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Investigation of the L_3–$M_{45}M_{45}$ Auger spectra of Cu, Cu_2O and CuO

S R Barman and D D Sarma

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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Abstract. We report a comparative study of the L_3–$M_{45}M_{45}$ Auger spectra of Cu, Cu_2O and CuO. The large intensity of the uncorrelated two-hole band-like spectrum in the L_3–$M_{45}M_{45}$ Auger spectra of Cu_2O and CuO and the spectral shapes for these transitions indicate strong Cu 3d–O 2p hybridization in the oxides. The L_2–L_3M_{45} CK rates obtained for these compounds indicate the stability of the Cu 3d level with increasing oxidation state of Cu. We also provide a quantitative estimate of the contributions of the different processes that lead to the formation of the L_3–$M_{45}M_{45}$ Auger satellite in Cu, Cu_2O and CuO.

1. Introduction

The L_{23}–$M_{45}M_{45}$ Auger spectra of Cu which show the most intense and distinctly recognizable features in the Auger spectra of solids have been the subject of many investigations [1–13]. It has been suggested that the satellite accompanying the Cu L_3–$M_{45}M_{45}$ spectrum is due to an L_3M_{45}–$M_{45}M_{45}M_{45}$ Auger transition following an L_2–L_3M_{45} Coster–Kronig (CK) transition of an L_2 hole [1]. This process effectively transfers spectral weight from the L_2–$M_{45}M_{45}$ Auger spectrum of Cu to the satellite region (containing an extra M_{45} hole both in the initial and final states) of the L_3–$M_{45}M_{45}$ Auger transition. The L_3M_{45} initial state, responsible for the satellite features, may also be generated following a CK decay of an L_1 hole, namely the L_1–L_3M_{45} transition. Recently [10–13] it has been recognized that the satellite in the L_3–$M_{45}M_{45}$ region may also be contributed by the direct generation of an L_3M_{45} state in the L_3 photoemission process due to shake-up and shake-off transitions. The quantitative estimates for the different processes such as photoemission shake-up and shake-off and the CK decay of the L_2 and L_1 photo-holes contributing intensity to the L_3–$M_{45}M_{45}$ Auger satellite of Cu have been worked out [13]. The oxides of Cu, namely Cu_2O and CuO, which have interesting electronic structures [14–17], also show intense Auger satellites accompanying the L_3–$M_{45}M_{45}$ spectra. While the Cu 2p photoemission satellite due to shake-up in Cu_2O is very weak and similar to that in Cu, the 2p spectrum of CuO exhibit intense satellites. Therefore one expects a much larger satellite intensity for the L_3–$M_{45}M_{45}$ spectrum of CuO compared with Cu_2O or Cu, but actually the satellite intensities in these three compounds are comparable. We decided to investigate the contributions of the different decay channels to the Auger satellite of L_3–$M_{45}M_{45}$ spectra in Cu_2O and CuO. We have found that the

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results for Cu and Cu_2O are similar, but that in the Auger spectrum of CuO the L_3 photoemission shake-up channel makes a considerably larger contribution. We also show that the higher kinetic energy uncorrelated band part of the L_3–$M_{45}M_{45}$ Auger spectra in Cu_2O and CuO exhibit pronounced effects of hybridization between the Cu 3d and O 2p states. We further calculate the transition probabilities of the L_2–L_3M_{45} CK processes in Cu, Cu_2O and CuO exhibiting the influence of the Cu 3d level energetics on the CK rates.

2. Experiment

The photoemission and the Auger spectra were recorded in the combined XPS-UPS-BIS instrument from VSW Scientific Instruments Ltd, UK. Measurements were carried out with laboratory sources (Al Kα and Mg Kα). The spectrometer resolution for the Auger spectra was 0.2 eV, whereas the 2p core-level photoemission spectra were recorded with a total resolution of about 0.5 eV for monochromatic Al Kα source and 0.9 eV for non-monochromatic Mg Kα source. Commercially available CuO powder was sintered in flowing oxygen in the form of pellets. The sample surface was scraped with an alumina file in order to obtain a clean reproducible surface. Cu_2O was prepared by precipitation following the reduction of concentrated copper acetate solution by 20% hydrazine hydrate solution [18]. Cu_2O was studied in powdered form. The possible reduction of copper acetate to metallic copper on addition of excess hydrazine could be eliminated because of the absence of any signal due to Cu metal in the L_{23}–$M_{45}M_{45}$ Auger spectra of Cu_2O. Also the possibility of contamination due to partial oxidation to CuO could be eliminated by noting the absence of the characteristic CuO 2p photoemission satellite signal. Metallic Cu was cleaned by argon-ion sputtering. The Auger spectra obtained with non-monochromatic Al Kα and Mg Kα and monochromatic Al Kα sources showed no dependence on the excitation source.

3. Results and discussion

We show the L_{23}–$M_{45}M_{45}$ Auger spectra of Cu, Cu_2O and CuO in figure 1. The most intense peak in each spectrum is due to the ^1G multiplet of the two-localized-hole d^8 final state [3]. The Auger spectra from the three samples have been aligned at the main peak for the purpose of comparison. The Auger satellite spectrum is distinct in each case, at about 4–8 eV kinetic energy below the ^1G peak. The sharp feature at about 921 eV kinetic energy in the spectrum for Cu is due to the ^3F multiplet of the localized d^8 final state [3]. This feature is not distinct in the spectra of Cu_2O and CuO, due to strong broadening of the spectra in the oxides. However, our data analysis in terms of spectral fitting (see the appendix) clearly indicates the presence of these multiplets at about the same relative energy with respect to the ^1G peak. The broad feature above 922 eV kinetic energy is the signature of the delocalized two-hole final state in terms of the Cini–Sawatzky model [19, 20]. Comparing the L_3–$M_{45}M_{45}$ Auger spectra of Cu, Cu_2O and CuO in the energy range between 922 eV and 930 eV kinetic energy clearly shows that the signatures of the delocalized two-hole state in the Auger spectra are more intense in Cu_2O and CuO than in Cu. This part of the Auger spectrum is hardly discernible in the case of Cu (see

figure 1). The relative intensity of this part of the Auger spectrum compared with the transition arising from the localized two-hole final state is a function of U/W [20], where U is the effective intra-atomic Coulomb correlation strength and W is the relevant bandwidth; the delocalized signature in the Auger spectrum is expected to gain intensity with decreasing U/W. Thus the enhanced intensity in the spectral feature due to the delocalized two-hole final state is an indication of the decrease of effective U/W in Cu_2O and CuO compared with Cu. It should be noted here, however, that the Cini–Sawatzky model which has provided the basis for the above interpretation, is itself based on a single-band model and is evidently of qualified use in the context of Cu_2O and CuO. However, if we interpret W as the effective Cu 3d–O 2p hybrid bandwidth and note that the intra-atomic effective U in these systems do not change significantly (see text later), it appears that the effective W is larger for Cu_2O and CuO than for Cu. This must be caused by the sizeable Cu 3d–O 2p hybridization interaction in the oxides, since the direct Cu 3d–Cu 3d interaction is expected to be very small in the oxides. It should also be noticed that the main peaks in the Auger spectra arising from the two-localized-correlated-hole final state are broader for Cu_2O and CuO compared with Cu. There are several possible origins of this width. The Cu 2p photoemission spectra in Cu_2O and CuO are considerably broader than that of Cu, contributing width to the Auger spectra. Of the two oxides, the Cu 2p photoemission spectrum of CuO has larger width. This may arise from the fact that the main peak of Cu_2O 2p spectrum corresponds to a 2p-hole $3d^{10}$ final state, while that of CuO is due to a 2p-hole $3d^{10}$ configuration *with another hole in the ligand O 2p levels*. This ligand hole spans the whole O 2p bandwidth leading to an increased width of the spectral feature. The same effect then also contributes to the increased Auger spectral width in CuO. Moreover we note that the Cini–Sawatzky model provides another contribution to the Auger spectral widths for Cu_2O and CuO. It has been shown that the width of the atomic-like correlated two-hole final state varies as W^2/U. Noting that W/U is larger in Cu_2O and CuO compared with Cu, due to an increase in the effective bandwidth W, it is obvious that W^2/U will be larger for Cu_2O and CuO than for Cu.

It is interesting to note that while the band-like uncorrelated two-hole final state feature is nearly absent in the spectrum of Cu and exhibits a broad pronounced feature in CuO, it exhibits a distinct two-peak structure in the case of Cu_2O (marked by arrows in figure 1). Since the band-like spectrum is essentially governed by the self-convolution of the relevant part of the density of states, modified by the matrix element effects, we have compared this part of the Auger spectra of Cu_2O and CuO to the self-convolution of the photoemission valence-band spectra of these compounds using 21.2 eV photon energy in a manner similar to that in [14]. The delocalized two-hole Auger spectra of CuO corresponds well in spectral shape and energy position to the self-convoluted density of states (DOS) obtained from valence-band photoemission [14]. We can estimate the effective screened intra-atomic Coulomb interaction strength, U_{dd}, within the Cu 3d manifold from the energy difference between the centroid of the self-convoluted DOS and the Auger spectral feature arising from the localized atomic-like two-hole final state; thus U_{dd} corresponding to the ^1G multiplet in CuO turns out to be 8.7 eV. In the case of Cu_2O, the self-convoluted DOS shows [14] two distinct peaks at about 6.7 eV and 9.4 eV binding energy. The first peak at 6.7 eV arises from the presence of two uncorrelated 3d holes and the peak at 9.4 eV is due to an O 2p and a Cu 3d hole. The Auger spectrum in figure 1 clearly exhibits two features at about the same energies as in the self-convoluted DOS, indicating

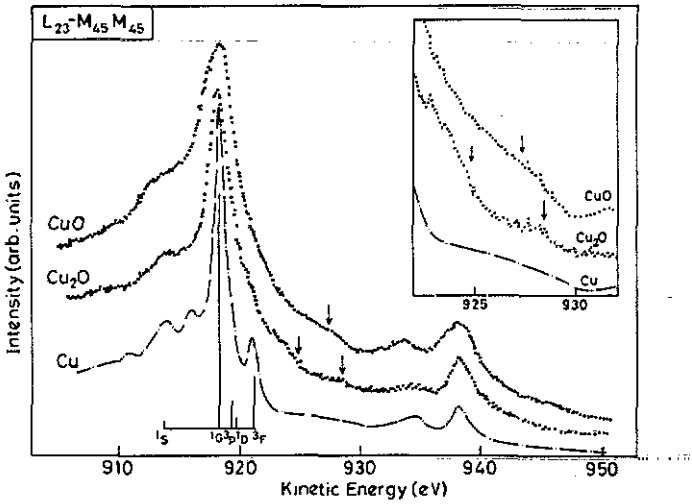

Figure 1. The L_{23}–$M_{45}M_{45}$ Auger spectra of Cu (dot-dashed), Cu_2O and CuO (dots). The Cu_2O and CuO main peaks have been aligned to the main peak of Cu. The positions of the atomic-like features (^1G, ^3P, ^1D and ^3F) are indicated. The arrows indicate the two-hole band-like density of states features (also shown on an expanded scale in the inset) in Cu_2O and CuO.

that the L_3–$M_{45}M_{45}$ Auger transition in the copper oxides not only generates two 3d holes, but also has a finite probability of generating an O 2p and a Cu 3d hole. This is only possible if there is a substantial overlap between the Cu 3d and O 2p states. The U_{dd} for Cu_2O is the energy difference between the feature due to the two uncorrelated 3d holes in the self-convoluted DOS and the localized atomic-like two-hole final state feature. Thus the estimate of U_{dd} corresponding to the ^1G multiplet turns out to be 10.0 eV for Cu_2O. These estimates of U_{dd} are in agreement with previous ones [14].

Table 1. The relevant relative intensity ratios extracted from the Cu 2p photoemission spectra and the Cu L_{23}–$M_{45}M_{45}$ Auger spectra of Cu, Cu_2O and CuO.

	Cu 2p photoemission shake-up satellite/main peak ratio (β)	Cu L_3–$M_{45}M_{45}$/ L_2–$M_{45}M_{45}$ main peak ratio (R)	Cu L_3–$M_{45}M_{45}$ satellite/main peak ratio
Cu	0.075	6.3	0.37
Cu_2O	0.05	5.7	0.36
CuO	0.45	4.2	0.47

We have extracted the intensities of the L_2–$M_{45}M_{45}$ and L_3–$M_{45}M_{45}$ transitions (without the satellite contributions) by spectral fitting as described in the appendix. The ratio (R) of the L_3–$M_{45}M_{45}$ and the L_2–$M_{45}M_{45}$ spectral intensities decreases from Cu ($R = 6.3$) to Cu_2O ($R = 5.7$) and is substantially lower ($R = 4.2$) in CuO (table 1). It is easy to see that the CK transition (L_2–L_3M_{45}) probability transferring spectral weight from the L_2–$M_{45}M_{45}$ region to the satellite of the L_3–$M_{45}M_{45}$ region is given by $(R-2)/R$, indicating that for $R = 2$ the CK process is absent. This is

evident since $R = 2$ implies that the intensity ratio between L_3– and L_2–$M_{45}M_{45}$ is exactly according to the statistical branching ratio for the generation of the L_3 and L_2 initial-hole states and there is no transfer of intensity from the L_2– to L_3–$M_{45}M_{45}$ transitions. The CK transition probabilities we get using the above expression are 0.68, 0.65 and 0.52 for Cu, Cu_2O and CuO respectively. The L_3–$M_{45}M_{45}$ CK transition probability for Cu calculated by Yin *et al* [1] and McGuire [7], performed with neutral atom potential, is 0.64 and is in good agreement with the value obtained here. Note that earlier experimental estimates [21] of the intrinsic life-time widths of the L_2 and L_3 hole states suggest that the CK process probability for Cu L_2 holes is 0.62, in good agreement with the probability obtained here. Based on atomic calculations, it has been further pointed out [1, 7] that the rate of the CK process is very sensitive to the binding energy of the M_{45} (3d) level, the rate of the L_2–L_3M_{45} CK process decreasing with increasing binding energy. Thus the decreasing rate of the CK process in the series Cu, Cu_2O and CuO can be related to the increasing stability of the Cu 3d level with increasing oxidation state of Cu.

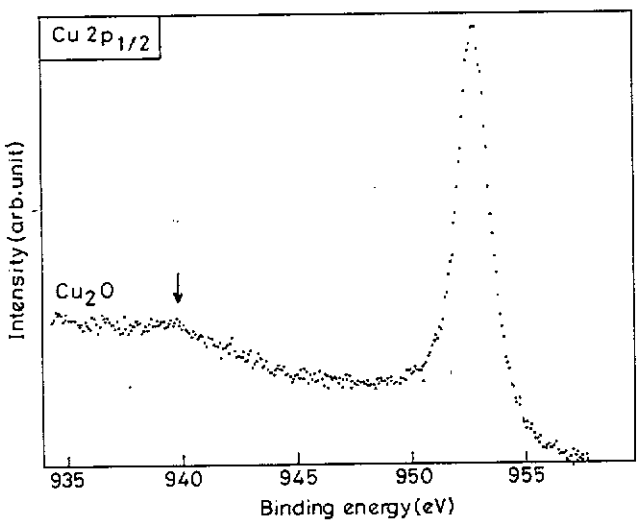

Figure 2. The Cu $2p_{1/2}$ photoemission spectra of Cu_2O, the arrow indicating the position of the weak satellite feature.

From our spectral fitting (see appendix), we have been able to obtain the intensity ratios between the satellite (three-hole and four-hole final states) and the main parts (two-hole final states) of the Auger spectra of Cu, Cu_2O and CuO and these values are shown in table 1. We find that the satellite to main peak ratio for the L_3–$M_{45}M_{45}$ Auger spectra is higher in CuO than in Cu or Cu_2O, the latter two compounds having comparable satellite intensity. In order to understand details of the origin of the Auger satellites in Cu_2O and CuO, we have recorded the corresponding Cu 2p photoemission spectra. A weak 2p photoemission satellite is observed for Cu_2O at about 12.7 eV higher binding energy from the main peak with a satellite to main peak intensity ratio of 0.05 (see figure 2 and table 1). This is comparable to the relative satellite intensity of 0.075 reported [13] for the 2p spectrum of Cu metal. For CuO, the 2p photoemission satellite to main peak intensity ratio (0.45) is much larger. The origin of these satellites has been discussed in detail in the literature; these represent primarily $L_{23}M_{45}$ shake-up satellites.

For the following analysis it is important to note that the 3–4 eV decrease in the satellite to main peak energy separation in the Cu 2p photoemission spectrum of CuO compared to those in Cu_2O and Cu has an important consequence. It is obvious that when $U_{pd}+E_d+U_{dd}$ (U_{pd} is the Coulomb interaction strength between a Cu 2p hole and a 3d hole, E_d the energy of the Cu 3d hole and U_{dd} the Coulomb interaction strength between two 3d holes) is greater than the L_2–L_3 spin orbit splitting, the L_2M_{45} initial photo-hole will have a very low transition probability to decay via the L_2–L_3M_{45} CK process. The energy separation between the photoemission satellite and the main peak in Cu provides an estimate of the strength of $(U_{pd}+E_d)$. Noting the satellite to main peak energy separation (about 12 eV) in the 2p photoemission spectrum and a U_{dd} of about 10 eV for Cu and Cu_2O, it is evident that the initial L_2M_{45} photo-hole (the shake-up/shake-off satellites) cannot decay via the CK process in the case of Cu or Cu_2O. But in CuO the 2p photoemission satellite is shifted 3–4 eV towards the main peak compared with Cu and Cu_2O. Since U_{dd} in CuO remains comparable to U_{dd} in Cu and Cu_2O, the decay of the L_2M_{45} shake-up satellite through the CK process becomes energetically allowed for CuO (unlike the cases of Cu and Cu_2O). Thus one of the channels contributing intensity to the Auger satellite in the L_3–$M_{45}M_{45}$ region of CuO is the decay of the initial L_2M_{45} shake-up state via the L_2M_{45}–$L_3M_{45}M_{45}$ CK process to the $L_3M_{45}M_{45}$ state which further undergoes an Auger decay to the $(M_{45})^4$ four-hole final state. On the other hand, the shake-off channel $L_2M_{45}O_p$ (O_p indicates a ligand hole) corresponding to the L_2 photo-hole in CuO is energetically forbidden to undergo the CK transition. For the L_1 photo-hole, the CK decay (L_1–L_2M_{45} and L_1–L_3M_{45}) of both the shake-up and shake-off satellites are energetically allowed for all the three systems. We show in figure 3 all the decay processes of the L_3, L_2 and L_1 photo-holes that are relevant for the L_3–$M_{45}M_{45}$ satellite intensity in these systems.

The different channels which contribute intensity to the L_3–$M_{45}M_{45}$ Auger satellite are the Auger decay of the L_3 ($2p_{3/2}$) photoemission shake-up/shake-off satellites and the CK decay of the photoemission main peak and the shake-up/shake-off satellites corresponding to L_2 and L_1 photo-holes (figure 3). The relative percentage contributions of these decay channels for Cu taken from [13] together with the satellite to main peak intensity ratio of 0.37 determined in the present study by spectral fitting indicate that the contributions of the above channels are 0.04, 0.07, 0.19 and 0.07 from shake-up, shake-off, L_2 induced CK and L_1 induced CK processes respectively. From these values for Cu, we can extrapolate the expected contributions of these channels to the satellite intensities in the L_3–$M_{45}M_{45}$ regions of Cu_2O and CuO, using the experimental values of the 2p photoemission shake-up satellite to main peak intensity ratio (β) and the L_3–$M_{45}M_{45}$/L_2–$M_{45}M_{45}$ main peak intensity ratio (R) in this series and the details of the decay channels as shown in figure 3. Thus we find that the expected contribution of the L_2 CK channel to the relative intensity of the satellite compared to the main peak in CuO is given by

$$0.19(1+\beta_{CuO})[(R-2)/R]_{CuO}/[(R-2)/R]_{Cu}$$

where $R=2[1+z/(x+y)]$ and the factor 0.19 is the L_2 CK contribution to the relative satellite intensity in Cu. In the numerator, 1 and $\beta_{CuO}(=0.45)$ are the photoemission main peak/main peak and the shake-up satellite/main peak intensity ratios respectively for the L_2 photo-hole of CuO. This way extrapolated contributions, the L_3 photoemission shake-up channel, the L_3 photoemission shake-off channel,

the CK decay of the L_2 photo-hole and the CK decay of the L_1 photo-hole to the relative intensity of the L_3–$M_{45}M_{45}$ Auger satellite are 0.03, 0.07, 0.18 and 0.07 respectively for Cu_2O. The corresponding numbers for CuO are 0.24, 0.09, 0.21 and 0.09 respectively. In this analysis it is assumed that the L_1 photo-hole which has the CK channels L_1–L_2M_{45} and L_1–L_3M_{45}, decays through these CK channels with probability of $k_2 = 0.18$ and $k_3 = 0.39$ (which implies $k_1 = 0.43$, see figure 3) in accordance with the calculations of McGuire [7]. Since it is difficult to estimate the probability of the shake-off channel, in this analysis it is assumed to remain the same for Cu_2O and CuO as in Cu. The ratio of the photo-ionization cross sections [22] for the L_3, L_2 and L_1 photo-holes is taken to be 2.0:1.0:0.55 in the calculation.

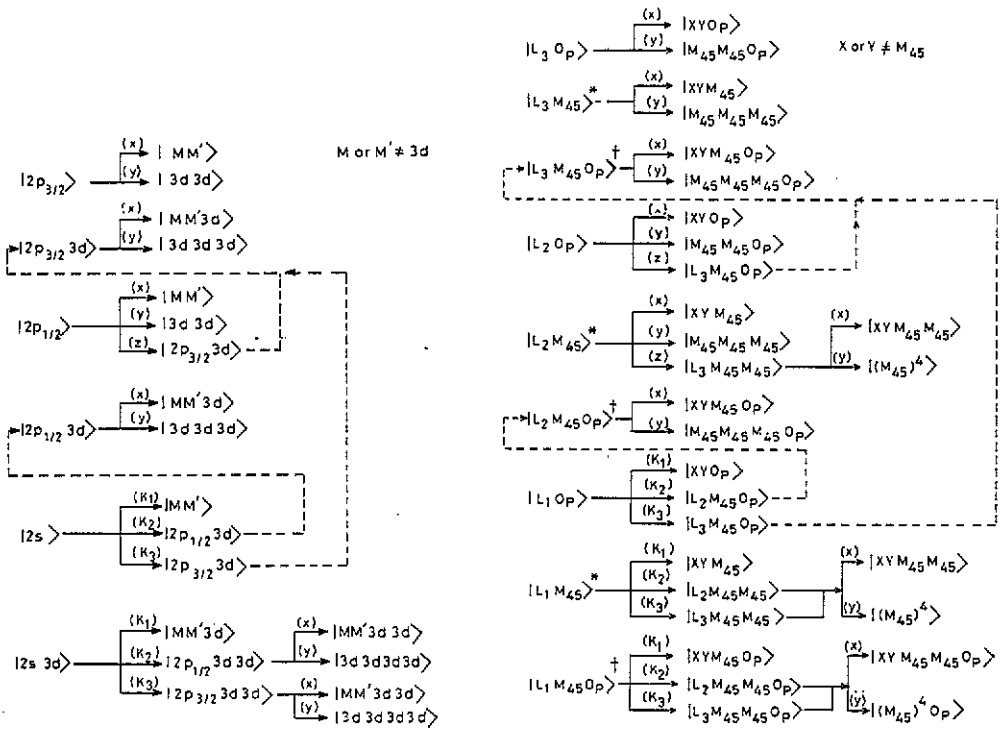

Figure 3. The decay processes for the L_3, L_2 and L_1 holes in CuO which contribute to the L_3–$M_{45}M_{45}$ satellite intensity. The states are represented in a hole picture and the quantities in brackets indicate the probabilities of the corresponding decay processes. The bold arrows show the CK channels and the dashed arrows are used to connect the final state of a CK transition to the initial state of a subsequent Auger transition. The shake-up and the shake-off states are indicated by star (*) and dagger (†) respectively. The symbol O_p indicates an O 2p ligand hole state which is present both in the initial and final state of an Auger decay. The decay channels for Cu and Cu_2O are similar to that of CuO except for the CK decay of the L_2 shake-up satellite which is energetically forbidden in these systems.

The contributions of the different decay channels in Cu_2O do not differ drastically from Cu. This is not surprising since the allowed decay channels for Cu_2O and Cu are the same (figure 3) and also the experimentally obtained inputs (i.e. β and R) to the estimation of the various contributions are very similar between the two. In contrast CuO shows a marked difference compared with Cu (table 2). The contribution from

Table 2. The contribution of the different decay channels (the 2p photoemission shake-up, the 2p photoemission shake-off, the CK decay of the L_2 photo-hole and the CK decay of the L_1 photo-hole) to the L_3–$M_{45}M_{45}$ Auger satellite to main peak intensity ratio in Cu, Cu_2O and CuO. The numbers in the brackets are the relative percentage contributions.

	Photoemission shake-up	Photoemission shake-off	L_2 induced Coster–Kronig	L_1 induced Coster–Kronig
Cu	0.04 (11)	0.07 (18)	0.19 (52)	0.07 (19)
Cu_2O	0.03 (9)	0.07 (20)	0.18 (51)	0.07 (20)
CuO	0.24 (38)	0.09 (14)	0.21 (34)	0.09 (14)

the initial state shake-up channel increases by a factor of $\beta_{CuO}/\beta_{Cu} \simeq 6$ compared with Cu. The L_1 CK contribution is also larger in CuO than in Cu. This is primarily because of the decrease of the L_3 Auger main-peak intensity in CuO due to large β. This leads to the relative increase of the Auger satellite to main peak intensity ratio for the L_1 CK channel contribution in CuO. Though the L_2–L_3M_{45} CK decay rate in CuO is lower than that of Cu, large β and the CK decay of the L_2M_{45} shake-up satellite (which is forbidden in Cu) are the reasons for the larger contribution from the L_2 CK process to the relative satellite intensity in the L_3–$M_{45}M_{45}$ Auger spectra.

The calculated relative intensity of the satellite for Cu_2O and CuO, which is the sum of the expected contributions from all four channels, should be in good agreement with the experimentally obtained relative satellite intensities. In the case of Cu_2O, the calculated value of 0.35 for the relative satellite intensity is in good agreement with the experimental value of 0.36 obtained from spectral fitting of the experimental Auger spectrum. For CuO the calculated relative satellite intensity is 0.63, whereas the experimental value is 0.47. This discrepancy is probably due to an overestimate of the shake-off probability in the CuO photoemission process, which was assumed to be equal to that in Cu. The overestimation of the shake-off probability results in increased contributions from the shake-off and the L_1 CK channel to the relative satellite intensity in the L_3–$M_{45}M_{45}$ Auger spectra of CuO. Besides the overestimation of the shake-off probability accompanying the initial state core-hole creation in the case of CuO, errors can also arise from the experimental estimates of different satellite intensities. In this context it should be realized that these estimates can contain upto a 20% uncertainty. The estimate of the other channels contributing to the relative satellite intensities in the L_3–$M_{45}M_{45}$ Auger spectra of these compounds are quite reliable however, since the processes responsible (e.g. the shake-up and the CK rates) have been experimentally determined here.

In conclusion we have shown that the U_{dd} values for Cu_2O and CuO are comparable. The uncorrelated two-hole band-like spectrum of the L_3–$M_{45}M_{45}$ transition has large intensity for CuO and Cu_2O compared with that for Cu, indicating an increase of the effective bandwidth due to the hybridization of the Cu 3d states with the O 2p states. The spectral shapes for these transitions provide further evidence for the extensive Cu 3d–O 2p hybridization in the oxides. The L_2–L_3M_{45} CK rates have been obtained for Cu, Cu_2O and CuO from the observed intensity ratio between the L_3–$M_{45}M_{45}$ and the L_2–$M_{45}M_{45}$ transitions, the trends in the CK rates indicating an increasing stability of the Cu 3d states in the series Cu, Cu_2O and CuO, in agreement with previous calculations. Using these CK rates and the experimentally obtained shake-up satellites intensities of the Cu spectra in these compounds, we

provide quantitative estimates for the contributions of the various decay channels to the Auger satellite intensity.

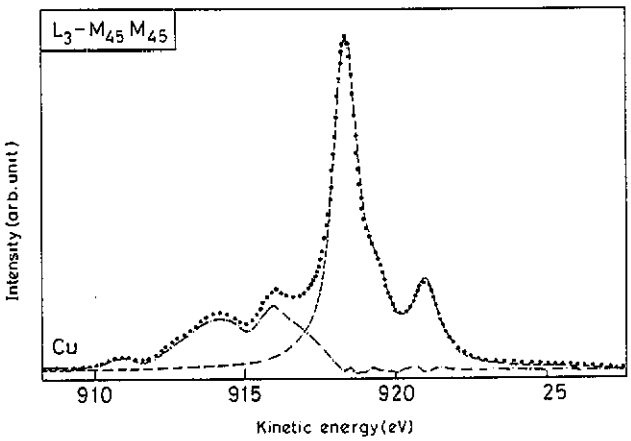

Figure 4. The L_3–$M_{45}M_{45}$ Auger spectrum of Cu (dots), the main peak of the L_3–$M_{45}M_{45}$ Auger spectrum obtained by least-square error fitting (dashed curve), and the satellite part of the L_3–$M_{45}M_{45}$ Auger spectrum (dot-dashed curve) obtained by subtracting the previous two curves.

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Appendix

We have analysed the spectral features by fitting the experimentally obtained L_3–$M_{45}M_{45}$ Auger spectra in terms of a least-square error approach. First, the spectra were background subtracted using an iteration proceedure. In each case, the most intense peak was associated with the ^1G multiplet of the final d^8 configuration. All the multiplets ^1G, ^3P, ^1D and ^3F which appear in the Auger main peak (excepting ^1S which is neglected assuming its intensity to be insignificant) were represented by a Gaussian of fixed width of 0.2 eV representing the spectrometer resolution function. These Gaussian broadened multiplets were then convoluted with a Lorentzian whose width was varied as a parameter in the fitting routine. Besides the main peak due to the ^1G state in all cases, the ^3F feature is also sharply defined for Cu. The position of the other two multiplets (^3P and ^1D) for Cu was determined using the least-square error routine by scanning the energy region between ^1G and ^3F. If we take the position of the ^1G as reference, the positions of ^3P, ^1D and ^3F on the basis of the above analysis turn out to be +1.0, +1.3 and +2.7 eV respectively. These values agree fairly well with the earlier theoretical calculations which give the relative separation

of the ^3P, ^1D and ^3F multiplets with respect to ^1G to be +0.6, +1.0 and +3.0 eV [2] and +0.7, +1.2 and +3.3 eV [3]. One important point to be noted here is that the least-square error fitting was done taking only the part of the experimental spectra on the higher kinetic energy side of the ^1G peak which has no satellite contribution. This is done to ensure that the fitted L_3–$M_{45}M_{45}$ Auger main peak spectral shape has no satellite contribution. A Gaussian was used to represent the uncorrelated two-hole band-like part of the Auger spectra. A scaling factor was also introduced in the fitting routine in order to vary the multiplet positions with respect to the ^1G multiplet by a multiplicative constant. The satellite was extracted by subtracting the least-square error fitted L_3–$M_{45}M_{45}$ main peak from the experimental L_3–$M_{45}M_{45}$ spectra containing both the satellite and the main peak contribution (figure 4). The same procedure was applied for Cu_2O and CuO. The relative multiplet positions in Cu_2O and CuO were found to be similar to that of Cu. We used two Gaussians in Cu_2O and one Gaussian in CuO to represent the uncorrelated two-hole band-like density of states.

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