhanced E_u(LO) mode near 412 cm^{-1}. Raman measurements on single crystals in *zx*, *zy* geometries may allow one to distinguish between these two possibilities.

B. Photoluminescence

We have observed midgap PL emission in insulating ceramic samples of $\mathrm{YBa_2Cu_3O_{6+x}}$ by exciting at 2.41 and 2.54 eV. The PL spectra obtained at both wavelengths are identical and rather weak. The PL intensity is much stronger at small oxygen doping near $x=0$. For samples with $x \geq 0.2$ no signal has been detected. As shown in Fig. 6, the intensity of low-temperature PL spectra decreases (note the scaling factors of spectra shown in the figure) and the PL maximum is shifted towards lower energies upon the increase of oxygen doping. The PL spectra of $\mathrm{YBa_2Cu_3O_{6.15}}$ at different temperatures are reported in Fig. 7. PL intensity increases at low temperatures and the maximum shifts towards higher energies; at liquid-helium temperature it is near the high-frequency limit of our detector sensitivity.

The observation of PL indicates the presence of a narrow band well inside the charge-transfer gap of semiconducting $\mathrm{YBa_2Cu_3O_{6+x}}$. We argue that the optical transition associated with this band be responsible for the observed resonant effect in the IR-excited Raman spectra. Since the PL is very weak, the dipole matrix element of this transition should be small. This is in agreement with the absence of a sharp intragap transition in optical absorption of $\mathrm{YBa_2Cu_3O_{6+x}}$ for $x \approx 0$.

In order to assign the PL spectrum observed in $\mathrm{YBa_2Cu_3O_{6+x}}$ we have studied PL of all materials which are usually present as impurity phases in YBaCuO. Only $\mathrm{Y_2O_3}$ exhibited luminescence near 1 eV. However, we exclude that $\mathrm{Y_2O_3}$ is responsible for the PL observed in our $\mathrm{YBa_2Cu_3O_{6+x}}$ samples. It would be difficult to explain the strong dependence of PL intensity on oxygen content (see Fig. 6) since $\mathrm{Y_2O_3}$ is a stable oxide which cannot be doped by oxygen. On the other hand, the observed doping dependence is rather natural for $\mathrm{YBa_2Cu_3O_{6+x}}$. The decreasing of PL intensity upon doping may be due to the opening of new radiationless processes mediated by doping induced electronic and hole levels inside the insulating gap which compete with radiative emission. The density of these levels increases with oxygen content. It should be mentioned that the temperature and doping dependences of all features in the PL spectrum are similar. This implies the same origin of these features confirming our interpretation of PL as an electronic transition (see Sec. III C).

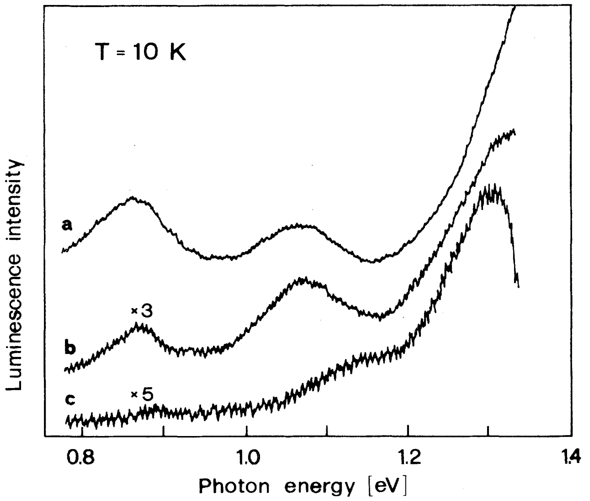

FIG. 6. Low-temperature (10 K) photoluminescence spectra by exciting at 2.41 eV of (a) $\mathrm{YBa_2Cu_3O_{6.0}}$, (b) $\mathrm{YBa_2Cu_3O_{6.05}}$ and (c) $\mathrm{YBa_2Cu_3O_{6.15}}$.

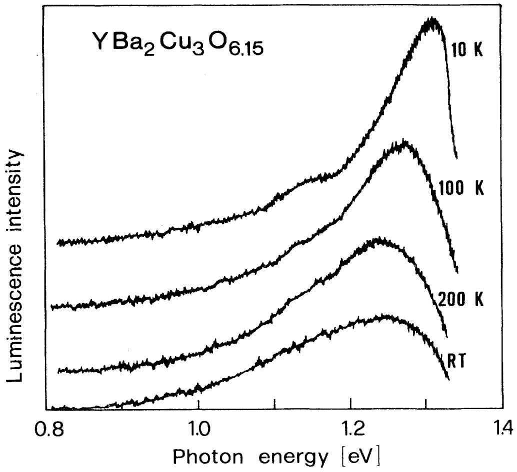

FIG. 7. Photoluminescence spectra of $\mathrm{YBa_2Cu_3O_{6.15}}$ exciting at 2.41 eV obtained at different temperatures.

C. Model

The resonant nature of the Raman scattering with laser excitation at 1.16 eV on insulating $\mathrm{YBa_2Cu_3O_{6+x}}$ is unambiguously proved by the high intensity of the observed Raman features, by their dramatic dependence on oxygen doping and by the appearance of overtones. One should expect that an insulating gap would provide opportunities for the appearance of narrow electronic states within the gap, which could be responsible for the resonant behavior of the Raman scattering. As shown in Ref. 16, impurity-induced localized electronic states inside the gap (midgap absorption) are present even at $x \approx 0$. It is extremely difficult to obtain samples with exactly $x=0$, and a small number of excess oxygen atoms in the basal plane sites acts as impurity giving rise to a broad electronic absorption band inside the gap. Such a broadband, however, cannot be accounted for by the interpretation of the resonant IR-excited Raman spectra, since only the 507 cm^{-1} vibrational band is strongly enhanced upon oxygen doping from $x=0$ to a higher oxygen content, while other resonance bands do not appreciably change their intensity. On the contrary, from our PL measurements we propose that a *narrow* electronic band already exists inside the semiconducting gap at $x=0$. At a higher oxygen content PL decreases monotonically in intensity.[17] The remarkable narrowness of the band observed in PL compared to the very broad midgap absorption caused by doping[16] strongly suggests that this band has an origin which is not connected with dopant oxygen atoms and that this narrow band is present inside the charge-transfer gap of $YBa_2Cu_3O_6$.

From currently available experimental data, Cu(1) sites at $x=0$ do not have a localized magnetic moment[18] indicating that these atoms are in the $3d^{10}$ state, unlike Cu(2) atoms which are in the $3d^9$ configuration. This also follows from high-energy spectroscopic measurements.[19] Hence, the band corresponding to the $3d^{10}$ state of Cu(1) is at least below the Fermi energy and therefore below the upper Hubbard empty $3d^{10}$ conduction band [see Fig. 8(a)]. The former band is narrow since it is weakly hybridized with electronic states of the planes from which the O(4)-Cu(1)-O(4) complexes are well separated at $x=0$. It has been shown in Ref. 19 that upon doping, holes initially appear on Cu(1) sites indicating that the Cu(1) $3d^{10}$ band is above the Cu-O plane valence band. Therefore, the assumption of the existence of a narrow band associated with the O(4)-Cu(1)-O(4) complexes inside the charge-transfer insulating gap seems to be quite reasonable. We can conjecture that the PL band is associated with a $3d^{10}$ configuration of Cu(1). We admit that such a rigid band proposal seems too crude. However, if the peak observed in PL is related to the same electronic transition giving rise to the resonance Raman effect, our conjecture gets stronger support.

The assumption of a narrow intragap band provides the clue to the understanding of resonance Raman scattering in the near infrared and PL. The latter is due to radiative recombination of excited electrons from the conduction band together with holes in the electronic band within the gap associated with Cu(1); more precisely this band is $O(4)p_z$-$Cu(1)3d_{(z^2-r^2)}$-$O(4)p_z$ antibonding orbital. From now on we will refer to this band as $Cu(1)3d^{10}$. A hole in the fully occupied $Cu(1)3d^{10}$ state (in $YBa_2Cu_3O_6$) can be generated through direct excitation of an electron from this band to the CuO_2 plane conduction band and/or through [path 1 in Fig. 8(b)] excitation of an electron from the valence band to the conduction band (valence and conduction bands are referred to the CuO_2 plane, i.e., to $O(2,3)2p$-$Cu(2)3d^9$ and $Cu(2)3d^{10}$ state, respectively) and the following migration of the hole to the $Cu(1)3d^{10}$ band. The latter possibility sketched in Fig. 8(b) seems to be more plausible since the PL is much weaker for excitation at 1.16 eV than at 2.41 eV. Also in $YBa_2Cu_3O_{6+x}$ there is no IR absorption[16] near 1 eV at small x. This means a small oscillator strength for electronic transitions from the intragap $Cu(1)3d^{10}$ band to the conduction band. Excited electrons on Cu(2)-O(2) planes are in an attractive Coulomb field of heavy holes on the O(4)-Cu(1)-O(4) complex. Due to this interaction, excitonic states appear near the bottom of the conduction band. These states provide a most effective channel for PL. The enhancement of PL near liquid-helium temperature is due to higher occupation of these states, and also less efficient radiationless transitions. The temperature dependence of the peak position in PL may be connected to contraction of the lattice, suggesting a strong dependence of the intragap state energy on the admixture of electronic orbitals of CuO_2 planes to this state.

In the ground state the intragap electronic band is occupied. Transitions from it to excitonic states below the bottom of the conduction band may account for the observed resonance effects in IR-excited Raman spectra of $YBa_2Cu_3O_{6+x}$, when x is close to zero [see Fig. 8(c)]. The strongest resonant Raman bands (*vide supra*) are associated with vibrations of O(4) oxygen atoms which are expected to couple most effectively with the electronic

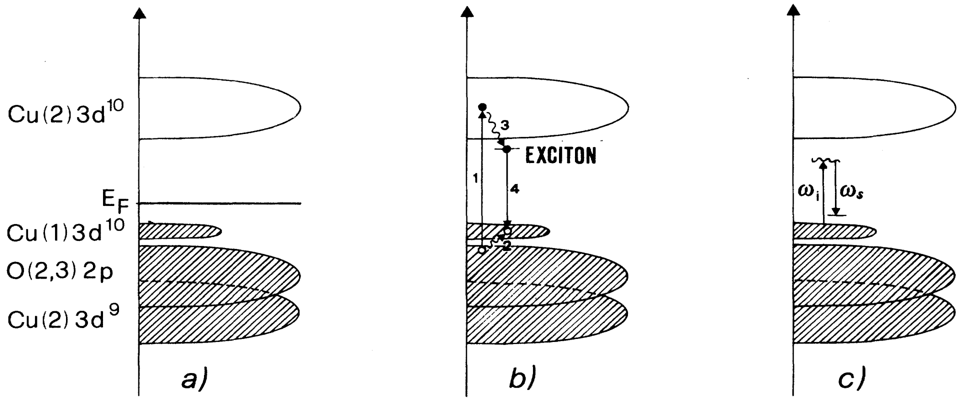

FIG. 8. (a) Illustration of the proposed band structure in $YBa_2Cu_3O_6$; the $O(2)2p$ and $Cu(2)3d^{10}$ bands are separated by a charge-transfer gap of 1.7 eV while the $Cu(1)3d^{10}$ and $Cu(2)3d^{10}$ are separated by a gap of about 1.3 eV. (b) Schematic representation of the luminescence process in $YBa_2Cu_3O_6$: (1) the incident photon generates an electron-hole pair; (2) the hole migrates from the valence band to the $Cu(1)3d^{10}$ band; (3) the electron, in Coulomb interaction with the hole in $Cu(1)3d^{10}$, forms an excitonic level below the bottom of the conduction band; (4) electron and hole recombine with the emission of one photon. (c) Schematic representation of the Raman scattering exciting at 1.16 eV in $YBa_2Cu_3O_6$ (ω_i is the incident photon; ω_s is the scattered photon).

states of the O(4)-Cu(1)-O(4) complex. Since the resonantly enhanced vibrational bands are observed in *xx/yy* geometry, the dipole matrix element for these transitions must be parallel to the *xy* plane. This means that excitonic states antisymmetric with respect to $x \rightarrow -x$ and or $y \rightarrow -y$ transformation are important.

A pronounced effect of this is the appearance of the ω_2^* vibrational band with overtones upon small doping. We have assigned this band *(vide supra)* to A_g vibrations of O(4) atoms in unit cells containing dopant oxygen atoms on O(1) chain sites. In these cells Cu(1) atoms are in the $3d^9$ configuration,[19] the same as in $YBa_2Cu_3O_7$ where this Raman band has been observed[9,20] near 500 cm^{-1}. Therefore, we may understand in this framework the shift on defect sites from 475 cm^{-1} in $YBa_2Cu_3O_6$ to 507 cm^{-1}. At first sight it seems that the sole effect of the oxygen atoms added to the O(1) sites is a donation of holes into the intragap band for $x \approx 0$. In this case the hardening of the O(4) A_g vibration directly follows from the fact that holes appear on the O(4)-Cu(1)-O(4) antibonding orbital. However, the oxygen atoms appearing on O(1) sites strongly distort the bonding configuration of Cu(1)-O(4) complexes. Nevertheless, it is reasonable to assume that we have defectlike electronic levels inside the gap induced by O(1) doping. In this case resonance transitions can involve these levels with a strong admixture of charge-transfer transitions of electrons from O(1) to Cu(1). It seems that these transitions strongly interact with the A_g O(4) vibrations leading to shifted positions of the O(4) atoms in the excited state. The appearance of strong overtones is associated with the reduction of selection rules due to the local distortion of the crystal associated with the random occupation of the O(1) site.

In connection with this strong coupling of O(4) vibrations to charge fluctuations on Cu(1)-O(4) a question arises: What is the situation in the metallic phase in $YBa_2Cu_3O_{6+x}$? It is not unreasonable to assume that the coupling between electronic and vibrational degrees of freedom leading to shifted position of O(4) atoms for different charged states of the Cu(1)-O(4) complex does not change drastically with doping from $x=0$ to 1. For slow enough charge fluctuations such an interaction may give rise in the ground state of the metallic phase to the appearance of double-well adiabatic potentials for O(4) atoms, each minimum of the well corresponding to different charged states of the Cu(1)-O(4) complex.[21] EXAFS measurements[22] have provided direct evidence of the existence of such a double-well potential for apex oxygen atoms in $YBa_2Cu_3O_7$ and have also shown that the splitting between the two minima and the fluctuation region near T_c are correlated. According to Refs. 6, 7, and 21 the existence of such an anharmonic potential can have a strong impact on superconducting properties of $YBa_2Cu_3O_{6+x}$ suggesting a crucial role played by apex oxygen vibrations in this oxide.[6,23–25]

IV. CONCLUSION

The Raman scattering of $YBa_2Cu_3O_{6+x}$ ceramics with 1.16 eV excitation, i.e., at energy lower than the charge-transfer gap of semiconducting samples with x close to zero have been studied. Resonantly enhanced vibrational bands have been observed. The strongest bands have been found to be related to vibrations of apex O(4) oxygen atoms. Some weak bands associated with E_u(LO) phonons which become Raman active probably due to the Fröhlich mechanism have also been observed. Dramatic changes in spectra have been found upon oxygen doping with the appearance of a new resonance vibrational band with strong overtones at relatively small x. This band has been assigned to A_g vibrations of O(4) atoms on sites adjacent to O(1) atoms in the basal plane introduced by doping from $x=0$. We have also observed PL with a peak round 1.3 eV in $YBa_2Cu_3O_{6+x}$ ceramic samples with small x. PL and resonance Raman scattering have been qualitatively described in the framework of a model where the existence of a narrow intragap electronic band associated to the O(4)-Cu(1)-O(4) complex has been assumed in $YBa_2Cu_3O_{6+x}$ for small x.

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