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Optical studies of gap, exchange, and hopping energies in the insulating cuprates

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We have measured the insulating energy gap Δ and the exchange interaction J in a series of cuprate crystals, including T'-phase M_2CuO_4 (M=Pr, Nd, Sm, Eu, and Gd), T^*-phase $(La,Tb,Sr)_2CuO_4$, and T-phase La_2CuO_4. We find that the energy gap scales predominantly with the in-plane Cu-O distance, scaling as $\delta\log\Delta/\delta\log d\sim -6$. Furthermore, contrary to simple expectations, the energy gap increases with decreasing Cu-O distance, suggesting that Coulomb and other repulsive energies dominate the effects of band hybridization. Using a three-band Hubbard-model expression, our studies of Δ and J in the cuprates allow us to estimate that the hopping energy t scales with Cu-O distance as $\delta\log t/\delta\log d\sim -4$.

Models of the high-T_c cuprates generally simplify the physics of these systems to model Hamiltonians involving a small number of fundamental electronic parameters that are presumed to characterize the dynamics of the Cu-O planes. These parameters generally include the charge-transfer energy gap Δ, the nearest-neighbor exchange interaction J, and the intersite hopping energy t. Consequently, it is important to elucidate how the gap, exchange, and hopping energies depend on structural features such as the in-plane Cu-O distance d, and the out-of-plane structural configuration. In this paper we report optical reflectivity and Raman scattering results on T'-phase M_2CuO_4 (M=Pr, Nd, Sm, Eu, and Gd), T^*-phase $(La,Tb,Sr)_2CuO_4$, T-phase La_2CuO_4, and $YBa_2Cu_3O_6$, in order to estimate these dependences. Our results indicate that the energy gaps of the insulting cuprates strongly *increase* as a function of decreasing Cu-O distance, and are less sensitive to structural variations outside the Cu-O planes. The increase in the gap with decreasing Cu-O distance suggests that changes in the hybridization bandwidth ($\propto t$) are outweighed by Coulombic and other repulsive energies in the insulating cuprates. An analysis of the changes in both the gap and exchange energies with Cu-O distance, combined with a standard three-band Hubbard model expression, allows us to estimate the dependence of the hopping parameter on the Cu-O distance. We find results that are consistent with theoretical estimates.

Optical reflectivity and Raman-scattering studies were performed at room temperature on single crystals of M_2CuO_4 (M=rare earth) grown using a technique described elsewhere.[1] The lattice parameters for all crystals were measured by x-ray and/or neutron diffraction and are accurate to within 0.1%. Reflectivity spectra from 100 to 20000 cm^{-1} (12.5 meV to 2.5 eV) were performed close to a normal incidence configuration using a rapid scanning interferometer. Raman-scattering measurements were also performed on the same crystals in the frequency range 0–8000 cm^{-1} using an Ar-ion laser at an excitation wavelength of 4880 Å. The scattered light was collected at right angles to the incident beam and passed through a Spex Triplemate spectrometer to a liquid-nitrogen-cooled charge-coupled-device (CCD) detector.

Figure 1(a) illustrates the optical reflectivity spectra for two of the T'-phase samples, Pr_2CuO_4 (d=1.983 Å) and Eu_2CuO_4 (d=1.953 Å). These spectra exhibit behavior characteristic of insulators, with sharp phonon features below 800 cm^{-1} and prominent reflectivity peaks near 11000 cm^{-1} due to electronic excitations above the Cu(d)-O(p) charge-transfer gap, Δ.[1-3] The most interesting change in the high-energy spectral features of Pr_2CuO_4 and Eu_2CuO_4 is a shift of the energy-gap peak to

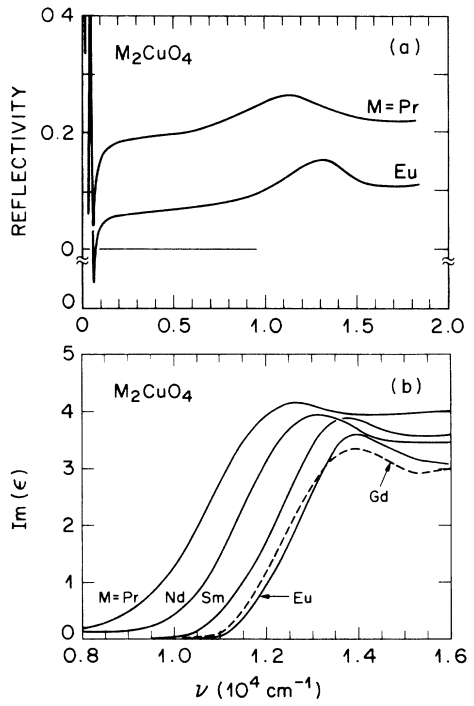

FIG. 1. (a) Room-temperature reflectivity spectra below 20000 cm^{-1} (2.5 eV) for two T'-phase samples, Pr_2CuO_4 (d=1.983 Å) and Eu_2CuO_4 (d=1.953 Å), illustrating the effects of changing Cu-O distance, d. The Pr_2CuO_4 spectrum has been offset by +0.1 relative to Eu_2CuO_4. (b) Imaginary part of the dielectric function, Im(ϵ), for all T'-phase samples in the vicinity of the energy-gap edge. These spectra were obtained from Kramers-Krönig transformations of the reflectivity.

higher frequencies as the lattice parameter decreases. A more detailed illustration of this shift is provided in Fig. 1(b), which plots the imaginary part of the dielectric function, $\mathrm{Im}(\epsilon)$, near the energy-gap edge for all T'-phase samples studied. These data were obtained through Kramers-Krönig transformations of the T'-phase reflectivity spectra. The energy-gap edge in Fig. 1(b) demonstrates a systematic shift to higher energies with decreasing lattice constant, indicating a strong sensitivity of Δ to the in-plane Cu-O distance, d. We have confirmed that this shift is not influenced by the Kramers-Krönig analysis by directly fitting the high-frequency reflectivity peaks in the T'-series with a single oscillator model. Such an analysis gives the same increase in Δ with decreasing d.

Figure 2 plots the energy gaps versus inverse Cu-O distance for all the insulating cuprates studied. The dramatic change of Δ throughout the isostructural T'-phase series (solid squares) indicates a surprising sensitivity of Δ to the in-plane Cu-O distance alone, as is illustrated by the fit of these data to the form $\Delta = \Delta_0 + a_0/d$ in Fig. 2 (dashed line, where $\Delta_0 \sim -8.5\times10^4\ \mathrm{cm}^{-1}$ and $a_0 \sim 1.9\times10^5\ \mathrm{cm}^{-1}\text{Å}$). These T'-phase results clearly illustrate the strong influence of Coulomb interactions within the Cu-O plane on Δ. The importance of in-plane contributions to Δ may be contrasted with the influence of structural contributions outside the planes by comparing the energy gaps in T^*-phase $(\mathrm{La,Tb,Sr})_2\mathrm{CuO}_4$ (fivefold coordinated Cu; open circle), T-phase $\mathrm{La_2CuO_4}$ (sixfold coordinated Cu; open triangle), and $\mathrm{YBa_2Cu_3O_6}$ (open square) to the trend established by the T'-phase series (fourfold coordinated; solid squares) in Fig. 2. While this comparison does indicate a small variation in Δ with structure [$< 5\%$ deviation of $\mathrm{La_2CuO_4}$, $(\mathrm{La,Tb,Sr})_2\mathrm{CuO}_4$, and $\mathrm{YBa_2Cu_3O_6}$ gap values from a best fit through the T'-phase data], it appears that the dominant contribution to Δ throughout the cuprate series involves the changing in-plane Cu-O distance. Indeed, a best fit through the entire cuprate series (solid line in Fig. 2) differs only slightly from a fit through the T'-phase data alone. These results are particularly surprising in view of recent suggestions that Δ is primarily sensitive to changes in Madelung energies associated with out-of-plane structural variations.[4–6] Torrance and Metzger,[6] for example, have proposed that Madelung energies, and hence Δ, should significantly *increase* with increasing number of oxygens coordinated around Cu. However, a comparison with the baseline established by the T'-phase series (dashed line in Fig. 2), which represents the contribution to Δ from the changing in-plane Cu-O distance, suggests that there is at best a small *suppression* of energy-gap values in $\mathrm{La_2CuO_4}$ and $(\mathrm{La,Tb,Sr})_2\mathrm{CuO}_4$ due to increases in the number apical oxygens.

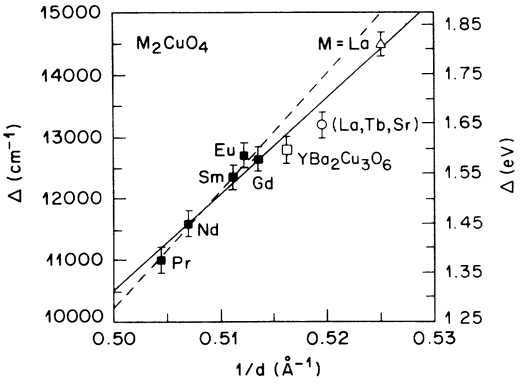

FIG. 2. The gap energy, Δ, defined as the center of trough-to-peak position in $\mathrm{Im}(\epsilon)$ [see Fig. 1(b)], plotted vs the inverse Cu-O distance, $1/d$ for T'-phase $M_2\mathrm{CuO}_4$ (M = Pr, Nd, Sm, Eu, Gd, solid squares), T^*-phase $(\mathrm{La,Tb,Sr})_2\mathrm{CuO}_4$ (open circle), and T-phase $\mathrm{La_2CuO_4}$ (open triangle). The energy gap for insulating $\mathrm{YBa_2Cu_3O_6}$ is also shown for comparison (open square). The dashed line is a least-squares fit to the T'-phase data, while the solid line is a fit to all the T'-, T^*-, and T-phase data.

Additionally, the large increase in Δ with decreasing d in Fig. 2 reveals the dominant contributions to the charge-transfer gap in the cuprates. The charge-transfer gap, Δ, may be described by the phenomenological expression,

$$\Delta = \Delta_0 + \frac{a_0}{d} + \delta - zt\,, \tag{1}$$

where Δ_0 represents all contributions to Δ that are independent of d to first order (e.g., electronic ionization and affinity energies), while the second term ($\sim 1/d$) represents Madelung and other Coulomb energies associated with the Cu-O planes. The $\sim 1/d$ contribution is expected to have a positive coefficient in the cuprates,[6,7] and thus favors an increasing Δ for decreasing d. The final two terms in Eq. (1) represent the influence of hybridization on Δ for z nearest neighbors: the first, which is expected to be positive in the cuprates ($\delta \sim +t^2/\Delta$), accounts for energy-level shifts due to Cu(d)-O(p) hybridization.[8] The last term, which decreases Δ as the Cu-O distance decreases, reflects the increasing hybridization bandwidth ($\propto t$) as the lattice contracts. Thus, while changes in bandwidth are expected to dominate Δ in many systems, as discussed by Mott and Davis[9] with regard to the metal-insulator transition, the insulating cuprates appear instead to be in a regime in which Madelung and level repulsion energies dominate bandwidth effects. This result is similar to that observed in some amorphous semiconductors.[10]

It is also interesting to estimate how the nearest-neighbor exchange interaction, J, scales with Cu-O distance by measuring the two-magnon Raman spectra in the 2:1:4 cuprate series. Characteristic two-magnon data in some 2:1:4 cuprates are summarized in Fig. 3, and the corresponding exchange interaction values have been extracted from the spectra using a procedure described elsewhere.[11] Like Δ, the two-magnon peak energy exhibits a systematic increase as the Cu-O distance decreases through the 2:1:4 cuprate series (plotted top to bottom in Fig. 3). Specifically, we find that $\delta \log J/\delta \log d = -4.3 \pm 2$ in the 2:1:4 cuprates [see solid line, Fig. 4(b)], which is consistent with the value of $\delta \log J/\delta \log d \sim -6$ that we have estimated by combining pressure-dependent Raman scattering[12] and neutron powder-diffraction[13] data on $\mathrm{La_2CuO_4}$. It is interesting that the value of J observed in $\mathrm{YBa_2Cu_3O_6}$ ($\log_{10} J \sim 2.9$; $\log_{10} d \sim 0.288$) (Ref. 9) falls well below the trend in Cu-

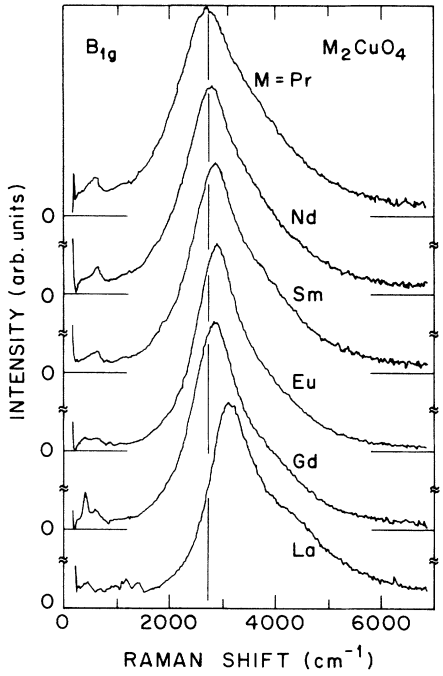

FIG. 3. Two-magnon Raman-scattering spectra for T'-phase M_2CuO_4 (M =Pr, Nd, Sm, Eu, Gd) and T-phase La_2CuO_4 at room temperature. The spectra have been offset, and have been plotted (top to bottom) in order of decreasing Cu-O distance d. For purposes of comparison, a solid vertical line has been drawn to illustrate the shift from the two-magnon peak position in Pr_2CuO_4.

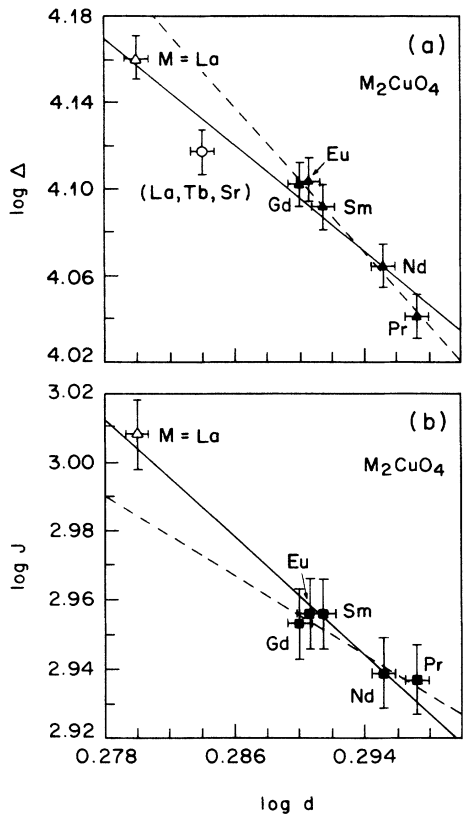

FIG. 4. (a) Log-log plot of the gap Δ vs the Cu-O distance d for all T'-phase (solid squares), T^*-phase (open circle), and T-phase (open triangle) samples. The dashed line is a least-squares fit to the T'-phase data, while the solid line is a fit to all the 2:1:4 data. (b) Similar plot for the exchange energy J in T'-phase (solid squares) and T-phase (open triangle) samples. The dashed line is a least-squares fit to the T'-phase data while the solid line is a fit to all the 2:1:4 data. The energy scales for both (a) and (b) are in $\log_{10}(cm^{-1})$, and the distance scale is in $\log_{10}$ (Å).

O distance exhibited either by the T'-phase series [dashed line, Fig. 4(b)] or the full 2:1:4 series [solid line, Fig. 4(b)]. This suggests that J may be more sensitive to the structural differences between these compounds than the energy gap, Δ (see Fig. 2). Nevertheless, structural differences associated solely with the different number of oxygens coordinated around Cu (i.e., among the 2:1:4 cuprates series) appear to have a lesser influence on J, as is suggested by the comparable scaling behavior found for both the entire 2:1:4 series, $\delta\log J/\delta\log d \sim -4\pm 2$ [solid line, Fig. 4(b)], and the isostructural T'-phase series alone, $\delta\log J/\delta\log d \sim -3\pm 2$ dashed line, Fig. 4(b)].

Significantly, when compared with the scaling behavior found in the $3d$-metal oxides, $\delta\log J/\delta\log R \sim -12$ (R =cation-anion separation),[14] the 2:1:4 or T'-phase series data in Fig. 4(b) and the pressure-dependent Raman data on La_2CuO_4 (Ref. 12) indicates a surprisingly weak sensitivity of J to in-plane Cu-O distance. This weak dependence of J on d in the cuprates appears to result from a near cancellation between changes in t and Δ with Cu-O distance—a conclusion that is suggested by the relationship between Δ, J, and t in a three-band Hubbard model,[15]

$$J \sim \frac{t^4}{U^*\Delta^2}, \tag{2}$$

where U^* is an effective on-site Coulomb energy for both Cu and O sites. Assuming the constancy of Coulomb energies (U^*) with respect to changes in d, the dependence of t on d may be related to corresponding changes in J and Δ, by

$$\frac{\delta\log J}{\delta\log d} = 4\frac{\delta\log t}{\delta\log d} - 2\frac{\delta\log\Delta}{\delta\log d}. \tag{3}$$

Thus, the Hubbard model expression in Eq. (2) implies that the large changes we observe in Δ with changing d [see Fig. 4(b)] can conspire with changes in t to give an unexpectedly small scaling of J with d. An estimate of $\delta\log t/\delta\log d$, as well as a more detailed examination of the relationship between Δ, J, and t, may be obtained from the data in Fig. 4, plotted as (a) $\log_{10}\Delta$ vs $\log_{10} d$ and (b) $\log_{10} J$ vs $\log_{10} d$. A least-squares fit to the entire 2:1:4 series data gives $\delta\log\Delta/\delta\log d = -6\pm 2$ and $\delta\log J/\delta\log d = -4\pm 2$, which may be written as power laws because of the small range of d measured: $\Delta = \Delta_1(d_0/d)^6$ and $J = J_1(d_0/d)^4$, where $\Delta_1 = 1.45\times 10^4\ cm^{-1}$ (1.8 eV) and $J_1 = 1\times 10^3\ cm^{-1}$ (0.13 eV) (normalized to La_2CuO_4 with $d_0 = 1.91$ Å). Therefore, using Eq. (3) and our values of $\delta\log\Delta/\delta\log d$ and $\delta\log J/\delta\log d$, we can estimate that t scales with d as $\delta\log t/\delta\log d \sim -4\pm 2$. This logarithmic derivative corresponds to a power-law dependence, $t = t_0(d_0/d)^\eta$, where $\eta = 4\pm 2$ and $t_0 = 1$ eV

(8×10^3 cm^{-1}), in agreement with theoretical estimates of Weber ($\eta\sim3$),[16] and Harrison ($\eta\sim3.5$–4).[17] The consistency of our empirical estimates of $\delta\log t/\delta\log d$ with theoretical estimates supports the conclusion that the weak dependence of J on d in the cuprates ($\delta\log J/\delta\log d\sim-4$) betrays a balance between changes in Δ^2 and t^4 with Cu-O distance [see Eqs. (2) and (3)]. It is interesting that an extension of these arguments to the stronger scaling behavior of J in the $3d$-metal oxides[13] suggests that Δ in these compounds does not scale as strongly with cation-anion distance, and thus cannot as effectively balance changes in the hybridization, $t\propto(R)^{-4}$.

The magnitudes and signs of $\delta\log\Delta/\delta\log d$, $\delta\log J/\delta\log d$, and $\delta\log t/\delta\log d$ in the 2:1:4 cuprates also provide interesting information about the size of the various contributions to Δ given in Eq. (1). Combining Eqs. (1) and (3), the Hubbard model assumption $t\ll\Delta$, and our results for $\delta\log J/\delta\log d$ and $\delta\log t/\delta\log d$, yields the relationship

$$6=\left|\frac{\delta\log\Delta}{\delta\log d}\right|<\frac{a_0/d}{\Delta}. \tag{4}$$

This result indicates that Coulomb contributions to the gap are much larger than the gap itself, suggesting that the observed gap value is given by a near cancellation of the various terms in Eq. (1). Furthermore, the results of Eq. (4) are consistent with the large Madelung and other Coulomb energies estimated previously by Varma, Schmitt-Rink, and Abrahams[18] and Torrance and Metzger.[6]

In summary, we have studied the dependence of the energy gap Δ and exchange parameter J on Cu-O distance and the out-of-plane structural configuration in the insulating cuprates. We find that the energy increases with decreasing Cu-O distance, suggesting that Madelung potential contributions within the Cu-O planes and hybridization shift energies dominate the energy gap in the cuprates. By contrast, the energy gap is less sensitive to variations in structure outside the Cu-O planes (for example, the presence or absence of apical oxygens) or to changes in the hybridization bandwidth ($\propto t$) with changing Cu-O distance. In addition, the exchange interaction J in the 2:1:4 cuprate series shows a sensitivity to Cu-O distance given by $\delta\log J/\delta\log d\sim-4$. This dependence is consistent with pressure-dependent Raman results on La_2CuO_4,[12] and is significantly weaker than that observed in transition-metal oxides.[13] We argue that this surprisingly weak dependence of J on Cu-O distance results from a cancellation between changes in the hopping parameter and the energy gap with Cu-O distance. Finally, from the scaling behavior of the gap and the exchange interaction with Cu-O distance obtained in our study, and assuming a standard three-band Hubbard model, we estimate a power-law dependence for the hopping parameter, $t\propto(d)^{-\eta}$ with $\eta\sim4$, which is consistent with theoretical estimates.

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