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Sub-band-gap electronic excitations in insulating $YBa_2Cu_3O_{6+x}$ observed by resonant Raman scattering

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Tunable ultraviolet laser light has been used to probe the electronic band structure of the charge-transfer insulator $YBa_2Cu_3O_{6+x}$. A 1.56-eV Raman-active excitation is observed for incident photon energy >3.5 eV. The excitation does not present clear selection rules in the low-energy wing of this resonance from 3.4 to 3.6 eV. We interpret the resonance and excitation as originating from in-plane Cu-O transitions. The excitation may be a crystal-field-like transition within the Cu d shell, a singlet two-hole state, or an excitonic state localized to a filled Cu $3d^{10}$ site.

The undoped insulating phase of the cuprates has unusual properties, some of which may be related to the high-temperature superconducting state reached when doped to the metallic phase. Single-particle electronic-structure calculations poorly describe the insulating behavior near the Fermi surface in systems whose weakly overlapping orbitals allow correlation energies to dominate. When single-particle descriptions fail, the less well understood Hubbard Hamiltonian more accurately includes the on-site repulsion that determines the electronic structure near the Fermi surface. Much theoretical work has been devoted to understanding this low-energy structure.[1-7]

It is generally accepted that the CuO_2 planes of the undoped cuprates such as $YBa_2Cu_3O_6$ are charge-transfer (CT) insulators as a consequence of the correlation effects. The undoped cuprates are observed to have a fundamental optical energy gap $E_g \approx 1.5$ to 2 eV between the highest occupied band of predominantly O $2p$ character and the lowest unoccupied band of predominantly Cu $3d$ character.[8] As free carriers are added by doping and the CuO_2 planes pass through the metal-insulator transition to the superconducting metallic phase, the behavior of electronic excitations that are comparable to the energy scale of the CT gap should give insight into the disappearance of the gap. Strong correlation effects in the electronic properties might lead to a description of the pairing mechanism in the superconducting state. The CT gap has a similar structure across the families of cuprate compounds, reflecting its common origin in the hybridization between the Cu d and O p orbitals of the CuO_2 planes and the on-site Cu Coulomb energy U_d. In $YBa_2Cu_3O_6$, E_g is 1.7 eV, and the resonant behavior of Raman-active phonons at this energy implies that the peak in absorption at 1.7 eV is not an exciton split off from a higher gap.[9]

We have observed a 1.56-eV transition that we identify as a Cu-localized excitonlike excitation. The large energy indicates an electronic origin. Since $1.56\ \text{eV} < E_g$, the transition is dipole forbidden and either arises from conduction and valence band (VB) states across E_g with 0.15-eV binding energy (likely a Frenkel-type exciton of dimension on the order of the atomic spacing), or simply involves a Cu intra $3d$-shell transition as discussed below. The 0.15-eV binding energy in this system can be compared to 0.10 eV for the dipole-forbidden exciton in Cu_2O.

A $YBa_2Cu_3O_{6+x}$ single crystal was studied with x approximately 0.1, well into the insulating phase. The crystal was oriented by well-defined edges, and checked by polarized Raman scattering. The commercially available apparatus was used for previous experiments.[10] Raman spectra were recorded with a Photometrics back-illuminated charged-coupled device after dispersal by a Spex Triplemate Raman spectrometer. The spectrometer was adjusted to minimize wavelength dependence throughout the spectral range of interest and the overall system response was verified with a tungsten filament lamp. Incident ultraviolet photons were generated by frequency doubling the output of a tunable dye laser. The fundamental and associated dye fluorescence were removed by a dichroic filter. The beam subsequently passed through two prisms and propagated more than 4 m to further purify the ultraviolet. Detector sensitivity and spectrometer transmission limited this experiment to observing photons shifted in energy by ~ 5000 to 16 000 cm^{-1} (0.6 to 2.0 eV). Regions of the crystal that had visible defects or varying amounts of weak luminescence were avoided in favor of those regions which appeared smooth, dark, and uniform, and yielded the strongest Raman intensity relative to the background. Measurements were performed at 300 K in a near backscattering geometry.

Figure 1 shows the Raman spectra for incident photon energy E_L spanning 3.4 eV to 3.6 eV. The incident polarization was oriented either along $x=(100)$ or $x'=(110)$, and scattered light was collected in the quasibackscattering geometry along the z axis perpendicular to CuO_2 planes. The Cu-O bonds lie along x and y. The polarization components of the scattered light were separately measured and summed for Fig. 1. The spectra are normalized by laser power but are not otherwise corrected. The series of spectra demonstrate that with increasing E_L, a peak grows out of the tail of lower energy excita-

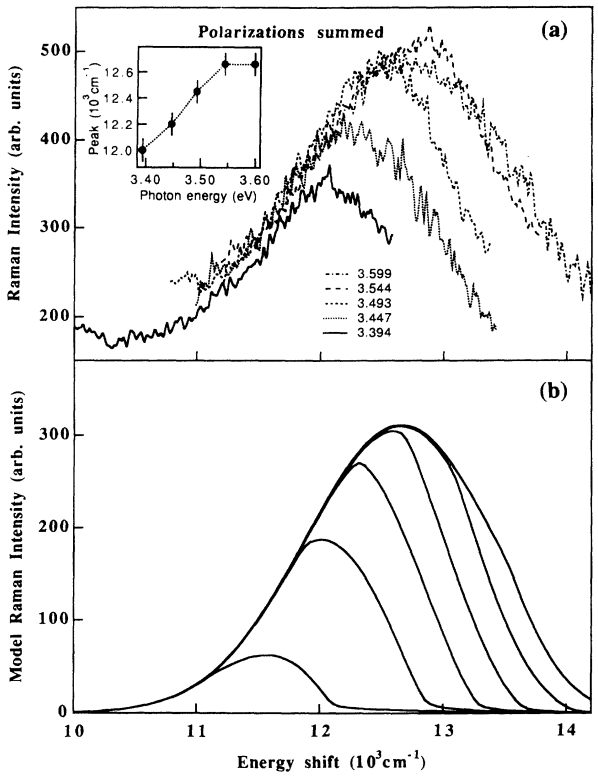

FIG. 1. (a) $YBa_2Cu_3O_{6+x}$ Raman spectra depicting the 1.56-eV excitation with E_L from 3.4 to 3.6 eV. (b) Model of the resonance as described in text. The E_L are the same as in (a) plus $E_L=3.3$ eV.

tions. For E_L below 2.8 eV, no feature is observed near 1.5 eV (1.2×10^4 cm^{-1}). The peak is not fixed in energy as expected for photoluminescence, and the perpendicular polarization ($x'y'$) is greater than the parallel ($x'x'$), a characteristic that implies inelastic light scattering. The first and second indices refer to the polarization of the incident and scattered photons, respectively. The generic nonresonant scattering process producing an excitation of energy $E_{\rm exc}$ is depicted in Fig. 2(a). The change in shape, peak position, and magnitude are due to the onset of the Raman resonance near 3.2 eV as we discuss below. Two questions arise from these Raman spectra: what are the optical transitions involved in the incident and scattered photons, and what is the nature of the 1.56-eV excitation?

Three constraints must be satisfied simultaneously: energy, momentum, and symmetry (selection rules). The inset in Fig. 1 details the shift in peak energy as a function of E_L. The intensity increases more slowly above 3.55 eV in agreement with the preliminary results of Liu *et al.*[11] who reported a more gradual increase in strength above 3.5 eV. We may extrapolate the resonance edge to predict that the peak will have vanishing small intensity for $E_L<3.2$ eV and a peak energy of 1.36 eV. Thus, there is clearly a kinematic cutoff that is relaxed only above 3.55 eV. We can model this constraint as arising from an outgoing resonance at the CT band edge. Each state within the distribution of allowed intermediate states has an energy denominator of the form,

$$I_R\sim\frac{1}{\Delta E^2+\Gamma_i^2}\ , \tag{1}$$

where ΔE is the energy separation from resonance and Γ_i, the energy damping term, is inversely proportional to the lifetime of the intermediate state. We model the dipole-allowed joint density of states $g(E)$ for optical transitions across E_g as a step function from 0 to g_0 at E_g. Taking the 1.56-eV peak as a Gaussian distribution of excitations $Q(E,E_c,\sigma_c)$, centered at E_c with $1/e$ width $2\sigma_c$, the Raman scattering intensity for a subset of $Q(E,E_c,\sigma_c)$ at a particular energy $E_0=E_L-E_{\rm exc}$ is described by the integration over the possible intermediate states:

$$I_R(E_0)\sim\int_{-\infty}^{\infty}\frac{\Gamma_i g(E')dE'}{[(E_L-E_{\rm exc})-E']^2+\Gamma_i^2}\ , \tag{2}$$

where we ignore momentum-conserving matrix elements and frequency factors. The overall resonant Raman profile is then

$$\begin{aligned}I_{\rm RRP}(E_0)&=\int_{-\infty}^{\infty}\frac{\Gamma_i g(E')dE'}{[(E_L-E_{\rm exc})-E']^2+\Gamma_i^2}\times Q(E,E_c,\sigma_c)\\&=Q_0g_0\exp-\left\{\frac{(E_L-E_c-E_0)^2}{\sigma_c^2}\right\}\int_{-E_g}^{\infty}\frac{\Gamma_i dE'}{(E_0-E')^2+\Gamma_i^2}\ .\end{aligned} \tag{3}$$

Finally,

$$\begin{aligned}I_{\rm RRP}(E_{\rm shift})=Q_0g_0\exp-&\left\{\frac{(E_{\rm shift}-E_c)^2}{\sigma_c^2}\right\}\\&\times\int_{-E_g}^{\infty}\frac{\Gamma_i dE'}{[E_{\rm shift}-(E_L-E')]^2+\Gamma_i^2}\end{aligned} \tag{4}$$

where $E_{\rm shift}=E_L-E_0=E_{\rm exc}$. To compare with the data, the abrupt step in $g(E)$ is smoothed to a single-sloped band edge spanning 0.15 eV with a constant density of states above 1.92. The peaks and line shapes generated by this model for several E_L, shown in Fig. 1(b), bear a strong similarity to the data of Fig. 1(a). The left (low-energy) side of the peak follows the low-energy shoulder of the excitation while the right side of the peak reflects $g(E)$ at the band edge until the peak reaches full strength. The model indicates that the rise in Raman intensity slows experimentally when E_L is near the minimum energy consistent with the allowed outgoing resonance, 3.55 eV. The energy in excess of E_g is $3.55-1.56-1.70\approx0.29$ eV, which is approximately the energy for flipping two spins in $YBa_2Cu_3O_{6+x}$ with B_{1g} symmetry.[12] This suggests either that the penultimate configuration involves two flipped spins which can relax to the ground state configuration with the emission of a

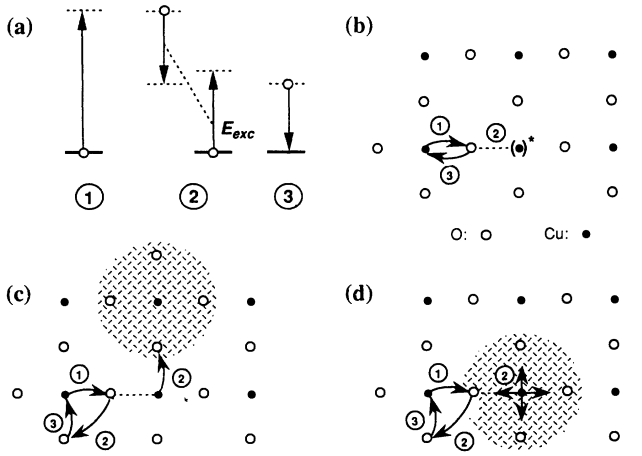

FIG. 2. Alternative scattering scenarios that describe the Raman process generating the spectra of Fig. 1, consistent with the energetics and electronic structure of $YBa_2Cu_3O_{6+x}$.

photon, or that the emitted photon arises from a VB hole in a 0.29-eV excited state. This model can be used with a more realistic band-edge density of states to determine the states participating in the Raman resonance.

The strongly hybridized Cu d-O p bands with mixed p and d character throughout the Brillouin zone[1,2] are too numerous to greatly restrict the possible optical transitions consistent with the energetics. Projecting out the p and d character of bands to consider optical transitions is not likely to substantially reduce the possibilities. The scattered photon polarization implies the possible symmetry of the excited state in the crystal. Within the C_{4v} symmetry pertinent to the CuO_2 planes, A_{1g}, B_{1g}, A_{2g}, and B_{2g} excitations are allowed with the following polarization selection rules:[13] (xx): $A_{1g}+B_{1g}$; (xy): $A_{2g}+B_{2g}$; $(x'x')$: $A_{1g}+B_{2g}$; and $(x'y')$: $A_{2g}+B_{1g}$.

The $(x'x')$ and $(x'y')$ spectra are plotted in Fig. 3 for different E_L. In this $YBa_2Cu_3O_{6+x}$ crystal we find that $(xx)\approx(xy)$, and $(x'y')\approx 1.5(x'x')$. This does not allow a complete determination of the intermediate state symmetry. Doing so requires measuring the scattering for circularly polarized light. Yet, B_{1g} and A_{2g} symmetries must both be present in the spectra with a mix approximately given by

$$\tfrac{1}{10}[(4x)A_{1g}+(1+4x)A_{2g}+(5-4x)B_{1g}+(4-4x)B_{2g}] \tag{5}$$

over the range $0\le x\le 1$. As pointed out in Ref. 12, selection rules that do not correspond to a single symmetry type in the tetragonal point group indicate a pair excitation at $\underline{k}$ and $-\underline{k}$. Superposition of all elements in the *star* of $\underline{k}$ produces a single symmetry type in the scattering selection rules. Liu *et al.* recently reported[11] the symmetry of a nearly identical excitation in Gd_2CuO_4 and other cuprates to be A_{2g} with very weak B_{1g} and B_{2g}. This implies a state that transforms as $(x^2-y^2)xy$, which would be consistent with the suggestion discussed below of an exciton or an intra-d-shell transition centered on a Cu. However, at the energies used here for $YBa_2Cu_3O_{6+x}$, the excitation is not seen to be solely A_{2g}. We speculate that the difference in these results might lie

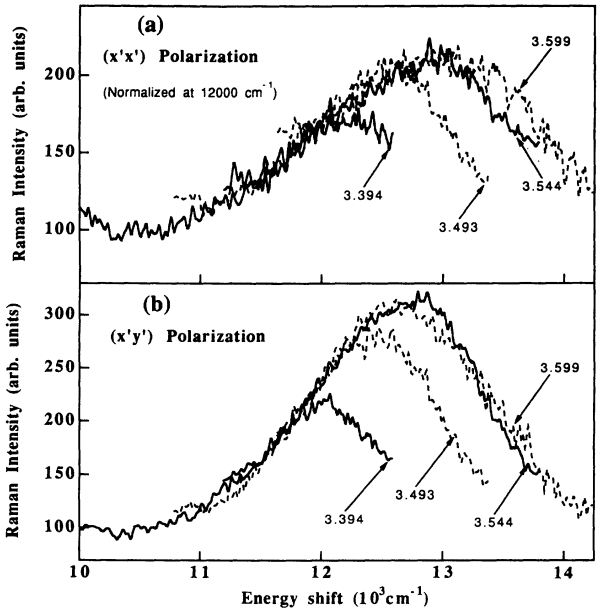

FIG. 3. Comparison of $YBa_2Cu_3O_{6+x}$ Raman spectra for $(x'y')$ and $(x'x')$ polarization geometries. E_L are labeled in eV.

in the projection of a subset of allowed states in the low-energy wing of the resonance forced by kinematic constraints. For $E_L > 3.4$ eV, the resonance can shift away from the E_g minimum in the Brillouin zone. This will change the mix of states participating in the process, and potentially give insight on the symmetry of states away from the band edge.

The Raman scattering process is schematically depicted in Fig. 2(a). Although the flexible selection rules and lack of consensus in electronic structure calculations bar a precise identification of the excitation at this time, we can still describe three specific scenarios consistent with the energetics and symmetry of the dipole-forbidden excitation. Because the ground state configuration is mainly Cu d^9-O p^6, the 1.56-eV transition must either be a d-d transition or directly involve the carrier created by the incident photon, e.g., a p-p transition localized at the O site. In detail these candidates are the following.

(1) An intrinsic Cu d^9 hole excited to a level deeper in the Cu d shell: $(d^9)^*$. Such d-d excitations are observed with Raman scattering in transition-metal oxide compounds and complexes[14] and could easily match the 1.56-eV energy with crystal-field splitting and hybridization with O $2p$ levels. The energy is also consistent with embedded cluster calculations by Annett *et al.*[4] Perkins *et al.* report a weak absorption below E_g in a compound with similar electronic structure, $Sr_2CuO_2Cl_2$.[15] They attribute the transition to a $d_{x^2-y^2}$-d_{xy} transition localized to a Cu site, and argue that random impurity potentials mix a little p character with the d state to slightly relax the dipole forbidden selection rule.

(2) A Zhang-Rice (ZR) two-hole singlet[3] with a nearby filled d^{10} site. The ground state of a hole in the VB is predicted by many calculations to consist of the hole distributed over the four nearest-neighbor O sites surrounding a Cu d^9 configuration. The $d_{x^2-y^2}$ symmetry of the

hole inhibits direct dipole excitation from the conduction band. Estimates of this state relative to an itinerant hole vary up to 1 eV, but a binding energy of ~ 0.2 eV is a reasonable value.[5] The 1.56 eV is then the CT energy needed to create the d^{10} configuration minus the energy binding the hole to a d^9 site. A two-hole excited state with different symmetry is possible but is likely to be unstable.

(3) A filled Cu-site exciton doublet. The Cu $3d_{x^2-y^2}$ level forms a narrow band of partially localized states. Exciting the intrinsic hole off the Cu site leaves a filled Cu d shell and creates a Coulombic potential in the surrounding O $2p$ bands to bind the hole. The O $2p\sigma$ orbitals strongly overlap Cu orbitals and are unlikely to produce a state whose lifetime is consistent with the energy width of the 1.56-eV peak. The O $2p\pi$ orbitals can distribute a hole over the four nearest neighbors in a d_{xy} or $g_{xy(x^2-y^2)}$ symmetry.[6] The latter is found by Goddard[8] to be nearly degenerate with the top of the VB although Annett *et al.* estimate this hole level lies 1 eV from the band edge.[4] The exciton doublet may couple antiferromagnetically to the neighboring Cu spins.

Optical transitions in the three step Raman scattering process which are compatible with each scenario are plausible. The 3.5-eV incident photon can excite an electron from the VB to Ba $5d$ hybridized with O p 1.8 eV above the Cu $3d^{10}$ level. These transitions are known to exist from electron energy loss spectra at the O $1s$ absorption edge.[16] The initially excited carrier then scatters a d_{xy} electron to the $d_{x^2-y^2}$ level, giving up 1.56 eV in the process. The scattered photon is emitted as the carrier returns to the hole in the O $2p$ band. The large U_d energy is avoided because the number of holes localized on the Cu site is unchanged. However, the outgoing resonance would be confined to the narrow $d_{x^2-y^2}$ band, and the intermediate scattering step would require a transition involving two Cu sites with the correspondingly small overlap. Thus the optical transition is instead most likely to be the excitation of a Cu hole deep into the O $2p$ VB.

In the second step, a p-p hole cascade in the VB will scatter a second Cu hole to one of the three excitations described above [Fig. 2(b), 2(c), or 2(d)]. This second step may be mediated by exchange scattering and involve mutual flipping of spins, particularly since the spin is on the O site after the first step, enhancing the exchange coupling with the second Cu.[6] The photon is emitted in the final step as the hole drops into the original $d_{x^2-y^2}$ level. The system is left in an excited state with a filled Cu $d_{x^2-y^2}$ level and a d-symmetric hole. Overlap-of-states arguments appear to favor the exciton, Fig. 2(d), but we are presently unable to reject any of the three.

Future work should seek to clarify the assignment of the excitation by correlating the low-energy onset of the resonance in other cuprate insulators with E_g. Comparison of the Y and Pr systems with doping across the metal-insulator transition would aim to distinguish between superconducting and nonsuperconducting character. $Ba_{1-x}K_xBiO_3$ can provide a check on the need for the CuO_2 planes to host the excitation. Application of an orienting magnetic field will clarify the spin state of the transition and shift the d levels at the Cu to assist in pinpointing the optical transitions. Additionally, weak photoluminescence at 1.56 eV at low temperature should be looked for with uv excitation. The width and energy of the luminescence peak would provide information regarding energy relaxation paths available to the excitation. And most important is the need to investigate in detail the effect that doping holes into the CuO_2 planes has on the resonance and excitation.

In summary, we have demonstrated the existence of a 1.56-eV dipole-forbidden excitation in the insulating cuprate $YBa_2Cu_3O_{6+x}$. The onset of the uv resonance from 3.2 to 3.5 eV indicates an outgoing resonance near the CT band edge in the CuO_2 planes. The experimental results point to candidates for the excitation but do not allow a definitive assignment at this time.

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