# Resonant photo- and Auger emission at the 3p threshold of Cu, Cu<sub>2</sub>O, and CuO

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We report photoemission spectra and intensity profiles of the 3*d* emission and the resonant valence-band satellites in Cu, Cu<sub>2</sub>O, and CuO. By analyzing the satellite separation energies, the multiplet structure, and the resonance shifts, we show that alternative resonance mechanisms are observed on Cu atoms in different electronic configurations. For Cu and Cu<sub>2</sub>O we find similar effective Coulomb interactions for the satellite final state. This emphasizes the contribution of the shake-up final state to the satellite separation energy, as evidenced by corresponding resonance shifts. Our results suggest that an alternate process can lead to the valence-band satellites observed in x-ray-photoemission spectroscopy studies of CuO (and many other compounds) which were previously interpreted as "ligand-to-metal charge-transfer" satellites. Finally no shift (<0.2 eV) of the  $M_{23}M_{45}M_{45}$  Auger emission is observed within 10 eV of the threshold. The increased effective Coulomb interaction for the Auger emission in Cu<sub>2</sub>O is attributed to the lack of metallic screening.

### I. INTRODUCTION

Resonant photoemission has attracted considerable interest in recent years. The observation of a strong resonance of the 6-eV satellite in Ni by Guillot et al.<sup>1</sup> suggested that empty 3d states are essential for the excitation of a two-hole bound state. The observation of the satellite far from resonance was explained by Penn<sup>2</sup> as being due to an intra d-shell Auger transition occurring simultaneously with the 3d-electron photoexcitation. At resonance, the same final state is reached if a  $3p \rightarrow 3d$ electron transition is accompanied by a super Coster-Kronig Auger transition (3p, 3d, 3d). The interference of these two channels leads to the resonant behavior of the satellite intensities. Recent reports of resonant satellites in systems with closed 3d shells such as Cu (Ref. 3), Zn (Ref. 4), and Ga (Ref. 5) show, however, that empty 3dstates are not essential for the existence and resonant behavior of these satellites. These reports propose a similar resonance mechanism with a  $3p \rightarrow 4s, p$  electron transition. The possibly excitonic 4s, p-like final state is then localized due to the presence of the two 3d holes in the satellite final state. Far from resonance the same satellite final state can then be reached if a  $3d \rightarrow 4s, p$  shake-up transition accompanies the photoexcitation of a 3delectron. While this intershell process can occur also in systems with empty 3d states, it should be

much weaker than the intrashell (nl=3d) process because of the stronger interaction within the 3d shell.<sup>2,6</sup> A more generalized model of the resonance was described by Davis and Feldkamp.<sup>6</sup> It takes into account the continuum character of the empty states. In this model the satellite is due to the strong interaction of the 4s,p conduction electrons with the 3d<sup>8</sup> electron configuration in the final state. These authors have calculated intensity profiles of both main line and satellites through the resonance which agree with experiment.

The object of this study is to compare the relative strength of these two resonance mechanisms (nl = 3d vs 4s) and the role of solid-state effects (screening) in this mainly local process. This is done by the comparison of the resonant behavior of Cu, Cu<sub>2</sub>O, and CuO at the Cu 3p threshold. Specifically, we compare a  $3d^{10}$  metal (Cu) to a  $3d^{10}$  insulator (Cu<sub>2</sub>O) and a  $3d^{9}$  semiconductor (CuO). We conclude that the satellite intensity profiles at and far from resonance, as well as the changes in satellite energy and in the 3p excitation energy, support the assumption that different processes are indeed being observed in open (CuO) and closed (Cu, Cu<sub>2</sub>O) shell systems. In addition, we identify the resonant satellite in CuO with the satellite observed in x-ray-photoemissionspectroscopy (XPS) studies of CuO (Refs. 7 and 8) based on the similar energy separation. This suggests that the valence-band satellites observed in

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XPS are not due to a "ligand-to-metal charge transfer" (Refs. 9 and 10) but rather to an intra-dshell shake-up process. This latter could also obey the monopole transition selection rules for shakeup processes in CuO far from resonance.9,11 The absence of such valence-band (VB) satellites for Cu and Cu<sub>2</sub>O for XPS data is then explained by the different shake-up process  $(3d \rightarrow 4s, 4p; \Delta l \neq 0)$  involved, which is prohibited by the monopole<sup>9,11</sup> selection rules far from resonance. Finally, an analysis of the  $M_{23}M_{45}M_{45}$  Auger emission shows no variation (< 0.2 eV) in the kinetic energy close to threshold. The effective Coulomb interaction  $U_{\text{eff},A}$  for the <sup>1</sup>G Auger components are determined.  $U_{eff,A}$  for Cu<sub>2</sub>O is larger than that of the satellite,  $U_{\rm eff, sat}$ . A similar difference was found for GaP and attributed to the lack of metallic screening.5

# **II. EXPERIMENT**

The experiments were made at the Synchrotron Radiation Center of the University of Wisconsin-Madison. The photoelectron energy was measured with a double-pass cylindrical mirror analyzer  $(\Delta E \simeq 0.3 \text{ eV})$ . Standard energy distribution curves (EDC's) were taken at closely spaced energy intervals with *p*-polarized light ( $\theta_{inc} = 45^{\circ}$ ). The working pressures ranged from  $6 \times 10^{-11}$  to  $2 \times 10^{-10}$ Torr. Cu samples were produced either by Ar bombardment ( $p = 5 \times 10^{-5}$  Torr, 800 V, 30 min) and annealing ( $\sim$ 700 °C) of a polycrystalline sample or by boat evaporation. CuO was obtained by exposing hot copper (~700 °C) to  $10^{-2}$  Torr oxygen while cooling down for 20 min. Annealing such samples for 30 min in vacuo finally produced spectra characteristic of pure Cu<sub>2</sub>O.<sup>7</sup> No impurities were detected in the EDC's during a 4-day measuring period for any one sample cycle under these conditions. However, weak emission from Cu<sub>2</sub>O sites in the CuO samples was observed by examining the Cu<sub>2</sub>O satellite region at the Cu<sub>2</sub>O resonance energy. Further oxidation lowered but did not entirely eliminate this contribution.

### **III. RESULTS AND DISCUSSION**

# A. Valence-band spectra

Figure 1 shows angle-integrated photoelectron spectra of the valence-band region of Cu, CuO, and  $Cu_2O$ . The spectra were taken close to the res-



FIG. 1. Valence-band spectra of Cu, CuO, and  $Cu_2O$  at photon energies close to resonance.

onance, at hv = 75, 74, and 76.5 eV, respectively, and all binding energies  $(E_i)$  are given with respect to the Fermi energy  $(E_F)$ . In addition to the 4s band emission up to  $E_F$  and the 3d emission at  $E_i \sim 3$  eV, Cu metal shows two rather sharp satellites at  $E_i = 11.9$  and 14.6 eV. We attribute them to a satellite state which, according to Iwan et al.,<sup>3</sup> leads to the observation of a  $3d^8$  multiplet. The two peaks then correspond to the strongest multiplet components, namely  ${}^{1}G$  (14.6 eV) and  ${}^{3}F$  (11.9 eV). For Cu<sub>2</sub>O only one satellite peak is clearly resolved (15.3 eV). Because  $Cu_2O$  has also a  $3d^{10}$ configuration (diamagnetic) we again expect the resonant shake-up satellite to have the  $3d^8$  configuration. Therefore, in analogy with Cu, the observed peak at 15.3 eV corresponds to the  ${}^{1}G$  component. The main 3d emission is slightly shifted to higher binding energy  $E_i \sim 3.2$  eV. Below it from 6-7 eV are the O 2*p*-derived bands. The O 2s band is at  $E_i \sim 22.2$  eV. The binding energies of the oxygen derived states are somewhat larger  $(\sim 2 \text{ eV})$  than expected from a recent bandstructure calculation.<sup>12</sup> Our Cu<sub>2</sub>O spectrum compares well with earlier XPS and ultraviolet photoelectron spectroscopy (UPS) measurements.<sup>7,8,13</sup>

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Finally, in the case of CuO,<sup>8</sup> the O 2s-derived emission shifts (0.6 eV) to lower binding energy (21.6 eV) in accordance with a further Cu $\rightarrow$ O charge transfer and the O2p bands more strongly overlap the 3d emission. CuO has an open-shell  $3d^9$  configuration (paramagnetic), and a slight broadening of the main 3d emission is observed. Two very strong components of the satellite are observed at 10.5 and 12.9 eV, with a third weak component located approximately at 16.6 eV.

#### B. Photon energy dependence

Figure 2 shows the intensity profiles of the maximum intensity of the strongest satellite component with a linear background subtracted. The results presented here have been normalized<sup>14</sup> to a ~1-eVwide background region of inelastic electrons immediately below the 3d emission. As the kinetic energy of this flat region at the 3p threshold is higher than the corresponding energy of the decay electrons (Auger, resonant satellite) no significant variation due to this normalization is expected in the region of interest, e.g., the threshold vicinity.



FIG. 2. Normalized intensity profiles (maximum intensity less interpolated linear background) of the resonant satellites in Cu, Cu<sub>2</sub>O, and CuO. The peak values are roughly 11%, 13%, and 23%, respectively, of the maximum 3d intensity (without background subtraction). Note that different intensity scales are raised for Cu and CuO. The numbers give the half-height position  $hv_{\text{thr}}$ . ELS gives values for the core ionization losses (Ref. 15) and XPS shows the binding energy of the Cumetal  $3p_{1/2,3/2}$  core levels determined by XPS (Ref. 10).

The resonance curves in Fig. 2 for all three systems show a characteristic two-peak structure with an energy separation of about 2.3 eV in each case. We attribute this doublet to the excitation of the spin-orbit split components  $3p_{1/2,3/2}$  of the 3p level with  $\Delta_{so}=2.2 \text{ eV.}^{10}$  For Cu the maxima occur at hv's corresponding roughly to the binding energies as determined by XPS:  $E_i(3p_{1/2,3/2})=75.07$  and 77.23 eV.<sup>10</sup> For Cu<sub>2</sub>O (CuO) the half-maximum of the lower edge is shifted to higher (lower) photon energy by 0.85 (1.4) eV. For comparison, recent electron-energy-loss spectroscopy (ELS) results<sup>15</sup> for the 3p ionization losses are also indicated in Fig. 2.

## C. Discussion

Resonant photoemission clearly involves the excitation of a 3p-core electron. Any shift in the binding energy of the core levels (such as chemical shifts or spin-orbit splitting) would result in a rigid shift of the entire resonance profile but have no implications for the satellite main line separation energy  $\Delta E_{sat}$ . Thus the occurrence of two maxima in the resonance profile with a separation equal to the spin-orbit splitting (see Fig. 2) indicates involvement of both  $3p_{1/2}$  and  $3p_{3/2}$  core levels in the resonance mechanism. Furthermore, since XPS measurements of these core levels show no chemical shift between Cu and Cu<sub>2</sub>O, the observed shift in the resonance threshold by 0.85 eV (Fig. 2) between Cu and Cu<sub>2</sub>O must be then due to a shift of the final state of the 3p excitation. In the case of resonance, this final state with energy E(4s) is also the final state of the shake-up process and constitutes a term in  $\Delta E_{sat}$  [see Eq. (1)]. The results listed in Table I show that for Cu<sub>2</sub>O the observed shift of the resonance profile can directly explain most of the increase in  $\Delta E_{sat}$ . For Cu and  $Cu_2O$  the satellite binding energy is given<sup>5</sup> by

$$E_{i,\text{sat}} = \overline{E}(3d) + \Delta E_{\text{sat}} = 2\overline{E}(3d) + E(4sp) + U_{\text{eff}} .$$
(1)

Equation (1) defines the effective Coulomb interaction  $U_{eff}$  between the two 3d holes in the 3d<sup>8</sup> final-state configuration. If we assume E(4sp) to lie at the Fermi level for Cu metal, we find  $U_{eff,Cu} = 8.2$  eV and  $U_{eff,Cu_2O} = 7.9$  eV for the <sup>1</sup>G component of the satellite. The value for Cu metal is in good agreement with the value (8.0 eV) found earlier by analyzing the  $L_3M_{45}M_{45}$  Auger emission.<sup>16</sup> Another feature in Fig. 2 is that the satel-

	Cu	Cu <sub>2</sub> O	CuO
$hv_{\rm thr}$	74.5(1)	75.35(10)	73.1(1)
hv <sub>sat max</sub>	75.6(2)	76.5(2)	74.2(2)
$E_i(3p_{3/2})$ XPS <sup>a</sup>	75.07	$\Delta E_{ m chem} = 0$	$\Delta E_{\rm chem} = 2$
$E_i({}^1G)$	14.6(1)	15.3(1)	12.9(1)
$\overline{E}_i(3d)^{\mathrm{b}}$	3.2(1)	3.3(1)	3.3(1)
$\Delta E_{\rm sat}$	11.4(1)	12.0(1)	9.6(1)
E(4sp)	≡0 <sup>c</sup>	0.85(1)	(-3.4)
	8.2(2)	7.9(2)	

TABLE I. Experimental values of some relevant energies referenced to  $E_F$  (eV). Estimated errors are given in parentheses.

<sup>a</sup>References 9, 10, and 15.

<sup>b</sup>Center of the 3*d* band at ~70%  $I_{\text{max}}$ .

°This is an assumption (see Sec. III C). A value of  $hv_{\text{sat max}} - E_i(3p_{3/2}) = 0.5$  eV could be deduced from the data, if one neglects the threshold character of the absorption. (The position of a threshold would be the half-height value,  $hv_{\text{thr}}$ .)

lite intensity is very weak (at hv = 90 eV, ca 2% of 3d intensity) away from resonance for Cu and  $Cu_2O$ . We interpret this as a result of the fact that the satellites involved include a  $3d \rightarrow 4sp$  shake-up transition  $(\Delta l = 1)$  forbidden in the atomic picture by the monopole selection rules<sup>9,11</sup> away from resonance. At resonance these selection rules may be partially relaxed due to interference with another excitation channel. This can be compared with very recent measurements on Cu vapor.<sup>17</sup> There the upper limit for the shake-up process at hv = 80eV was observed to be  $\sim 2\%$  of the main 3d emission. The similarity with our results is surprising in that for Cu metal hybridization could cause the presence of 3d character in the empty states. That the hybridization is not the dominant cause for the resonance, i.e., a process like the one observed in Ni, is experimentally verified by the fact that similar resonances are also observed in Zn (Ref. 4), Ga (Ref. 5), and Ge (Ref. 18) where the 3d core levels are certainly full and up to 29 eV below  $E_F$ . Our results on CuO [and also NiO (Ref. 18)] suggest that changes in *d*-band occupancy have a strong effect on the satellite intensity profiles.

For CuO the situation is different. Although available XPS binding energies for the  $3p_{3/2}$  core level are somewhat conflicting, they indicate a chemical shift of  $\sim 2$  eV to higher binding energies<sup>9,15</sup> with respect to Cu metal in agreement with a charge transfer. The observed energy shift by 1.4 eV to lower hv for the 3p excitation would, therefore, lead to a final state 1.4 + 2 eV = 3.4 eV below  $E_F$  in CuO indicating that the single-particle model fails. We propose that this apparent discrepancy<sup>19</sup> between XPS-derived binding energies for the 3p levels and those derived from resonant photoabsorption are due to the different final states involved in each process for CuO.

For XPS (Ref. 20) we have

$$h\nu + 3p^{6}3d^{9}(V) \rightarrow 3p^{5}3d^{9}(V) + e$$
. (2)

Here, filled core levels are omitted and (V) denotes the energy of the *sp* portion of the valence bands. The  $3p^{5}3d^{9}$  final state is evidenced by the rather complicated 3p XPS spectrum due to the exchange and correlation interaction of the 3p hole with the 3d hole.<sup>9,21</sup> Photoabsorption at threshold is described by

$$h\nu + 3p^{6}3d^{9}(V) \rightarrow 3p^{5}3d^{10}(V)$$
 (3)

In this case the 3*d* states are full and the excited state spectrum contains only the spin-orbit splitting of the 3*p* hole state. If the resonant intensity in the satellite is proportional to the number of 3*p* excitations, this can account for the similar shape of the intensity profiles (Fig. 2) showing the spin-orbit splitting of Cu metal. The lower energy of the  $3p^5d^{10}$  state, as compared to the  $3p^5d^9$  state, is probably due to screening by the additional *d* electron.<sup>22</sup>

The involvement of the excited  $3d^{10}$  state in CuO leads again to a  $3d^8$  satellite state after the resonant decay. This is strongly supported by the exact correlation ( $\pm 0.1$  eV) of the multiplet term splitting ( ${}^{1}S = 16.6$  eV,  ${}^{1}G = 12.9$  eV,  ${}^{3}F = 10.5$  eV) with the values obtained earlier from the  $L_2M_{45}M_{45}$  Auger multiplets<sup>16</sup> in Cu metal. These results therefore confirm the assumption made by Penn<sup>2</sup> that in open shell systems the satellites are described by a resonance involving these empty states. The satellite is then given by an n-1 state (n is the initial occupation of that level). As the 3d direct emission also represents a  $3d^{n-1}$  final state in transition-metal oxides,<sup>23</sup> one can describe the satellite far from resonance as an intra-d-band shake-up process. It can therefore satisfy the monopole selection rules ( $\Delta S = \Delta l = 0$ ) required for shake-up processes at higher photon energies.<sup>9,11</sup> This accounts for the strong persistence of the satellite intensity in CuO far from resonance where considerable satellite intensity is readily observed for hv=30 eV and hv=90 eV (~8% of 3d intensity). Based on the same separation energy (9 eV), we identify the XPS valence-band satellites<sup>7,8</sup> with those observed in UPS. [The same identification was made in the open shell elements Ni (Ref. 2) and Pd (Ref. 24).] We therefore conclude that the satellites observed in XPS valence-band spectra of CuO (and possibly most divalent transition metal monoxides) are not due to a "ligand (O 2p) to metal (empty 3d) charge-transfer" process,<sup>10,11</sup> but, rather, due to an allowed intra-d-shell excitation.

Our interpretation agrees with a recent XPS study of the satellites of the copper dihalides.<sup>25</sup> There the VB satellites were also observed to have a  $3d^8$  electron configuration, which therefore excludes the ligand  $2p \rightarrow$  metal 3d charge transfer. That study,<sup>25</sup> however, points out the possibility that the main 3d peak could be due to a  $3d^9 \underline{L}$  final state. L denotes a hole in the ligand orbital due to the charge transfer to the metal 3d bands. The  $3d^9 L$  state can also be identified with direct emission from the ligand p levels. With our resolution (0.3 eV) and the energy dependence of cross sections,  $\sigma(3d)$  vs  $\sigma(2p)$ , we can show that at least part of the ligand 2p emission is nondegenerate in energy with the 3d main peak. As its intensity for CuO seems to be roughly twice as strong as in Cu<sub>2</sub>O we assume that the charge transfer contribution to this emission is not strong. We will therefore describe the 3d main emission with a  $3d^8$ band-like final state where the two holes are separated and do not interact. Such a  $3d^8$ -bandlike state was described for Ni.<sup>2,26</sup>

#### D. Direct recombination

Direct recombination of the excited 3p electron causes interference effects in the photoemitted intensity. This can be observed in constant initial-

state (CIS) energy curves, with the initial states chosen at the top of the VB. If photoemitted electrons from those states at  $(hv)_{res}$  have higher kinetic energy than Auger electrons due to the decay of the core holes, then the resonant behavior of the intensity is not due to the Auger channel.<sup>27</sup> Figures 3, 4, and 5 show CIS curves for the initial states corresponding to the 3d and satellite maximum intensity for Cu, Cu<sub>2</sub>O, and CuO, respectively. In all cases a significant decrease ( $\sim 10\%$ ) of the 3d emission intensity is observed at roughly the same hv where the satellite emission has its maximum. This feature has also been observed for Ni (Ref. 27) and quasiatomic copper in phthalocyanine.<sup>28</sup> This dip in the 3*d*-band emission at resonance is in agreement with recent theoretical calculations.<sup>6</sup> It should be noted that this decrease is in contrast to the behavior at the 4d core threshold of systems with empty 4f states where strong enhancements in the direct VB emission have been observed.<sup>29</sup> The latter were attributed to resonant recombination of the excited  $4d^94f^{n+1}$  states to  $4d^{10}4f^{n-1}+e$  states that are identical to the offresonance photoemission final state as demonstrated, e.g., by a study on Yb  $4f^{14}$  and its oxide  $(4f^{13})$ .<sup>30</sup> The absence of such a valence emission enhancement in the case of CuO  $3d^9$  is therefore a significant difference between resonance effects involving  $3p \rightarrow 3d$  and  $4d \rightarrow 4f$  transitions.



FIG. 3. Accumulated intensity in a 0.5-eV region centered at the 3d-maximum intensity and  ${}^{1}G$  component maximum intensity for Cu metal.



FIG. 4. Same as Fig. 3 but for Cu<sub>2</sub>O instead of Cu.

# E. Auger emission close to threshold

A further point of interest lies in the Auger emission close to threshold. In Fig. 6 we show the position of the half-maximum of the lower edge<sup>31</sup> of the  $M_{23}M_{45}M_{45}$  Auger emission for Cu metal versus  $h\nu$ . The data points for this half-maximum lie on a line of constant kinetic energy. This agrees with the assumption that within ~10 eV of threshold the Auger energy is always given by a two-hole final state that is completely screened in a metal. This result must be compared to a recent report of strong energy shifts of the *electron* stimulated  $L_3M_{45}M_{45}$  Auger emission<sup>32</sup> in Cu metal.

Another feature of the  $M_{23}M_{45}M_{45}$  Auger emis-



FIG. 5. Same as Fig. 3 but for CuO instead of Cu.

sion is that it consists of two  $3d^8$  multiplets. Since the  ${}^{1}G$  component is the strongest one,  ${}^{3,16}$  the entire spectrum exhibits two peaks ("Augermax" in inset of Fig. 6) corresponding to the  ${}^{1}G$  components of the two Auger transitions  $M_2M_{45}M_{45}$  and  $M_3M_{45}M_{45}$ , separated by the spin-orbit splitting of the 3p core levels. The final state energies of these two peaks were determined by measuring their separation from the lower edge half-maximum ("Auger $_{(1/2)}$ ") part of the Auger structure of the EDC's. The two resonances of the  ${}^{1}G$  component of the satellite observed in Fig. 2 are marked by two vertical lines in Fig. 6 and occur at the same final-state energy as the Auger maxima ( ${}^{1}G$  components) corresponding to the  $M_2M_{45}M_{45}$  and the  $M_3M_{45}M_{45}$  Auger transitions. This suggests that for Cu metal the Auger channel makes a significant contribution to the satellite resonance. A similar conclusion was derived from an angleresolved study of the resonant satellite in nickel.33

In the case of the oxides a direct evaluation of the Auger emission is difficult because it is very weak and is obscured by the O2s level. We used two different ways to determine the half-height po-



FIG. 6. Auger<sub>(1/2)</sub> gives the final-state energy of the lower edge half-height of the  $M_{23}M_{45}M_{45}$  Auger emission (see inset) at  $h\nu \simeq 90$  eV for Cu. Also shown is the photon-energy-dependent final-state energy  $E_f$  of the 3d emission (reduced by 10 eV) and of the <sup>1</sup>G component of the satellite. For Cu it is seen (circles) that the maxima in the satellite emission occur at the final state energies of the Auger maxima, see text.

sition of the low energy edge: (a) subtraction of a spectrum close to resonance from a spectrum above resonance, and (b) CIS curves at various  $E_i$  below the resonant satellite, thus locating the photon energy at which the Auger edge coincided with the energy  $E_i + hv$ . Both methods basically eliminate any other features of the photoemission spectrum but contain variations due to the core hole decay. The accuracy of the method is estimated to be  $\pm 0.4$  eV. Figure 7 shows the results for Cu<sub>2</sub>O and CuO. For both oxides the Auger energies remain roughly constant close to threshold.

The effective Coulomb interaction  $U_{\text{eff},A}$  for the Auger two-hole final state is defined as the difference between the measured kinetic energy of a given Auger multiplet component and the value expected from the binding energies of the electron states involved in the Auger transition. For the  ${}^{1}G$  component of the  $M_{3}M_{45}M_{45}$  Auger emission this gives

$$U_{\text{eff},a} = E(3p_{3/2}) - 2\overline{E}(3d) - E_A({}^1G) .$$
 (4)

 $E_A({}^1G)$  is the kinetic energy of the Auger maximum<sup>5,16</sup> given in Figs. 6 and 7:  $E_A({}^1G)=61.0$ , 60.0, 60.9 $\pm$ 0.2 eV for Cu, Cu<sub>2</sub>O, and CuO, respec-



FIG. 7. Same as Fig. 6 for CuO and Cu<sub>2</sub>O. Because the  $M_{23}M_{45}M_{45}$  Auger emission is weak and overlaps the O 2s emission, the measured Auger<sub>(1/2)</sub> values were determined differently (see text):  $\bigcirc$  measured on an EDC;  $\square$  measured on a difference spectrum subtracting an EDC taken slightly below resonance;  $\bullet$  and + measured on two sets of CIS curves with various initial state energies below  $E_i(\text{sat})$ .

tively. The value for Cu agrees well with a recent report<sup>3</sup> (61.3 eV). With the data in Table I we find the corresponding values  $U_{\text{eff},A} = 7.7(3)$ , 8.5(4), and 9.6(4) eV. Differences in  $U_{eff}$  for the satellite (Table I) and the Auger emission are believed<sup>4,5</sup> to be due to different screening processes involved. Thus the increase (0.6 eV) for  $Cu_2O [E_{gap} = 2.16]$ eV (Ref. 15)] is attributed to the lack of metallic screening as observed in GaP.<sup>5</sup> The decrease in Cu metal [0.5 eV, also reported for Zn (Ref. 4)] is harder to explain and needs further study, because both final states are usually assumed to be completely screened in metals.<sup>26</sup> Finally, the value found for CuO is equal to the observed satellite separation energy. This further supports our assumption that both direct 3d emission and satellite are  $3d^8$  states, the only difference being the effective Coulomb interaction of the two localized 3dholes in the case of the satellite. This can be verified by reducing  $\Delta E_{sat}$  in Eq. (1) by the  $3d \rightarrow 4s$ shake-up energy E(3d) + E(4s,p), as no such transition occurs in the resonance mode for systems with open d shells.

#### **IV. SUMMARY**

The energy positions of the resonant satellites and their intensity profiles at the 3p core-level photoexcitation threshold were measured with photoemission using synchrotron radiation for Cu,  $Cu_2O$ , and CuO. We find evidence that the shake-up state differs for Cu atoms in different electron configurations. In CuO far from resonance the satellite represents an intra-d-shell transition as proposed for systems with unfilled dstates. Because the excitation fulfills the monopole transition selection rules for shake-up processes, the satellite can have considerable intensity far from resonance. Based on the similar energy separation we can apply this mechanism to explain the strong satellite observed in XPS valence-band spectra of CuO. This is a plausible alternative to the hitherto postulated ligand-to-metal chargetransfer process that would lead to a  $3d^9$  final state. For Cu and Cu<sub>2</sub>O the satellites require a  $3d \rightarrow 4sp$  transition far from resonance and are therefore forbidden by selection rules; thus their intensity is rapidly reduced away from resonance so that no satellites are observed in XPS spectra. In  $Cu_2O$  the shift in the resonance energy and the change in satellite separation energy is explained by a 0.85-eV increase of the possibly exitonic 4sp state with respect to Cu metal. In all three samples the

An analysis of the  $M_{23}M_{45}M_{45}$ -Auger emission shows no evidence of an energy shift close to threshold. Differences of  $U_{eff}$  for satellite and Auger emission can be due to screening. For the insulator Cu<sub>2</sub>O the absence of the 4sp electron in the Auger emission cannot be compensated by interatomic screening. This leads to an increased energy of the two-hole state for the Auger emission. The observed increase  $\Delta U_{eff} \simeq 0.6$  eV in Cu<sub>2</sub>O is somewhat smaller than to the value 0.9 eV found earlier in GaP.<sup>5</sup>

Finally, we find that the 3d-band intensity goes through a minimum at resonance. This was al-

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ready observed earlier for nickel<sup>27</sup> and Cu phthalocyanine.<sup>28</sup> Further studies are needed to see if this is a general effect in 3*d* metals and compounds in contrast to the strong enhancements found so far in measurements involving  $4f^n$  (n < 14) systems.

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