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Cu-O network dependence of optical charge-transfer gaps and spin-pair excitations in single-CuO_2-layer compounds

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Spectra of optical conductivity and magnon Raman scattering have been investigated in single crystals of a parent family of cuprate superconductors with various types of Cu-O single-layer networks. The analysis of the spectra shows the systematic dependence of the charge-transfer gaps and covalent character of Cu—O bonds on the pattern of the Cu-O network, while the spin-exchange energy is rather convergent for all the single-CuO_2-sheet compounds.

Superconducting copper-oxide compounds with high transition temperature (T_c) possess two-dimensional (2D) sheets of corner-linked CuO_4 squares ("CuO_2" sheets) as a common structural unit. The first discovered high-T_c compound,[1] alkaline-earth-substituted La_2CuO_4 shows the 2D sheets of Cu-O octahedra, while most of the other copper-oxide compounds with higher T_c's show adjacent multilayers of pyramidal CuO_2 sheets. Recent work[2] on electron-doping-induced high T_c shows that the CuO_2 sheets without apical oxygens can also sustain superconducting carriers, as observed in Ce-doped Nd_2CuO_4. In this Rapid Communication we have spectroscopically investigated how the electronic parameters (e.g., the charge-transfer gap, spin-exchange energy, and degree of *p-d* hybridization in Cu—O bonds) vary with the change in the pattern of Cu-O networks in single crystals of parent compounds for high-T_c superconductors.

Single-crystal compounds investigated here are (a) La_2CuO_4, (b) $Sr_2CuO_2Cl_2$, (c) $LaGdCuO_4$, (d) Nd_2CuO_4, (e) (Ca,Sr)CuO_2, and (f) Ca_2CuO_3. These compounds represent the typical patterns of the 2D Cu-O networks presently known[1-5] (see the inset of Fig. 1). All the structures show a well-defined network of a *single* Cu-O sheet within a repeated unit. Therefore, there is no complication in these compounds due to the coexistence of two or more types of Cu-O planes as observed, for example, in the Y-Ba-Cu-O systems which have both pyramidal sheets and chain(s). This feature is important to get clear-cut observations about the Cu-O network dependence of the electronic structures by spectroscopic methods.

Of particular interest among these are the compounds which can sustain charge carriers in their CuO_2 sheets; (a) $La_{2-x}Sr_xCuO_4$ (T phase), (c) $(La,Gd)_{2-x}Sr_xCuO_4$ (T^* phase),[4] and (d) $Nd_{2-x}Ce_xCuO_4$ (T' phase).[6] These represent the three prototypical patterns of Cu-O networks—i.e., octahedra, pyramids, and squares and are all superconducting at a suitable doping level (e.g., $x=0.15$) with maximum T_c's of ca. 40, 35, and 25 K, respectively. The important aspect is that the former two compounds associated with apical oxygens possess the hole-type carriers (p type) and the T'-phase compound with no apex only sustains the electron-type carriers (n type).[2,6,7] Such an observation about the types of charge carriers in single-CuO_2-sheet compounds may be generalized to the multisheet systems: Other superconductors with pyramidal or octahedral CuO_2 sheets all show hole-

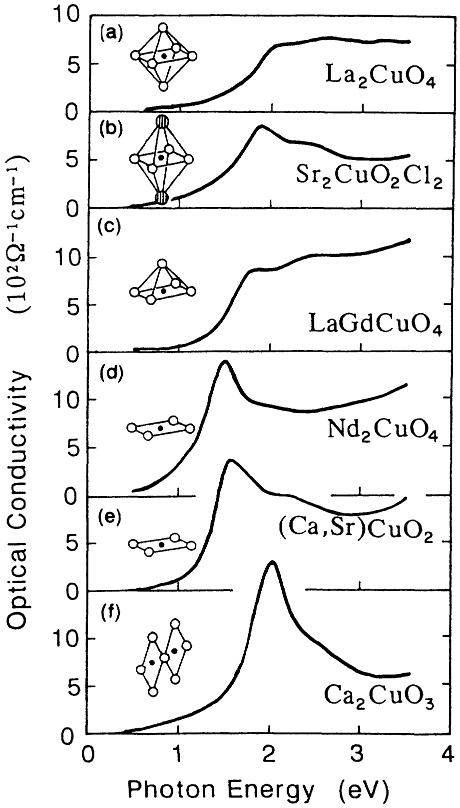

FIG. 1. Optical conductivity spectra of single crystals of Cu-O layered compounds. In all the spectra the light E vector is parallel to the basal plane.

type conduction, at least at low carrier concentrations, whereas the no apex compound[5] (e) (Ca,Sr)CuO_2 with Ca-to-Sr ratio of ca. 85/15 appears to show the *n*-type behavior from our preliminary measurements of its thermopower. Such an exclusive *p*- or *n*-type behavior implies an important variation in the background electronic structures in CuO_2 sheets depending on the pattern of Cu-O networks.

Single crystals of the "carrier-undoped" compounds (a)-(f) listed above (see the inset of Fig. 1) were grown from the melt by using CuO or CuO-Bi_2O_3 mixture as flux, detailed procedures will be described elsewhere. All the crystals show insulating or semiconducting behavior: The compounds (b), (e), and (f) show in-plane resistivity (ρ_{ab}) larger than 10^3 Ω cm at room temperature. To eliminate or reduce the charge carriers arising from oxygen nonstoichiometry, single crystals of (a) *T*- and (d) *T*′-phase compounds were annealed at 900 °C under a reducing and oxygenating atmosphere with oxygen partial pressures of 10^{-4} and 1 atm, respectively. After this procedure, the single crystals show well insulating behavior with $\rho_{ab}(300\ K) > 10$ Ω cm. The Néel temperature for the *T*-phase (La_2CuO_4) single crystal adopted in the measurements is around 240 K.

In Fig. 1, we plot the optical conductivity spectra for the six Cu-O layered compounds (a)-(f). The conductivity spectra were obtained by Kramers-Kronig transformations of the reflectivity data, which were measured on the (001) faces of those single crystals at 290 K with the polarization parallel to the Cu-O basal planes. Concerning the reflectivities at photon energies above 6 eV, reflectance data[8] taken by use of the synchrotron radiation source were utilized. In all the compounds investigated here, we have observed strong optical transitions with peak energies of 1.5-2.0 eV, below which the compounds show no optical-active bands except for the optical-phonon modes. The energies of the absorption bands in these semiconducting compounds are roughly in agreement with the result reported recently on ceramics samples.[9] However, the present study on single crystals can bring about much more reliable and quantitative information about the anisotropy, peak energy, intensity, and spectral shape which may subtly but significantly depend on the pattern of Cu-O networks.

The absorption bands observed in the single-CuO_2-sheet compounds [(a)-(e)] are all strongly polarized along the basal plane and the reflectance spectra for the polarization normal to the basal plane (i.e., parallel to the *c* axis) show no prominent structure in the energy region shown in Fig. 1. In addition, the optical-absorption band around 2.0 eV in the compound Ca_2CuO_3 with the Cu-O chain [see Fig. 1(f)] is strongly polarized along the chain axis (*a* axis) and neither $\mathbf{E} \parallel b$ nor $\mathbf{E} \parallel c$ reflectance spectra show any prominent feature below 3 eV. Since the polarized bands in these single crystals are considered to be of the same origin, their large anisotropy strongly indicates the importance of the anisotropic hybridization between Cu $3d_{x^2-y^2}$ and O $2p\sigma$ orbitals in the optical-excitation process. According to the photoemission studies,[10] the topmost valence band is dominantly composed of O 2*p* orbital. On these bases, the anisotropic bands observed at 1.5-2.0 eV can be assigned to charge-transfer-type excitations mainly associated with the transition from O 2*p* to Cu $3d_{x^2-y^2}$ (d^{10}) states.

The fairly sharp profile of the absorption peaks as observed should be considered due to the excitonic character of the transition. However, rather blurred features are observed in the spectra of *T*-phase La_2CuO_4 and T^*-phase $LaGdCuO_4$ [Fig. 1(a) and 1(c)]. This may be attributed to extra charge carriers, which are inevitably present due to the nonstoichiometric oxygens in the *T* phase and due to a small amount of Sr in the T^* phase.[4] Similar but less prominent tails below the main conductivity peaks observed in other compounds may be attributed to the broadening of the strong charge-transfer (CT) exciton, which may be similarly caused by a small amount of extra carriers and/or by strong coupling of the CT exciton with lattice phonons or magnetic excitations.

Looking at Fig. 1, one may notice the systematic change in the peak position with the number of oxygens coordinated around Cu; 2.0 eV in octahedral CuO_2 sheets of La_2CuO_4, 1.8 eV in pyramidal-CuO_2-sheets of $LaGdCuO_4$, and 1.5 eV in square-type CuO_2 sheets with no apex in Nd_2CuO_4 and (Ca,Sr)CuO_2. In addition, the CT peak is observed at the intermediate position (ca. 1.9 eV) in $Sr_2CuO_2Cl_2$ [Fig. 1(b)], in which the single-CuO_2-sheet has two apical halogens [hatched circles in the inset of Fig. 1(b)] per Cu atom instead of apical oxygens. These facts indicate that the relative position of the topmost filled (dominantly of O 2*p* character) and lowest unoccupied (dominantly of Cu $d^{10}_{x^2-y^2}$ character) bands is quite sensitive to the number and valence of apical ions (oxygen or halogens).

In Fig. 2 are plotted the Raman spectra in the single-CuO_2-sheet compounds shown in Figs. 1(a)-1(e). The spectra for the B_{1g} excitations were measured at 300 K with the polarization configuration (x',y') by utilizing the Ar laser 4880-A line as an exciting light. Fairly strong but broad Raman bands around 3000 cm^{-1} have been attributed to the spin-pair (two-magnon) excitations.[11-14] The spectra for La_2CuO_4 and Nd_2CuO_4 agree well with the previously reported ones.[11-14] We have observed similar Raman bands in $Sr_2CuO_2Cl_2$, $LaGdCuO_4$, and (Ca,Sr)CuO_2, with different "shapes" of CuO_2 sheets. Remarkably, the Raman shifts for the spin-pair excitations appear not to be sensitive to the pattern of CuO networks, which is in marked contrast to the systematic change of the CT gap energy.

Based on the observed results for CT and spin-pair excitations, important features of electronic structures in CuO_2-sheets can be discussed for various Cu-O networks. Hereafter, we focus on the systematic change in electronic parameters in the three single-CuO_2-sheet compounds, *T*-phase La_2CuO_4, T^*-phase $LaGdCuO_4$, and *T*′-phase Nd_2CuO_4. These compounds have the common chemical formula of $M_2{}^{3+}CuO_4$ [M = La, (La,Gd), and Nd] and similar *c*-axis values (12-13 A) but different CuO networks, which may enable us to compare the electronic parameters with each other. In Table I, we show the energy of the CT excitation (Δ_{CT}), its oscillator strength (f_{CT}) and the Raman shift for the B_{1g} excitation (ω_s). The value of ω_s is directly correlated with the antiferromag-

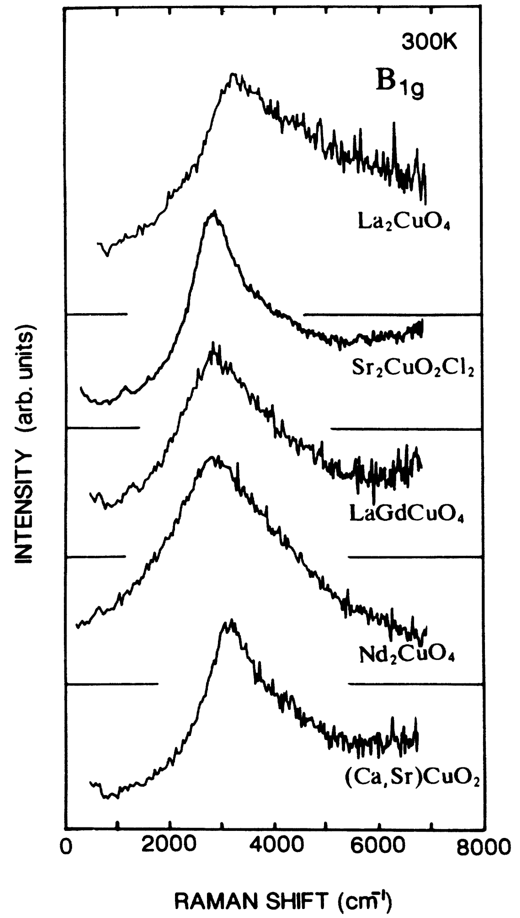

FIG. 2. Raman spectra for B_{1g} spin-pair excitations in single-CuO_2-sheet compounds shown in Figs. 1(a)–1(e).

netic exchange energy (J_s) between localized Cu spins ($\hbar\omega_s \approx 3J_s$).[15] The oscillator strength f_{CT} was approximately estimated by fitting the CT exciton peak using a Lorenzian profile.

The observed oscillator strengths of the CT excitations are quite high (f_{CT}=0.2–0.5), as shown in Table I, supporting again our interpretation of these optical-absorption bands. However, they show a large variation in the three (T-, T^*-, and T'-phase) compounds. The CT excitation process mainly occurs on the nearest-neighbor pair of Cu-O and hence its oscillator strength (f_{CT}) is approximately proportional to the degree of p-d hybridization. The quantity may be approximated by $(t_{pd}/\Delta)^2$, when $\Delta \gg t_{pd}$. Here, t_{pd} and Δ represent the nearest-neighbor-pair transfer energy and energy gap between the Cu 3d and O 2p one-hole levels, respectively. Judging from the systematic change in f_{CT}, the p-d hybridization (i.e., the covalent character of in-plane Cu—O bond) is increased as the oxygen coordination around Cu is decreased in going from octahedral to square-type sheets. According to Harrison's rule,[16] t_{pd} is expected to vary as d^{-n} with $n \approx \frac{7}{2}$, d being the Cu—O bondlength. Then, t_{pd} for the T^*- and T'-phase compounds are approximately $0.94t_0$ and $0.87t_0$, t_0 being the t_{pd} value for La_2CuO_4 (T phase). This tendency is in contradiction to the increase in the p-d hybridization from the T to T' phase through T^* phase. This is apparently due to the fact that the change in Δ is superior to the change in t_{pd}. In fact, the observed CT gap energy (Δ_{CT}), which is a good measure for Δ, becomes smaller, as shown in Table I, with the decrease of the oxygen coordination number.

On the other hand, the J_s value probed by the Raman measurements are rather convergent for different compounds (see Fig. 2 and Table I) in spite of such a large variation in the CT gap energies. To explain this, we have to consider that the exchange energy J_s is more strongly dependent on the t_{pd} values. Let us tentatively adopt here the simplified two-band (p-d) model. Let U_d and U_p be the correlation energies for Cu d-holes and O p-holes, respectively. Then, with the perturbation treatment of this model ($U_d,U_p,\Delta \gg t_{pd}$), the exchange energy J_s is approximately given by the relation[17]

$$J_s = \frac{2t_{pd}^4}{\Delta^2}\left[\frac{1}{U_d}+\frac{2}{U_p+2\Delta}\right].$$

In the real situation, such a perturbation treatment may not be valid for quantitative discussion because t_{pd}($\simeq$1 eV) is rather comparable with Δ (=1.5–3.5 eV).[17] Nevertheless, the leading term which governs possible material dependence of J_s should be t_{pd}^4/Δ^2, since U_d and U_p are considered to be constants in a series of compounds. (Note that the degree of hybridization probed by f_{CT} is t_{pd}^2/Δ^2 within the same approximation.) If the power-law dependence of t_{pd} on the Cu—O bond length (d) is taken into consideration again, it is very likely that the large variation of t_{pd}^4 term is compensated by the variation in Δ^2, which seemingly gives rise to network-insensitive ω_s values.

TABLE I. Physical parameters in CuO_2 sheets.

Compounds	La_2CuO_4	$(La,Gd)_2CuO_4$	Nd_2CuO_4
Cu-O network	Octahedron	Pyramid	Square
(oxygen coordination)	(6)	(5)	(4)
$d_{Cu\text{-}O}$	1.905 A	1.936 A	1.973 A
Δ_{CT}	2.0 eV	1.8 eV	1.5 eV
f_{CT}	0.2_8	0.3_3	0.4_3
ω_s	3200 cm^{-1}	2800 cm^{-1}	2900 cm^{-1}

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