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THE CONFIGURATION-ENERGY SCHEME FOR CUPRATE MATERIALS

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RE-ANALYSIS OF PHOTOEMISSION DATA FOR CuO: REVISION OF THE CONFIGURATION-ENERGY SCHEME FOR CUPRATE MATERIALS

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INTRODUCTION

We have recently carried out a very careful analysis of photoemission and inverse photoemission (BIS) data for CuO,¹ probably the most refined and thorough such analysis for any transition-metal compound to date. This has led to a configuration-energy scheme for cuprate materials which is quite different from the generally-accepted one, due largely to Sawatzky and co-workers.²⁻⁴ For example, it is commonly believed that the "doping holes" in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are hosted almost entirely within oxygen 2p orbitals. We find instead that these holes are shared roughly equally by 2p and 3d orbitals. In this report we shall sketch the motivations for this study, the main results, and some of the lessons and surprises encountered along the way.

Valence-band photoemission and BIS data provide the main phenomenological access to parameter values for the model Hamiltonians used in studying cuprate superconductivity. The material CuO is particularly convenient for detailed study here. It contains only the elements of most interest (copper and oxygen), without any chain coppers to complicate the interpretation. Furthermore, the ratio of copper to oxygen is much larger than in most cuprate materials, so details of the 3d photoemission can be more clearly resolved. Each copper is square-planar coordinated with four nearby oxygens, as in the superconducting materials. On the other hand this is a magnetic insulator (Mott insulator), like the parent compound La_2CuO_4 , which simplifies the data analysis. Thus, CuO deserves to be carefully studied.

Photoemission data for CuO and other cuprates have already been presented and analyzed by a number of workers.^{2,5,6} We were skeptical that any of the previous results were sufficiently reliable, however, for several reasons: (1) Previous workers have typically focussed on XPS data, where the high energy of the photons (>1000 eV) suggests that the photoemission is due almost entirely to 3d electrons. Data at lower photon energies reveals additional features, which can be attributed to 2p photoemission, but this 2p information had not been utilized. (2) BIS data is essential for a reliable determination of the Hubbard parameter U , but this data was unavailable for most of the earlier studies. BIS data was used by Eskes, Tjeng, and Sawatzky² (hereafter, ETS), which is the most refined of the previous analyses, but, as we shall argue below, this data was used incorrectly. (3) The resulting energy level scheme for CuO was quite different from what had been obtained in the 1970's for the classic Mott insulators NiO, CoO, etc. Although this older scheme⁷ was never universally accepted,

and was not worked out as thoroughly as is now possible, it did have the support of several additional lines of evidence, including 2p photoemission.^{8,9} (We have reviewed this other evidence in Ref. 1.) One should expect CuO to be quite similar to its neighbor NiO. On the other hand, the "new" scheme for CuO (which has also been applied to NiO etc.^{3,4}) appears to be nicely confirmed by evidence from resonant photoemission.^{10,11}

We were thus faced with an intriguing problem -- a major inconsistency between the old and new pictures, each of which could claim support from a number of other kinds of evidence, but neither of which was based on sufficiently thorough analysis. The most troubling problem, for us, was a paradoxical inconsistency between the 2p data, which supported the old picture, and the resonant photoemission, which favored the new one.

THE MODEL AND ANALYSIS

Our analysis is based on the most refined previous work, by ETS,² together with a number of further refinements. Thus, we calculate the full multiplet structure for two holes in D_{4h} symmetry, as appropriate for square-planar oxygen coordination. The Coulomb (direct minus exchange) interactions between the various 3d orbitals are represented by the Racah parameters A, B, C, using the matrices of Zaanen.^{2,12} (B and C are obtained from free-ion data, leaving only A to be fitted to the CuO data.) All of the charge-transfer configurations (d^8 , $d^9\bar{L}$, $d^{10}\bar{L}^2$) are included ($\bar{L}$ = "ligand" (oxygen 2p) hole). These features are the same as in ETS.

We use an Anderson-impurity model, rather than the CuO_4 cluster of ETS. This model has only one Cu ion, the "impurity." However, the oxygens are assumed to form a simple cubic lattice of infinite extent. (This idealization is obtained by "undistorting" the monoclinic CuO structure, which makes it essentially the same as the PdO structure.) Furthermore, on *every* Cu site (the empty Cu sites as well as the impurity) we place 4s orbitals. Bloch states are then calculated for this combined 2p-4s tight-binding basis. We then return to the simple four-oxygen cluster of the corresponding CuO_4 cluster model, and combine the twelve 2p spatial orbitals into twelve symmetry-adapted orbitals ϕ_γ for the D_{4h} point group. Then for each ϕ_γ we calculate its overlap with the Bloch 2p-4s eigenstates $\psi_{k\nu}$ (ν = band index) and evaluate the projected state density

$$\rho_\gamma(\epsilon) = \sum_{k\nu} |\langle \phi_\gamma | \psi_{k\nu} \rangle|^2 \delta(\epsilon - \epsilon_{k\nu}) . \quad (1)$$

Five of these symmetries γ are the same as those of the 3d orbitals, and thus can hybridize with the corresponding 3d's while the remaining seven are nonbonding with respect to the 3d's. For each of the hybridizing γ 's we discretize $\rho_\gamma(\epsilon)$ into 10 states, so that a hole of symmetry γ is then represented by 11 states, 10 for the projected 2p band and 1 for the 3d orbital. It is then a straightforward matrix problem to find the two hole eigenstates resulting from photoemission. The spectral weight for 2p removal and for 3d removal are then constructed according to the sudden approximation, equivalent to the usual Green's function expression. These results are then Lorentzian broadened, for the sake of illustration. To this "hybridizing" 2p removal spectrum we then add the sum of the seven nonhybridizing densities $\rho_\gamma(\epsilon)$, similarly broadened, to get the total 2p removal spectrum.

Further refinements include a parameter to allow for the *nonhybridizing component* of the phenomenological crystal field splitting of the 3d orbitals. Such a contribution was found to be significant in *ab initio* cluster calculations,¹³ where it was found to arise mainly from the extra kinetic energy due to constructing orthogonal Wannier

orbitals out of overlapping ionic orbitals. (ETS assumed that the 3d splitting comes entirely from the 2p-3d hybridization.) The use of projected state densities $\rho_\gamma(\varepsilon)$ likewise provides an effective crystal field splitting for the 2p's, as is apparent if one takes the centroid of each $\rho_\gamma(\varepsilon)$ to represent the energy of the associated four-oxygen cluster orbital ϕ_γ . This feature is similar to the 2p splitting in the cluster model of ETS, although the 4s-2p hybridization now substantially increases this effective splitting. We also further modify the effective crystal field for the $a_{1g} = z^2$ channel, to allow for a further strong effect of the 4s orbital in this symmetry. This refinement was necessary to fit the multiplet structure of the main peak region, and is consistent with previous experience with other square-planar complexes.¹⁴

In order to obtain sufficient intensity in the satellite region, we found it necessary to allow for a charge dependence of the hybridization strength, i.e., we assume that the magnitude $|t_{pd}|$ of the transfer integral is larger for d^8 - d^9 transitions than for d^9 - d^{10} transitions. There is independent evidence for this in an *ab initio* cluster calculation,¹⁵ and in a previous photoemission study.¹¹

We want to emphasize that each one of these added refinements was motivated in two different ways: (a) by the empirical fitting process, i.e., it was indicated by the data, and (b) it had precedents, usually from previous *ab initio* studies.

RESULTS AND DISCUSSION

We have used the same data⁶ as ETS. However, in addition to the XPS spectrum (1478 eV photon energy), which is the one that they analyzed, we have also analyzed the 70 eV (synchrotron radiation) and 21.2 eV (HeI lamp) spectra from Ghijsen *et al.* The main features of the XPS data are a "main peak" with a narrow high-intensity maximum and some multiplet structure, and a considerably weaker "satellite" centered at about 8 eV higher binding energy, also with some multiplet structure.

In comparing the lowest-energy (HeI) and highest-energy (XPS) data, three features can be identified as due to 2p photoemission. There is a strong shoulder on the high-binding-energy side of the main peak, and at higher binding there are two weaker features in the energy range of the satellite. The spacing and relative intensities of these 2p features are well explained by our model. Also, the required 2p-2p and 2p-4s transfer integrals agree well with those deduced from band calculations for La_2CuO_4 ,¹⁶ especially so for the 2p-2p transfer. It turns out that the calculated 2p removal intensity spectrum has almost the same shape as the state density of the 2p-4s tight-binding band.

The charge-transfer energy parameter Δ , nominally defined as $E(d^{10}\underline{L}) - E(d^9)$, is determined mainly by the position of the strongest 2p feature with respect to the main peak, which comes from 3d removal. This determination is as straightforward and unambiguous as one could reasonably hope for, so the resulting Δ value should be reliable. Similarly, the Racah A parameter is determined mainly by the total energy separation (2.9 eV) between the threshold photoemission feature (a rather weak bump at 1.1 eV binding energy, with 1A_1 symmetry), and the BIS peak, at 1.8 eV above the " ε_F " reference energy. The A value should therefore also be reliable. The various hybridization strengths (for different symmetries γ , and different charge states, three free parameters) are determined by the position, shape, and intensity of the satellite, including some very weak but apparently genuine features seen in the 70 eV data (which has the highest resolution) at around 16 eV binding energy, which ETS had also fit. The quality of the fit in the satellite and 16 eV regions is very good, provided that we also include a significant amount of 2p intensity. We return to the latter issue below.

Figure 1. The present configuration-energy scheme for two holes of $x^2 - y^2$ symmetry, compared with the result of ETS, Ref. 2.

The Hubbard U parameter is not uniquely defined, but depends on the quantum numbers of the two-hole eigenchannel. The 1A_1 eigenchannel is the one of most interest for understanding superconductivity, since this is the one containing two d holes of $b_{1g} = x^2 - y^2$ symmetry. (As expected, this channel contains the photoemission threshold state.) It would be pointless to present all of the fitting parameters of our model without carefully defining them, so we shall now focus on only the Δ and U obtained for this 1A_1 eigenchannel. Here the effective U is

$$U_{eff}(^1A_1) = A + 4B + 3C', \quad (2)$$

for which we find 7.0 eV. (ETS found 8.8 eV.) Our charge-transfer energy, $\Delta = 7.55$ eV, is now very different from the corresponding ETS value of 1.75 eV (by our definition -- we measure from the *centroid* of $\rho_\gamma(\epsilon)$ for $\gamma = b_{1g}$). Using the definitions of the configuration-energy differences (for two $b_{1g} = x^2 - y^2$ holes),

$$E(d^{10} \underline{L}^2) - E(d^9 \underline{L}) = \Delta, \quad (3)$$

$$E(d^9 \underline{L}) - E(d^8) = \Delta - U, \quad (4)$$

the present configuration-energy scheme is compared with that of ETS in Fig. 1. The difference is quite drastic, and this deserves an extended discussion.

For a qualitative understanding of the main peak and satellite states, according to our scheme, one can visualize these as the bonding and antibonding combinations of d^8 and $d^9 \underline{L}$, ignoring the high-lying $d^{10} \underline{L}^2$ configuration. The latter is important only for high-lying states which have negligible intensity. This picture is valid for every one of the two hole eigenchannels. The two hole ground state (photoemission threshold state -- present “bonding” state) corresponds to the state of a doping hole in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Since the energy separation of d^8 and $d^9 \underline{L}$ is far smaller than their very strong hybridization matrix element, it is clear that the doping holes should have roughly equal amounts of 3d and 2p character. This is quite contrary to the generally

accepted picture, where these holes are nearly pure 2p, but this is consistent with the near-threshold intensity behavior (*vs.* photon energy) in photoemission from metallic cuprates.¹⁷

All previous analyses of cuprate photoemission, done to obtain effective Hamiltonian parameters, have been based on the premise that the necessary information can be obtained from the 3d photoemission alone, where the 3d removal spectrum is assumed to be the XPS spectrum. In a simplified model¹⁸ containing only the holes of b_{1g} symmetry, the final states are obtained from an energy matrix of the form

$$\begin{pmatrix} \varepsilon_8 & T & 0 \\ T & \varepsilon_9 & T \\ 0 & T & \varepsilon_{10} \end{pmatrix}.$$

We now observe that the diagonal elements ε_8 and ε_{10} (energies of the d^8 and $d^{10}\underline{L}^2$ configurations) can be *interchanged* without affecting the final-state eigenvalues. This indicates that *two different solutions* are possible, when attention is restricted to the customary choice of data. The two schemes in Fig. 1 do indeed differ by a rough interchange of the d^8 and $d^{10}\underline{L}^2$ energies, although this interchange is imperfect because of multiplet effects.

One might suppose that a careful treatment of the two-hole multiplet structure would suffice to resolve this ambiguity. We found that this is not so, at least not definitively, because of the extra free parameters we have introduced to treat the crystal-field aspect. (Nevertheless, we believe that these extra parameters have more reasonable values for our solution.) By appealing to the 2p spectrum, however, our solution is selected quite unambiguously.

Our result is qualitatively the same as the old picture for NiO, CoO, and MnO, obtained in the early 1970's.⁷ This picture has been buttressed by several independent observations.¹ For example, the strong 2p feature has an essentially constant energy separation from the oxygen 2s peak, independent of the material, for a series of transition-metal oxides.⁸ Likewise, the main 2p signal always falls between the “main peak” and “satellite” of the 3d spectrum.⁹ Our interpretation of CuO is consistent with these old observations, provided we identify this “main 2p feature” with the strong state-density peak at the *top* of our 2p band.

In this original picture, the insulating gap (identified with the threshold for strong optical absorption) was assigned to transitions from 3d orbitals to 4s/4p band states. We believe that this conclusion remains correct for *all* of the late 3d transition-metal oxides including CuO, and that the more recent $2p \rightarrow 3d$ assignment^{2-4,19} is wrong. In other words, we are arguing that these materials are *not* “charge-transfer insulators.” This can be deduced from Fig. 1, with allowance for the energy shifts from p-d hybridization, and with a band-theoretic estimate for the 2p-4s band gap.

ETS were quite convinced that the photoconductivity threshold (insulating gap) of 1.35 eV²⁰ is due to $2p \rightarrow 3d$ transitions. They therefore used this gap value (raised to 1.8 eV to allow for some bandwidth of the relevant 2p state) in place of the experimental d-d gap value of 2.9 eV, the separation between the centers of the BIS and photoemission threshold features. We consider this illogical, because one ought to *deduce* the assignment of the insulating gap transitions from the results of the data analysis, rather than presuming a particular choice as input. Furthermore, the calculated d-d gap value should be made to agree with its experimental value, 2.9 eV, instead of the value for a different property. Using the 3d-removal spectrum (XPS data) and their value of 1.8 eV for the d-d gap, but *without* considering the available 2p data, we obtained two solutions, as expected from the argument above, with one of these solutions closely matching their solution. But when we raised the d-

d gap value to 2.9 eV, this sufficed to eliminate the Sawatzky-type (small Δ) solution, *even without* constraining Δ to match the 2p spectral information. (At small Δ but large d-d gap, the required U or A became unphysically large.) This provides further evidence against their assignment.

In contrast, the resonant photoemission¹¹ appears to be very strong evidence *for* the Sawatzky (ETS) solution in Fig. 1. Our response to this is necessarily rather subtle. At 70 eV photon energy, which is just outside the copper 3p $\rightarrow$ 3d resonance region centered around 74 eV, the satellite intensity (relative to the main peak) is only about 1/4 of its intensity in the XPS data. This loss of satellite intensity is surprising. The only explanation we could find, which is consistent with similar data over a broad range of photon energies,¹¹ is that the sudden approximation is failing quite seriously here. Using a semiclassical analysis, we have found¹ that the adiabatic corrections to the “direct” and “resonant” channels are sufficient to qualitatively account for the fact that the resonance is strongly concentrated in the satellite region. Thus, a high energy for the d^8 configuration is *not* demanded by this resonance data.

In matching our calculations to the spectra for 1478 eV, 70 eV, and 21.2 eV photon energies, in each case we treated the orbital photoemission cross section ratio σ_{2p}/σ_{3d} as a free parameter. That is, we added the 3d and 2p removal spectra with an adjustable intensity ratio. At 1478 eV, our empirical value for this ratio was an order of magnitude larger than the very small theoretical value,²¹ based on neutral-atom orbitals. This surprising result is consistent with the appearance of rather prominent 2p-like features in XPS spectra of some other 3d-metal oxides.⁸ To account for this, we came up with two explanations which are presumably working together: (a) The removal of a d electron allows the orbitals of the remaining occupied d electrons to collapse suddenly (in XPS), thus reducing the “passive electron” overlap and suppressing the d removal intensity with respect to the 2p intensity. This is analogous to the band-narrowing in polaron theory. (This happens also for 2p’s, but less strongly.) (b) Since the theoretical analysis presumes orthogonal orbitals, our “2p” orbitals are actually Wannier functions containing bits of 3d and several of the other copper-ion orbitals. At 1478 eV these “Wannier tail” components can contribute substantially to the photoemission cross section, and can thus enhance the apparent 2p intensity.

An important lesson here, as in the cases of the weakened satellite intensity and the resonant photoemission, is that one should be prepared for surprises in intensity behavior, and not rely too heavily on the standard recipes for intensities.

A few more remarks are needed to put these results in perspective. The present model has no Coulomb interactions involving 2p electrons (no U_p or U_{pd}), so the results should not be compared directly with models which do include such interactions. The present parameter set gives a Heisenberg magnetic coupling J which is too small, by about a factor of two, so there is room for some modest revision of the parameters. Finally, it should be emphasized that our results are specific for the *insulating state* of CuO. In applying these parameters to superconducting cuprate materials, one should be wary about possibly important changes due to metallic screening, especially for U and Δ . Also, Δ can be significantly affected by the Madelung potential effects of the ions between the CuO_2 layers, and especially by the presence or absence of apical oxygens.²²

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REFERENCES

1. B. H. Brandow, J. Solid State Chem. **88**, 28 (1990).
2. H. Eskes, L. H. Tjeng, and G. A. Sawatzky, Phys. Rev. B **41**, 283 (1990).

3. G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. **53**, 2339 (1984); J. Zaanen, G. A. Sawatzky, and J. W. Allen, *ibid.* **55**, 418 (1985).
4. J. Zaanen and G. A. Sawatzky, Canad. J. Phys. **65**, 1262 (1987); J. Solid State Chem. **88**, 8 (1990).
5. A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987); Z. Shen *et al.*, *ibid.* **36**, 8414 (1988); D. D. Sarma, *ibid.* **37**, 7948 (1988); F. Mila, Phys. Rev. B **38**, 11358 (1988); D. E. Ramaker, *ibid.* **38**, 11816 (1988); K. Okada and A. Kotani, J. Phys. Soc. Japan **58**, 1095 (1989).
6. J. Ghijsen *et al.*, Phys. Rev. B **38**, 11322 (1988).
7. R. J. Powell and W. E. Spicer, Phys. Rev. B **2**, 2182 (1970); D. Adler and J. Feinleib, *ibid.* **2**, 3112 (1970); L. Messick, W. C. Walker, and R. Glosser, *ibid.* **6**, 3941 (1972).
8. G. K. Wertheim and S. Huffner, Phys. Rev. Lett. **28**, 1028 (1972).
9. D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. **34**, 395 (1975).
10. S.-J. Oh, J. W. Allen, I. Lindau, and J. C. Mikkelsen, Phys. Rev. B **26**, 4845 (1982); M. R. Thuler, R. L. Benbow, and Z. Hurych, *ibid.* **27**, 2082 (1983).
11. J. Ghijsen *et al.*, Phys. Rev. B **42**, 2268 (1990). See also M. R. Thuler, R. L. Benbow, and Z. Hurych, *ibid.* **26**, 669 (1982); Okada and Kotani, in Ref. 5.
12. J. Zaanen, Ph.D. thesis, Groningen (unpublished).
13. T. F. Soules, J. W. Richardson, and D. M. Vaught, Phys. Rev. B **3**, 2186 (1971); A. J. H. Wachters and W. C. Nieuwpoort, *ibid.* **5**, 4291 (1972).
14. P. Ros and G. C. A. Schuit, Theor. Chim. Acta (Berl.) **4**, 1 (1966); B. Roos, Acta Chem. Scand. **20**, 1673 (1966); H. Basch and H. B. Gray, Inorg. Chem. **6**, 365 (1967); F. A. Cotton and C. B. Harris, Inorg. Chem. **6**, 369 (1967); J. Demuyne, A. Veillard, and U. Wahlgren, J. Am. Chem. Soc. **95**, 5563 (1973).
15. R. L. Martin, Physica B **163**, 533 (1990), and private communication.
16. A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988); M. J. DeWeert, D. A. Papaconstantopoulos, and W. E. Pickett, *ibid.* **39**, 4235 (1989); L. F. Mattheiss and D. R. Hamann, *ibid.* **40**, 2217 (1989); M. S. Hybertsen, M. Schluter, and N. E. Christensen, *ibid.* **39**, 9028 (1989); A. K. McMahan, J. F. Annett, and R. M. Martin, *ibid.* **42**, 6268 (1990).
17. R. S. List *et al.*, Phys. Rev. B **38**, 11966 (1988) and Physica C **159**, 439 (1989).
18. Z. Shen *et al.*, in Ref. 5.
19. S. Hüfner, Z. Phys. B **61**, 135 (1985).
20. F. P. Koffyberg and F. A. Benko, J. Appl. Phys. **53**, 1173 (1982).
21. J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).
22. J. B. Torrance and R. M. Metzger, Phys. Rev. Lett. **63**, 1515 (1989).