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UNDERSTANDING ELECTRONEGATIVE EFFECTS IN CORE-
LEVEL ELECTRON SPECTROSCOPES; APPLICATION TO
THE HIGH TEMPERATURE SUPERCONDUCTORS

By

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2. THE CORE-LEVEL IN XPS

2.1 The Nature of the Satellites

The metal 2p XPS data for TM compounds generally exhibit a main peak plus one or two satellite peaks at higher binding energy (5-14). Figure 1 summarizes the energy separation, ΔE , between the main and satellite peaks, and Fig. 2 shows XPS data for titanium and copper halides (7,12); examples at the left and right sides of the TM series. Several mechanisms have been proposed to explain the origin of these satellites (15). The models involving charge transfer (CT) seem to be gaining the most acceptance for explaining at least some of the 2p core level satellites (7,8,10). A different mechanism, the excitonic satellite mechanism (19), appears to be the most promising for explaining the satellites at larger energy separation. Fig. 1 distinguishes between those features identified as charge transfer and excitonic

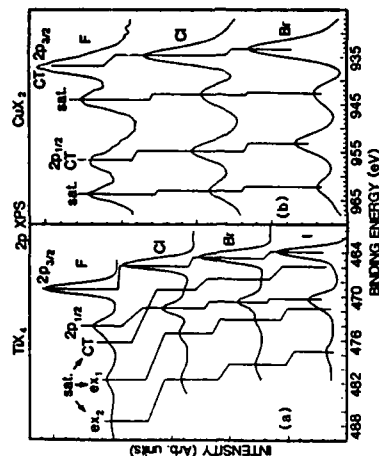
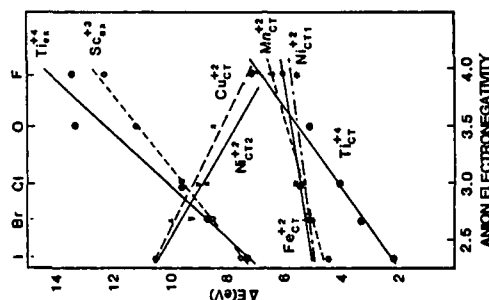


Fig. 1. Experimental main-satellite peak separation, ΔE , vs. anion electronegativity, χ . Experimental data obtained from the following: TiX_4 (12), TiO_2 (13), Sc (9), Cu (7), Mn (10), and Ni (8). Anion electronegativity from Ref. 5. Although the data are not necessarily linear, the straight lines help to give clarity to the plot.

Fig. 2. a) Ti 2p XPS data (12) for TiX_4 complexes taken in the gas phase. Comparison with data taken in the solid phase for $TiCl_4$ (14) indicates very little differences. b) Cu 2p XPS data for CuX_2 (7). The data for $X = Cl$ and Br have been Gaussian broadened by 3 eV to allow better comparison with that for $X = F$, which generally reveal much broader peaks.

UNDERSTANDING ELECTRONEGATIVITY EFFECTS IN CORE-LEVEL ELECTRON SPECTROSCOPES; APPLICATION TO THE HIGH TEMPERATURE SUPERCONDUCTORS

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SUMMARY

The nature of the core level reflected in x-ray photoelectron spectroscopy, Auger electron spectroscopy, and x-ray absorption near edge structure is considered. An understanding of the effects of anion and cation electronegativity on spectra for the transition metal halides is obtained. This knowledge is applied to understand similar spectra for the high temperature superconductors.

1. INTRODUCTION

Since the discovery of the copper oxide based high temperature superconductors (HTSC) just a few years ago, a deluge of electron spectroscopic data on these materials has appeared. In spite of this great effort to elucidate their electronic structure, many basic questions remain on just how to interpret some of the data. In an effort to provide answers, some investigators have examined the more basic CuO and Cu_2O materials (1-4). In this work we shall examine some core-level electron spectroscopic data of various transition metal (TM) halides. By emphasizing the effects of anion electronegativity (χ_a) on the spectra, some basic understanding can be obtained, which we then apply to the HTSC's.

This paper will consider three different reflections of a core-hole state. In Sec. 2 we examine the transition metal 2p x-ray photoelectron spectra (XPS), which reflect the initial creation of a core-hole (i.e. within the escape time of the photoelectron, typically much less than 10^{-17} sec.). Sec. 3 examines the nature of the core-level which decays in the Auger and x-ray emission processes (AES and XES), and thus reflects a more relaxed core-hole generally much later than 10^{-15} sec. after creation. Sec. 4 discusses the nature of the anion core-level in x-ray absorption near edge spectra (XANES), which reflects the unoccupied density of states after a completed response to creation of the core-hole.

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satellites. The excitonic satellites result from the polarization response to the core hole, and are believed to involve shakeup of an electron on the anion (9). ΔE will obviously increase with x for these satellites, since the binding energy of the anion valence band increases with x . The excitonic satellites exist only for metals near the beginning of the TM series, i.e. for Sc, Ti, and perhaps Cr, etc (9). We will not discuss them further here, but rather concentrate on the CT satellites.

It is clear from Fig. 1 that electronegativity has a dramatic effect on the separation and intensity of the CT satellite peaks. Two very different CT models exist for explaining this data. Veal and Paulikas (the VP model) (5), examining primarily the left end of the TM series, utilized a relativistic local density atomic code to calculate transition energies for atoms with different outer electronic configurations. In their work, replacement of a localized 3d electron with a more extended 4p electron simulates the movement of charge from a metal cation to a more electronegative anion (i.e. local vs. nonlocal screening). It was concluded from these calculations that the main peak arises from a locally screened final state reflecting a 2p to 3d CT response to the core hole, and the satellite from a state reflecting a more nonlocal polarization response to the core hole. Within the VP model, ΔE increases with x , because the non-local screening response is decreasing with x , while the local CT response remains unchanged. The larger "chemical shift" of the satellite compared with the main peak for the TiX_3 complexes in Fig. 2, and the positive slope for all but the CuX_3 and NiX_3 materials in Fig. 1, appears to be consistent with this model.

On the other hand, Larsson (6) and Sawatzky and co-workers (the LS model) (7) utilizing an Anderson impurity Hamiltonian in a correlated cluster theory, examined the XPS data for the Cu and Ni dihalides. More recently Park et al (10) have extended the model to the Co, Fe, and Mn dihalides. The ground state is viewed as a hybridized mixture,

$$\psi_g = A(d^n + \alpha d^{n+1}L^{-1} + \beta d^{n+2}L^{-2}) \quad [A^2 = (1 + \alpha^2 + \beta^2)^{-1}] \quad (1)$$

of the three indicated configurations, where n is the number of TM 3d electrons assuming a completely ionic compound, and L^{-1} or L^{-2} indicate the number of holes on the ligand. The diagonal energy of these configurations is given by $d^n = 0$, $d^{n+1}L^{-1} = \Delta$, and $d^{n+2}L^{-2} = 2\Delta + U_d$ where U_d is the effective d-d Coulomb interaction and Δ is the CT energy (7). The parameters α and β are determined by diagonalization of the 3×3 matrix with off diagonal matrix elements characterized by T , the p-d hybridization parameter. The eigenstates,

$$\psi_i = A(2p^i d^n + \alpha' 2p^i d^{n+1}L^{-1} + \beta' 2p^i d^{n+2}L^{-2}) \quad (2)$$

appropriate for after creation of the core hole involve the indicated configurations with energies, $2p^i d^n = E_c$, $2p^i d^{n+1}L^{-1} = E_c + \Delta - Q$, and $2p^i d^{n+2}L^{-2} = E_c + 2(\Delta - Q) + U_d$, where E_c is the core-hole excitation energy, and

Q is the effective core-hole, d-electron Coulomb attraction energy (7). The final state energies are obtained by diagonalization of the corresponding Hamiltonian matrix. Within the sudden approximation the XPS intensities are given by $I_n = |\langle \psi_f | 2p^i \psi_g \rangle|^2$.

Assuming $U_d = 5.0$ eV, $Q = 7.0$ eV, and $T = 2.0$ eV (parameters appropriate for Ni^{2+} when $n = 8$), Zaanen et al (8) have presented the results in Fig. 3, which gives the energy separation, ΔE , and the satellite intensities relative to the main peak, I_s/I_m , for the two possible satellites. We have also indicated in Fig. 3b, the dominant configurations in the main peak and each of the satellites. Fig. 3a also indicates the optimal Δ/T for each halide anion which provide nearly quantitative results for the NiX_3 (8). These results show that ΔE is nearly constant with Δ and ΔE decreases with Δ in agreement with Fig. 1 (it is assumed that Δ is proportional to x). Fig. 3b shows that for NiF_3 , the main peak is primarily $2p^i d^{n+1}L^{-1}$ and for the remaining Ni halides, it is primarily $2p^i d^{n+2}L^{-2}$, i.e. the core hole is primarily locally screened by CT. Note that only Δ changes significantly as the halide changes.

These results can be utilized to qualitatively understand the satellites for the other TM's as well. For Cu^{2+} when $n = 9$, of course the $2p^i d^{n+1}L^{-1}$ configuration is no longer valid. In this case the curves for S_1 map qualitatively into M, and those for S_2 into S_1 (7,8). Fig. 3a shows the optimal Δ for the CuX_3 , showing that indeed ΔE then decreases with Δ in agreement with experiment (Fig. 1) (11). The results obtained by Park et al (10) for Co, Fe, and Mn are qualitatively similar to those in Fig. 3, although they included the additional configurations $cd^{n+1}L^{-1}$ ($i=3$ to $10-n$). As we go left in the TM series, the 3d orbitals become more diffuse and shift to lower binding energy, and the lattice constant gets larger, having the effect of increasing Δ , and decreasing T and Q (10,16). Thus we move to the right in Fig. 3 as we go left in the TM series (the optimal values (10) for Δ/T and Q are shown for Mn in Fig. 3) showing that the slope of ΔE vs. x should shift from negative to positive in agreement with Fig. 1, and the intensity of the CT satellites should decrease in intensity (compare the Ti vs. Cu data in Fig. 2). Evidently the experimental XPS data (i.e. at least the CT satellites) for the entire TM series can be qualitatively explained by Fig. 3 and the general LS model.

Although both the VP and LS models appear to be consistent with Fig. 1, closer analysis shows the two models assign the various peaks very differently. Fig. 3 shows that as Δ/T increases, the final state forming the main peak is not the CT locally screened state, but rather the non-locally screened state. This is because as we proceed left in the TM series when Δ becomes greater than Q , the CT costs more energy than that returned from screening. This main-satellite peak reversal between Cu^{2+} and Ti^{2+} is evident from the absolute peak energies (Fig. 2), which show that the "chemical shift", due to the change in Δ ,

is largest in the CT peak; i.e. the CT satellite peak for TiX_3 , the main peak for CuX_3 (7,12). It is also evident from the narrow main peak widths, which according to the LS model have primarily a $2p^{-1}d^8$ (Ti^{3+}) or $2p^{-1}d^9L^{-1}$ (Cu^{3+}) core-hole state which offer no opportunity for multiplet splitting between the

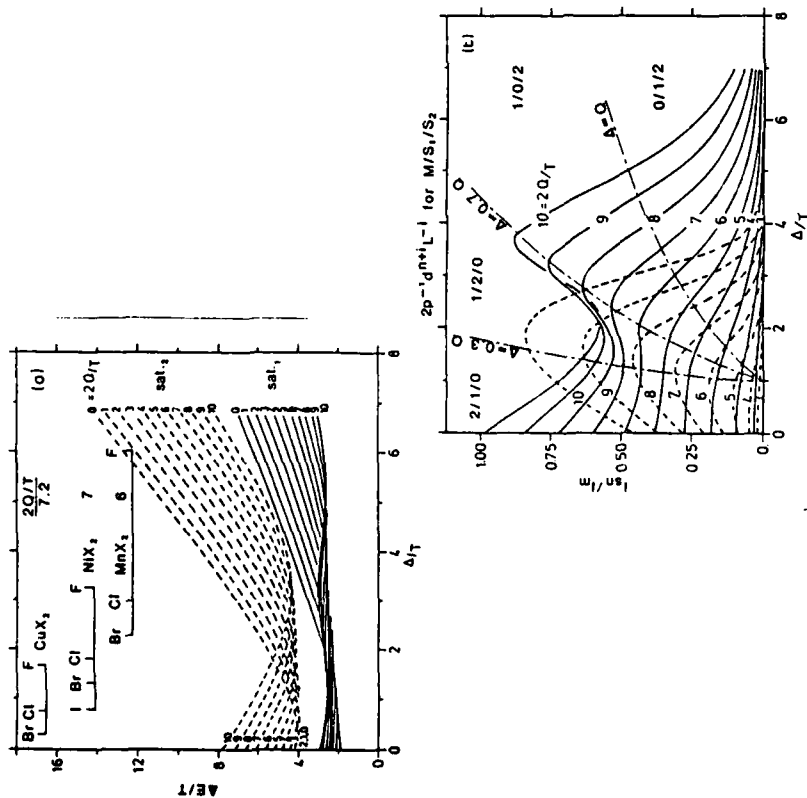


Fig. 3. Calculated results obtained by Zaanen et al. (8) utilizing the LS model for $U = 0.5$ eV, $Q = 7$ eV, and $T = 2$ eV; the parameters most appropriate for NiX_3 . a) ΔE vs. Δ/T . The optimal Δ/T and $2Q/T$ are indicated as obtained by comparison with experimental data for CuX_3 (7), NiX_3 (8), and MnX_3 (10). b) $1/L_0$ vs. Δ/T . The lines for $\Delta = 0.3, 0.7$ and 1.0 Q are the points where the dominant character of the main and satellite peaks are switching the fastest with change in Δ . The dominant character within each region between these lines is indicated by the number of electrons, i , transferred to the core-hole atom for each main and satellite ($M/S_1/S_2$) feature (i.e. i in the expression $2p^{-1}d^{n+1}L^{-1}$). Dotted lines are for satellite 2, and solid for satellite 1.

excited electron and the core hole (9). In contrast the satellites reflect $2p^{-1}d^i$ (Ti^{3+}) and $2p^{-1}d^8$ (Cu^{3+}) states, which indeed are broadened by multiplet splitting in each case. Finally the very similar multiplet structure (such structure is often more important at the 3s and 3p levels than at the 2p levels) exhibited in the 3s and 3p core level XPS data for MnF_3 , MnO and atomic Mn (17) indicates that the CT does not occur in the primary state for these two materials either, a fact consistent with Fig. 3.

This CT main-satellite peak reversal between the left and right ends of the TM series is contrary to the VP model (5), which assumed that the main peak was always representative of the locally screened state. Of course the atomic model utilized in the VP model did not take into account the cost of the CT, and thus their basic assumption was incorrect. It seems quite ironic that although the basic VP assumption is correct for the right end of the TM series, there ΔE decreases with X , rather than increases. We believe that the VP model therefore does not correctly interpret the XPS data anywhere, although it qualitatively is consistent with the trends in Fig. 1 for most of the TM series.

2.2 Application to the HTSC's

Recently Nepela and McKay (18) reported a remarkable correlation of T_c in the HTSC's with the electronegativity difference, ΔX between the average for all of the metal atoms, X_M , and that for the anions, X_A (see Fig. 4). They further utilized the VP model and the data in Table 1 to conclude that the Cu-O bond is becoming more ionic as T_c increases, consistent with their reported T_c vs. ΔX correlation. The data in Table 1 and the LS model indicates more correctly that the Cu-O bond is actually becoming more covalent for the HTSC's, i.e. a large Cu-O hybridization occurs and the holes or electrons are more equally shared between the Cu and the O in the HTSC's, consistent with other data (25).

If the Cu-O ionicity decreases with T_c , how can the T_c vs. ΔX correlation be explained? Newns et al (26) have suggested that ΔX does not reflect the Cu-O bond ionicity, but rather the ionicity of the remaining "counter" ions which regulate the number of holes introduced in the CuO_2 planes. It has been shown experimentally that T_c is proportional to the number of holes on the O atoms in the CuO_2 planes (27-29). Newns et al (30) have shown that this is dependent on the binding energy, E_* , relative to vacuum of the top of the O nonbonding valence band. This is because when the Fermi level drops to E_* , no additional holes will be introduced into the CuO_2 planes. Furthermore, Phillips and van Vechten (31) have shown that the ionic band gap, and hence E_* , is proportional to ΔX .

3.1 Relaxation vs. Decay

Evidence for relaxation of the CT shakeup satellites before Auger decay in CuX₂ is clearly evident from Figs. 2 and 5. The primary 2p-d₁₀⁹ core-hole state decays to a d₁₀¹⁰ primary Auger final state in the Cu L_{2,3}V case and

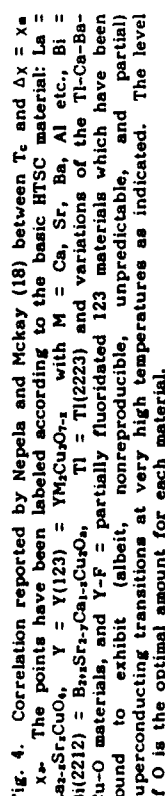


Fig. 5. a) Comparison of $L_{2,3}VV$ Auger spectra for the CuX , from ref. (7). The data for $X = Cl$ and Br were shifted by -1.5 and -2.5 eV, respectively, to bring them into registry with that for $X = F$. The data for Cl and Br were Gaussian broadened by 2 eV for clearer comparison with the F data.

b) Comparison of $L_{2,3}M_{2,3}V$ Auger data for the CuX , from ref. (7). The data for $X = Cl$ and Br were shifted by -2.75 and 3 eV for registry with the F data. The Cl and Br data were broadened by 2 eV.

c) Comparison of $L_{2,3}VV$ Auger data for CuO (7), CuO (7), and $Bi(2212)$ data reported by Weaver (22), Hillebrecht (24), and Kohiki (21)]. No shifts or broadening were performed here.

d) Comparison of $L_{2,3}M_{2,3}V$ data for $CuCl$, Cu and $CuCl_2$ (7). The data for Cl is exactly as in b) above, and the Cu and $CuCl$ were broadened by 2 eV. The $CuCl_2$ data were placed in registry with that for $CuCl$.

Data showing the correlation of ΔE and I_V/I_m with T_c for the HTSC's.

All results directly reported by author. The data varies because of different background subtractions but trends within a single investigator's results are clearly shown.

The Bi 4s XPS feature may also be contributing to the satellite peak in this case (22,24).

Ramakrishna has also shown that $I_{\text{L}}/I_{\text{M}}$ correlates with T_{c} within the Y(123) samples.

Kohiti used a variety of samples with different T_{c} 's.

The above results show that clearly all CT shakeup states relax before core-hole decay (33). This is not unexpected because the shakeup excitation energy is much larger than the core-level width (34). In contrast, the additional valence-hole states resulting from Coster-Kronig decay and shakeoff do not dissipate before decay, because the extra hole is apparently bound on the local CuO_4 cluster (33).

3.3.2 The Nature of the Core-level Width

At least two mechanisms have been given to explain the nature of the large widths for the main Cu $2p$ XPS peak. Assuming that the main peak indeed reflects predominantly the $2p_{1/2}L_{2-3}$ state, it has been suggested that the large width arises from the width of the anion band, i.e. from the spread of

the L hole (24,35). However, Fig. 2 shows that the width of the main 2p XPS peak increases from Br to F; however, the width of the valence band as reflected in XPS data is essentially constant for CuX_2 (7).

A second mechanism suggests that the width arises from multiplet splitting (7). The large width of the satellite is known to arise from the spread of the $2p\text{-}d^9L^{-1}$ multiplets (7). In the LS model, the mixing of the $2p\text{-}d^9L^{-1}$ and $2p\text{-}d^{10}$ configurations in the XPS final state, eq. (2), then causes the width of the primary peak, since the d^{10} configuration has just a single multiplet. This mechanism is consistent with the observation that the width of the main peak directly correlates with the relative intensity of the satellite as seen in Fig. 2 for the CuX_2 (7). Sacher et al (36) have also shown that the width correlates with the inductive character (or electronegativity) of the ligand for a large number of different ligands consistent with the LS model.

The Cu $L\alpha$ XES data (2,4) for CuO has a width (FWHM) of 1.7 eV, much narrower than the Cu 2p main XPS peak (3-4 eV) (1-3). One might question how the XES spectrum can be narrower than the XPS peak which reflects the initial state of the XES process. To understand this we need just to realize that in XES, the mixed $2p\text{-}d^9/2p\text{-}d^9L^{-1}$ core-hole state decays to a mixed d^9/d^9L^{-1} two-hole valence-band state. The XES spectrum is dominated by the d^9L^{-1} component with the d^9 component fairly small at 12-13 eV. Therefore, consistent with Fermi's golden rule or final state rule (37), only the narrower $2p\text{-}d^9L^{-1}$ character projects onto the d^9L^{-1} final state. From another perspective, the entire spread of multiplets in the initial state does not contribute to the width of the XES. We note, however, that the widths of the AES peaks in Fig. 5 do increase with the widths of the XPS peaks in Fig. 2 for the CuX_2 . Apparently some small component of the primary state width does project onto the AES or XES final state width.

3.3 Application to the HTSC's

Fig. 5 indicates that the $L_{2,3}V$ Auger spectrum for Bi(2212) exhibits an increased satellite intensity. This satellite intensity is also enhanced for the Y(123) materials, but it varies considerably (19,38,39), apparently because of the presence of Cu^{+} character near the sometimes O depleted surface under vacuum (40,41). Note that Fig. 5 shows the $L_{2,3}V$ Auger peak for CuO at the kinetic energy for the satellite in CuO and the HTSC's (1). This O depletion problem is particularly true of the Y(123) samples (40); but, this is much less of a problem for the Bi(2212) samples (at least the Bi samples exhibit a UPS intensity at the Fermi level) (42-51). In light of the above, this increase cannot arise from decay of the shakeup core-hole state, since it relaxes prior to the Auger decay. Furthermore, an enhanced satellite is not evident in the $L_{2,3}V$ Auger spectra, and it should be visible in both if the core-hole

shakeup states are Auger decaying (33). We have suggested previously that the enhanced satellite arises from d^9L^{-1}/d^9L^{-1} hybridization in the Auger 3-hole final-state (33). This hybridization is larger in the HTSC's because of the increased covalency of the HTSC's compared to CuO or the CuX_2 . The difference in energy between the d^9L^{-1} and d^9L^{-1} states, as effectively reflected by the O KVV and Cu $L_{2,3}V$ Auger line shapes, decreases from 3.1 eV in CuO (1), to 2.1 eV in CuO (1), to around 1.0 eV in Bi (2212) (22), supporting this point.

4. THE CORE LEVEL IN XANES

4.1 Excitonic Effects

The final state rule (37) generally dictates that XANES data should directly reflect the unoccupied density of states (DOS) relaxed in the presence of the core hole. Although not completely applicable for highly-correlated systems, it should be qualitatively correct for the HTSC discussed here. However, when a band is nearly full, such as the O 2p or X 3p valence bands in metal oxides or halides, the XANES excitation, $p^1 \rightarrow 1s^{-1}p^4$, completely fills these bands. In this case the XANES spectra reflects the initial unoccupied DOS without the core hole. We have termed this the initial-state/final-state rule applicable for the nearly filled VB /empty CB cases (52).

Figure 6 shows anion K edge XANES data for several TM oxides and chlorides (53-59). These data clearly show the empty O 2p/Cl 3p states in the valence band just above the Fermi level for all but CuCl , which has a filled Cl 3p valence band as expected. This initial peak has been shown to depend on the O hole density (25,60), the symmetry of the p orbitals (51,62), and the van Hove singularity (63). The peak around 531 eV in the Bi(2212) data in Fig. 7, is believed to arise from Bi-O antibonding orbitals (64-66).

Above these valence band peaks we see excitation into the O 3p/Cl 4p extended conduction bands. Here the final state rule is applicable, so that the line shapes reflect the 3/4 p DOS in the presence of a core hole. The 3/4 p DOS has remarkably similar structure (albeit different energy scales) for all of the materials shown except for the absence of the peak around 2826 eV in the CuCl data. To understand this we need to ascertain the nature of the peak around 2826 eV at the Cl K and 533 eV at the O K edges. Multiple scattering calculations, but which do not account for the core hole, reproduce all of the structure in the spectra except for this peak, as seen for the NIO and CuO data in Fig. 6 (54,55). Those calculations which include the core hole (i.e. excitonic effects) naturally obtain this peak (53,67,68). There seems to be little doubt that this peak arises from an excitonic-like state involving the 3/4 p extended bands. Its absence in CuCl must mean that the highly polarizable filled 3d shell on the Cu atoms surrounding the Cl anion can more effectively screen the

core-hole, 4p-electron interaction, than the unfilled 3d shell in the other systems. The reason for this, however, is not entirely clear.

4.2 Application to the HTSC's

We have been unable to locate O K edge XANES data for Cu_2O . Nevertheless, we believe a similar polarization phenomenon is occurring for Cu_2O as well for some of the HTSC materials studied. Fig. 6 shows data (56) for Y (123x) with x equal to 6.98 and 6.26. Notice the much reduced feature at 533 eV in the data for $x=6.26$. At these very low O levels, the peak at 528.6 eV is also much reduced. At intermediate O levels (data (56) not shown in Fig. 6) the 530 eV peak decreases without reduction of the 533 eV feature. This indicates that with O reduction, the 2p DOS just above the Fermi level decreases as expected, but finally at $x = 6.26$, Cu^{1+} is formed (56) as indicated by the reduced 533 eV peak. Thus the O K edge can be used to track the reduction in O 2p holes, as well as the production of Cu^{1+} .

One of the most important Hubbard parameters still not accurately known is the p-p Coulomb interaction, U_p , on the O atom (69-71). Values from 4.5 to 14 eV have been reported (1,20,72-76). The O KVV AES data rather directly indicates the two-hole binding energy which for Cu_2O is equal to $2\epsilon_p + U_p$, and UPS data directly reflect the value of the one-electron binding energy, ϵ_p . Thus a U_p of 4.6 eV is indicated for Cu_2O (1) compared to estimates as large as 12 eV for ZnO, which also has a filled 3d shell but apparently much more core-

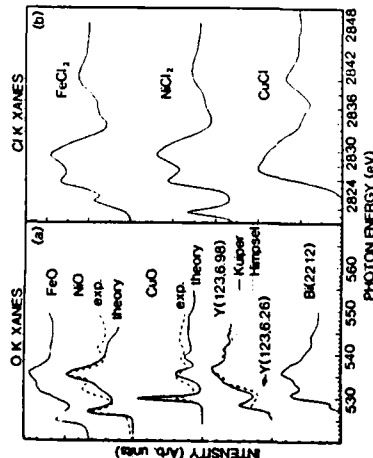


Fig. 6. a) Comparison of experimental O K XANES data for FeO (53), NiO (53), CuO (55), Y(123, 6.98) [Kuiper (56) and Himpsel (57)], Y(123, 6.26) (56), and Bi(2212) (57). Theoretical results without the inclusion of effects from the core-hole are shown for NiO (54) and CuO (55).

b) Comparison of experimental O K XANES data for FeCl_2 (58), NiCl_2 (58), and CuCl (59). The CuCl data was shifted up by 2 eV for alignment of the features above 2830 eV.

like and thus less polarizable (77). In CuCl , the free ion p-p interaction of 10.2 eV is reduced to 3.8 eV by polarization effects (78), again showing the large polarizability of the neighboring closed shell Cu^{1+} ions. Similar Auger data for CuO and the HTSC's is not so easily interpreted because now the Auger final state is a 3-hole state (7,33), and the UPS final state a 2-hole state, so the values of ϵ_p and U_p for these systems remain very uncertain (69-72, 79-81). Often, it has been assumed that U_p is the same for Cu_2O , CuO and the HTSC's (1,82).

In light of the relatively small 1s-core-hole, 3p-electron interaction experimentally deduced above for Cu_2O , one might also expect U_p to be relatively small for Cu_2O . Thus we anticipate U_p to be somewhat larger for CuO and the HTSC's, most probably around 6-8 eV (71-73).

5. CONCLUSIONS

Analysis of XPS, AES, and XANES data for TM halide and oxide data has led to the following conclusions:

1. The Larson-Swatzky model adequately explains the satellite structure in TM 2p XPS.
2. The satellite states visible in XPS do not produce comparable satellites in AES or XES, but rather relax before the decay process.
3. The filled 3d shells in Cu^{1+} atoms which surround the anion in Cu halides or oxides, are uniquely strongly polarizable and thus decrease the intra-atomic anion Coulomb interactions.

Applying these findings to the HTSC's, we find the following:

1. The covalency of the Cu-O bonds increase with increasing Tc.
2. The increased L₂₃V Auger satellite visible for the HTSC's arises from final state mixing due to the increased covalency.
3. The O p-p coulomb interaction in CuO and the HTSC's is probably significantly larger than that for Cu_2O .
4. The O K edge XANES data can be used to track the reduction of unfilled O 2p DOS at the Fermi level as well as the production of Cu^{1+} .

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