Charge-Transfer Gap and Superexchange Interaction in Insulating Cuprates

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A cluster-model analysis is made on the material dependence of the optical charge-transfer gap and antiferromagnetic superexchange interaction of a variety of insulating cuprates. It is shown that the electronic structure of cuprates typically of the charge-transfer type is characterized by the unique energy-level separation that reflects the three dimensionality of the crystal via the long-range Madelung potential; such characteristics are absent in the Mott-Hubbard regime.

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The electronic structure of insulating cuprates has been understood to be in the charge-transfer (CT) regime rather than in the Mott-Hubbard (MH) regime.[1] Their energy gap should thus be determined basically by the energy-level separation of orbitals between copper and ligand oxygens, and the separation may well be characterized by the ligand electronegativity and the Madelung potential, not by the on-site Coulomb interaction of copper. Quantitative studies of the electronic structure of CT insulators have not, however, been explored much until the recent intensive investigation of the cuprate high-T_c superconducting materials.

Experiments on the optical conductivity and magnon Raman scattering spectra recently made by two groups[2,3] for a large variety of insulating cuprates have shed light on their electronic structure and provided an important opportunity for a deeper understanding of the CT insulators. Explicit information from such studies also contributes to establishing a quantitative basis for the description of the electronic states of the high-T_c superconducting cuprates.

In this Letter, we analyze the material dependence of the reported CT gap E_g and superexchange interaction J by means of the combined ionic- and cluster-model approach, and deduce the characteristics of the electronic structure of the cuprates representative of the CT insulators. We will show that the material dependence of E_g is predominantly determined by the unique energy-level separation between copper and in-plane oxygen which reflects the three-dimensionality of the crystal via the long-range Madelung potential. The small material dependence of J is also due to the effect. We will see that such characteristics become apparent in the CT insulators but are absent in the MH regime.

The electronic structure of cuprates has two features: (i) the relevant electrons are highly correlated and (ii) the ligand oxygens play an explicit role. To describe the dynamics of the electrons of such a system, we take an accepted view[4] that the $3d_{x^2-y^2}$ orbital of copper and the $2p_\sigma$ orbitals of in-plane oxygens are essential. The electronic parameters characterizing the system are then as follows:[5] (i) The on-site Coulomb interactions U_d and U_p. They are of the atomic character and assumed independent of the neighbors. (ii) The hopping interactions T_{pd} and T_{pp}. They measure the overlap of the wave functions and are assumed to depend only on the bond length between two atoms. (iii) The level separation Δ between the $3d_{x^2-y^2}$ and $2p_\sigma$ orbitals. This parameter has a long-range nature as discussed below, in contrast to the parameters in (i) and (ii). We also examine the contributions of the Cu $3d_{3z^2-r^2}$ and apex-oxygen $2p_z$ orbitals.

First, we specify the level separation Δ and demonstrate its unique variation. Considering that the system in the insulating state exhibits no metallic screening, we take the ionic model and write[6]

$$\Delta=\Delta V_M/\epsilon(\infty)+\Delta_0, \tag{1}$$

where ΔV_M is the difference in the Madelung site potentials (V_i at the i site) for a hole between the copper and in-plane oxygen: i.e., $\Delta V_M=V_{\mathrm{O}}-V_{\mathrm{Cu}}$.[7] The dielectric constant $\epsilon(\infty)$ represents the nonlocal charge relaxation at infinite frequencies due to core polarization of the background ions. Δ_0 involves the second electron affinity of the O^{2-} ion and second ionization energy of the Cu^{2+} ion, representing the atomic limit of the level separation. ΔV_M turns the large negative Δ_0 into the small level separation Δ of positive sign. This treatment of Δ is our basic assumption. Δ coincides with E_g if there are no hopping interactions. We calculate ΔV_M for a variety of compounds by the Ewald method using the reported crystal structures.[8] The formal ionic charge is assigned to each ion. Note that ΔV_M does not scale with the inverse of the lattice constant among the compounds since it directly reflects the out-of-plane structure (as well as the volume) of the crystal. This is the case even within the T'-phase compounds because by different rare-earth substitutions the lattice is about twice as easy to expand or contract along the c axis as along the a and b axes. A characteristic material dependence thus comes out in ΔV_M. In Fig. 1, we examine the correlation between the calculated ΔV_M and observed E_g and find that E_g scales predominantly with ΔV_M. This result suggests that the Madelung potential plays an important role in the CT gap energy of the cuprates. Actually, the variation of Δ appearing via Eq. (1) offers,[9] as we will show, the origin

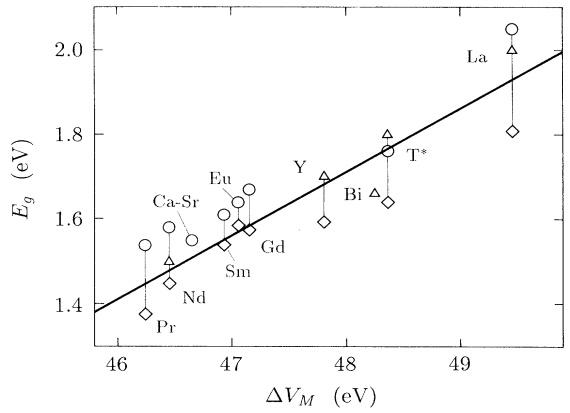

FIG. 1. The correlation between the observed E_g and the calculated ΔV_M. Collected are the data for T' phase L_2CuO_4 (L=Pr, Nd, Sm, Eu, and Gd), T phase La_2CuO_4, T^* phase $(La\text{-}Ga\text{-}Sr)_2CuO_4$ and $(La\text{-}Tb\text{-}Sr)_2CuO_4$ (where the same crystal structure in Ref. 8 is assumed for the calculation of ΔV_M), $(Ca\text{-}Sr)CuO_2$, $Bi_2Sr_2YCu_2O_8$, and $YBa_2Cu_3O_6$. ◇ after Ref. 2; ○ after Ref. 3; and △ after Tokura *et al.*, Tajima *et al.*, and Terasaki *et al.* of Ref. 15. The solid line is a guide to the eye.

of the material dependence of E_g of this class of compounds.

We now explore the calculation including the hopping interactions. A quantitative treatment is essential because the detailed changes of the parameters contribute to the material dependence of E_g and J. We follow the prescription proposed by Tohyama and Maekawa,[10] who have calculated the doping effects on the optical conductivity of high-T_c materials. The real part of the optical conductivity, $\sigma(\omega)$,[11] is given by the Kubo formula as

$$\sigma(\omega) = -\frac{1}{\omega}\,\mathrm{Im}\langle 0|j_x^\dagger \frac{1}{\omega + i0 + E_0 - H} j_x|0\rangle , \qquad (2)$$

where $|0\rangle$ is the ground state with energy E_0 of the Hamiltonian H and j_x is the x component of the current operator $\mathbf{j}$. We take the cluster-model approach. The current operator is then defined as

$$\mathbf{j} = ied_{\text{Cu-O}}\left(T_{pd}\sum_{mls}\mathbf{u}_{ml}(p_{ls}^\dagger d_{ms} - d_{ms}^\dagger p_{ls}) + \sqrt{2}T_{pp}\sum_{l'ls}\mathbf{v}_{l'l}p_{ls}^\dagger p_{l's}\right) , \qquad (3)$$

where e is the electron charge, $d_{\text{Cu-O}}$ is the Cu-O bond length, $\mathbf{u}_{ml}$ and $\mathbf{v}_{l'l}$ are, respectively, the unit vectors directed from the m and l' sites to the l site, and $p_{ls}^\dagger$ (p_{ls}) and $d_{ms}^\dagger$ (d_{ms}) are the creation (annihilation) operators for the O $2p_\sigma$ and Cu $3d_{x^2-y^2}$ orbitals with spin s, respectively. The m, l, and l' summations are over the orbitals on the neighboring sites. We calculate $\sigma(\omega)$ by the continued-fraction expansion of Eq. (2) via the Lanczos algorithm.[12] The ground state is evaluated by the modified Lanczos method.[12] The CT gap energy E_g is obtained as the energy of the lowest peak of $\sigma(\omega)$. The Cu_4O_{13} cluster with the free boundary condition is employed, where four CuO_4 clusters are linked linearly in the x direction by sharing the corner oxygens. This cluster is sufficient in size to examine the material dependence of E_g. The superexchange interaction J is calculated as the difference between the lowest energies of the singlet and triplet spin states of the coupled Cu_2O_7 cluster.[13] The clusters contain one hole per Cu ion to simulate the insulating state. We choose the values of the parameters as follows: U_d=8.5 eV and U_p=4.1 eV. T_{pd}=0.873 eV and T_{pp}=0.366 eV for Sm_2CuO_4 and are assumed to have the standard bond-length (d) dependence of d^{-4} and d^{-3}, respectively, for the other compounds. Δ is given by Eq. (1). Values of $\epsilon(\infty)$ and Δ_0 are chosen to give an overall agreement with the observed values of E_g; $\epsilon(\infty)$=3.5 and Δ_0=−10.88 eV, independent of the compound,[14] which are consistent with the work in Ref. 6. Note that the material dependence of Δ then comes only through ΔV_M.

The contribution from the hopping interactions through the apex-oxygen $2p_z$ and Cu $3d_{3z^2-r^2}$ orbitals is examined first of all. We expect that their contributions to E_g and J are small because the symmetry of the undoped ground state is orthogonal to the symmetry of these orbitals in the CuO_5 cluster. Calculations in the extended clusters actually show that the presence or absence of these orbitals changes E_g and J by less than 3% and has a negligible effect. This result leads to a statement that the contribution to E_g and J from the three dimensionality (or out-of-plane structure) of the crystal enters solely through Δ.

Calculated results for E_g and J are compared with the experimental results[2,3,15] in Figs. 2 and 3 for a variety of insulating cuprates. A good agreement is obtained. Noted in particular is a comparatively small (large) value of E_g (J) in $(Ca\text{-}Sr)CuO_2$ which has the smallest $d_{\text{Cu-O}}$ among the compounds with no apex oxygens. The material dependence of E_g and J may be further examined by a decomposition into three contributions, Δ, T_{pd}, and T_{pp}, as shown in Fig. 4, where each of the parameters is varied independently from the Sm_2CuO_4 reference. We note that the effects of T_{pd} and T_{pp} on the material dependence of E_g are one order of magnitude smaller than the effect of Δ.[16] The effect of the level repulsion due to band hybridization is mostly canceled out by the d-band-width effect due to the indirect d-d hopping. The effect of oxygen bandwidth is also very small. We thus conclude that the material dependence of E_g is caused only by Δ. Remember that Δ, as given by Eq. (1), reflects the three dimensionality of the crystal, namely, its volume and out-of-plane structure, via the long-range Madelung potential. The short-range contributions specified by the bond lengths are of little significance. The pressure coefficient of E_g, dE_g/dP, may then be positive in cuprates (due to the negative

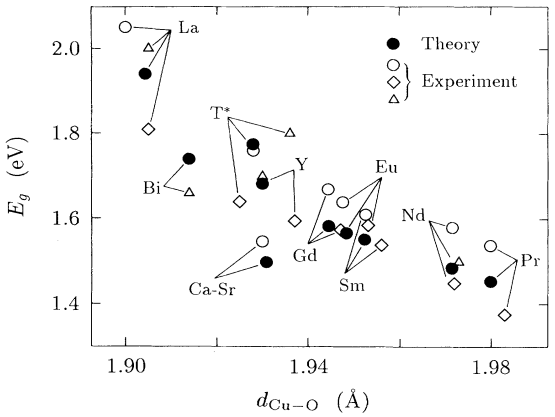

FIG. 2. The calculated CT gap energy E_g compared with the data of the optical conductivity measurements. ◇ after Ref. 2; ○ after Ref. 3; and △ after Tokura *et al.*, Tajima *et al.*, and Terasaki *et al.* of Ref. 15.

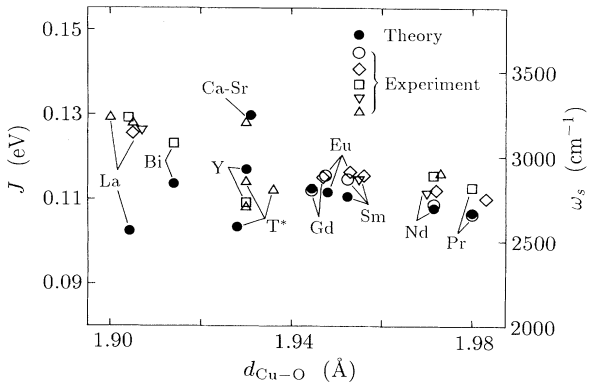

FIG. 3. The calculated superexchange interaction J compared with the two-magnon Raman peak position ω_s. Two scales on the ordinate are given by assuming an approximate relation $\hbar\omega_s = 3.1J$ (see Ref. 21). ◇ after Ref. 2; ○ after Ref. 3; □ after Sugai *et al.* of Ref. 15; ▽ after Sulewski *et al.* of Ref. 15; and △ after Tokura *et al.* and Tajima *et al.* of Ref. 15.

volume derivative of Δ), which is in contrast to the MH insulators where the pressure-induced metal-insulator transition has been observed.[17] This contrast has not yet been well recognized, but it is not surprising that the positive pressure coefficient of the energy gap may be a common feature of the typical CT insulators. Experimental studies on this point are desirable. For the superexchange interaction J, the most important effect is that the strong positive contributions of T_{pd} and T_{pp} to the bond-length dependence of J are canceled largely by the negative contribution of the above-mentioned Δ (see Fig. 4), to give a small material dependence of J. A recent magnon Raman scattering measurement under pressure for La_2CuO_4 (Ref. 18) supports this result. The MH insulators, in contrast, exhibit a strong bond-length dependence of J due to the d-d hopping contribution.[19] Thus, the small material dependence of J may also be characteristic of the CT insulators. We have assumed the standard bond-length dependence of the hopping interactions throughout the work; the possibility of an anomalously large or small bond-length dependence is ruled out because such a dependence does not explain the behaviors of E_g and J on the same footing.

We see that among transition-metal oxides cuprates are unique in the sense that the Madelung potential plays an explicit role in their electronic structure via the level separation Δ, and its importance was recognized first after the intensive examination of the high-T_c cuprates. The highest phonon frequency of the measured optical-phonon spectra assigned as the Cu-O-bond-stretching mode has been reported[20] to show an anomalously strong bond-length dependence, whereby its strong interaction with the electronic system has been suggested. We believe that this anomaly is also due to the above-mentioned uniqueness of the cuprates where the virtual CT excitation with energy characterized by Δ can couple to the phonons of the bond-stretching mode. Since our combined ionic and cluster model is applicable to the intermediate and other classes[1] of compounds, a future accumulation of experimental data will enable us to clarify what are the crucial parameters for their electronic structure.

In conclusion, we have analyzed the material dependence of E_g and J for a variety of the insulating cuprates quantitatively via the combined ionic- and cluster-model approach, and have shown that their electronic structure is predominantly characterized by the unique level separation Δ that reflects the three dimensionality of the crystal through the long-range Madelung potential. Such characteristics become apparent in the CT insula-

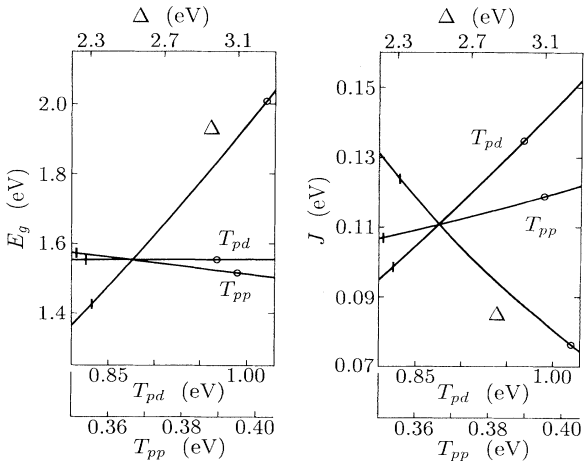

FIG. 4. The contributions to E_g (left-hand panel) and J (right-hand panel). The crossing point of the curves corresponds to Sm_2CuO_4, and circles and bars on the curves indicate the parameter values for La_2CuO_4 and Pr_2CuO_4, respectively.

tors but are absent in the MH insulators.

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[9]Equation (1) produces a strong material dependence of Δ from ΔV_M. These dependences, if they could be regarded as functions only of the bond length d, would roughly be $\Delta V_M \propto d^{-1}-d^{-2}$ and $\Delta \propto d^{-7}-d^{-8}$.

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[11]$\sigma(\omega)$ stands for the xx component of the optical conductivity tensor. The x direction will be taken along the -Cu-O-Cu- bond.

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