Role of charge-transfer in formation of x-ray and x-ray photoelectron spectra of cupric compounds

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The 1*s* and 2*p* x-ray photoelectron spectra and the *Kα* x-ray line of copper in copper (II) compounds are analyzed theoretically on the basis of Larsson's model and the *Xα*-PB method. Both methods independently indicate an intense shake-up satellite in the Cu*Kα* spectrum; the satellite is at a distance ≈0.4 eV from the main line on the long-wavelength side. It is shown that in the case of CuO this satellite corresponds to a *Kα* transition in the presence of an electron transferred from the $2b_{1g}$ to the $3b_{1g}$ level of the cluster CuO_4^{6-}. A relation is established between this satellite and the corresponding satellite of the 1*s* and 2*p* x-ray photoelectron spectra of Cu. The applicability of Larsson's model for interpreting the x-ray and x-ray photoelectron of copper (II) compounds is discussed.

INTRODUCTION

The determination of the charge state of copper atoms in high-T_c superconductors is still a controversial question. Without this knowledge it is impossible to explain the mechanism of high-temperature superconductivity. In order to solve this problem it is necessary to have a method that is sensitive to the charge state of the atom but not to the charge state of other atoms, as through the valence shell of the given atom. X-ray emission spectroscopy of the core levels meets these requirements, since x-ray spectra respond to any change in the valence shell and at the same time they are insensitive to the Madelung potential,[1] while changes in the valence state of other atoms are manifested in these spectra only through the valence shell of the given atom.

X-ray photoelectron spectroscopy also makes it possible to obtain information about the charge state of atoms, in particular, by studying the satellite structure. In addition, the satellite structure is, as a rule, much richer and more intense in x-ray photoelectron spectra than in x-ray spectra,[1] since x-ray spectra are subject to additional selection rules (see below).

The application of both methods together could significantly aid in the solution of the problem under study.

With the goal of interpreting data from x-ray photoelectron and x-ray emission spectroscopy, using Larsson's model[1–4] and the *Xα*-PB method[5–7] we investigated the structure of 2*p* and 1*s* spectra of copper as well as the Cu*Kα* line in copper (II) compounds.

1. LARSSON'S MODEL

In the mid-1970s Larsson[1–4] proposed a significantly nontraditional mechanism for the formation of 2*p* x-ray photoelectron spectra of copper in copper (II) compounds. This method was later developed in Refs. 8 and 9.

In accordance with Larsson's model, the ground state, for example, of CuO, can be represented in the form[9]

$$\Psi_G=\cos\theta|3d^9\rangle-\sin\theta|3d^{10}\underline{L}\rangle, \qquad (1)$$

where $|3d^9|$ and $|3d^{10}\mathrm{L}\rangle$ are orthonormalized wave functions and L is a 2*p* hole on the ligand. Here $|3d^9\rangle$ is a wave function characterized by the value of the *d*-density on the copper atom, which is close to 9*e*, while $|3d^{10}\mathrm{L}\rangle$ corresponds to *d*-density of about 10*e* with a simultaneous decrease of the electron density on the ligands (which is customarily referred to as a 2*p* hole on oxygen). It should be noted that this manner of writing the wave function is simplified and does not mean that the system contains molecular orbitals which are almost pure 3*d*-orbitals of copper. In the general case the molecular orbital clusters are delocalized and, in addition, they contain contributions from the 4*s* and 4*p* orbitals of copper; this is consistent with the possibility of writing the wave function in the form (1), but underscores the arbitrariness of the notation $|3d^9\rangle$ and $|3d^{10}\underline{L}\rangle$.

Following Ref. 8 we introduce the transfer integral

$$T=\langle 3d^9|H|3d^{10}\underline{L}\rangle,$$

where H is a Hamiltonian; the charge-transfer energy is

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

We write $\tan 2\theta = 2T/\Delta$ (Ref. 8).

A 1*s* hole formed at the first stage of the x-ray *Kα* process results in the presence of the states

$$\begin{aligned}\Psi_M^{(1s)}&=\cos\theta_1|\underline{1s}3d^9\rangle-\sin\theta_1|\underline{1s}3d^{10}\underline{L}\rangle,\\ \Psi_S^{(1s)}&=\sin\theta_1|\underline{1s}3d^9\rangle+\cos\theta_1|\underline{1s}3d^{10}\underline{L}\rangle,\end{aligned} \qquad (2)$$

where Ψ_M corresponds to the main line and Ψ_S is the satellite line. (Here and below, in contradistinction to Ref. 2, we take as the main line the strongest and narrowest component of the x-ray photoelectron spectrum and we take as the satellite the less intense component with pronounced multiplet structure. This, however, does not change the essence of the matter, since, as will become evident below, such a separation is arbitrary.) The 2*p* hole formed at the final stage of the *Kα* transition leads to the presence of the states

$$\begin{aligned}\Psi_M^{(2p)}&=\cos\theta_2|\underline{2p}3d^9\rangle-\sin\theta_2|\underline{2p}3d^{10}\underline{L}\rangle,\\ \Psi_S^{(2p)}&=\sin\theta_2|\underline{2p}3d^9\rangle+\cos\theta_2|\underline{2p}3d^{10}\underline{L}\rangle.\end{aligned} \qquad (3)$$

The following formula is satisfied:

$$\mathrm{tg}\, 2\theta_i = 2T/(\Delta - Q_i), \quad i=1, 2,$$

where, in accordance with Ref. 8, Q_1 and Q_2 are, respectively, the 1s-3d and 2p-3d effective interactions. In the sudden approximation, the ratio of the intensities of the satellite and main lines in the 2p x-ray photoelectron spectrum of Cu is determined by the relation[9]

$$I_S^{(2p)}/I_M^{(2p)} = |\langle\Psi_G|\Psi_S^{(2p)}\rangle|^2/|\langle\Psi_G|\Psi_M^{(2p)}\rangle|^2 = \mathrm{tg}^2(\theta-\theta_2)$$

(taking into account the difference noted in the terminology).

An analogous relation can also be written for the case of 1s spectrum:

$$I_S^{(1s)}/I_M^{(1s)} = |\langle\Psi_G|\Psi_S^{(1s)}\rangle|^2/|\langle\Psi_G|\Psi_M^{(1s)}\rangle|^2 = \mathrm{tg}^2(\theta-\theta_1).$$

The energy splitting between the diagram and satellite lines in the x-ray photoelectron spectrum is equal to

$$W_i = [(\Delta - Q_i)^2 + 4T^2]^{1/2}, \tag{4}$$

where $i = 1$ corresponds to the 1s spectrum and $i = 2$ corresponds to the 2p spectrum.

2. ROLE OF SATELLITE SHAKE-UP IN THE FORMATION OF THE Cu*K*α LINE

The shift of the energy of the $K\alpha$ line is widely employed for determining the charge of the atom of interest (see, for example, Refs. 10 and 11). For this, the change in the energy of the maximum of the $K\alpha_1$ ($K\alpha_2$) diagram line must be determined from experiment. This is possible if the diagram line can be separated from the spectrum, i.e., separated from the satellites, which means that there can be no overlapping of satellite and diagram lines whatever.

As the discussion below shows, in the case of the spectra of copper (II) compounds there is no justification for neglecting the contribution of the satellites, since an intense shake-up satellite, whose energy is close to the $K\alpha_1$ ($K\alpha_2$) diagram line, is present. In addition, according to what we have said above, the position and intensity of this satellite must be sensitive to the charge state of the atom under study, so that analysis of this satellite should give additional possibilities for studying the charge state. We shall examine the form of the $K\alpha$-line of copper, taking this satellite into account, for the case of CuO.

The results of investigations of the 1s and $2p_{3/2}(2p_{1/2})$ x-ray photoelectron spectra of copper play an important role in analysis of the $K\alpha$ line, since the 1s and 2p hole states are the initial and final states in the $K\alpha$ transition. In copper (II) compounds two components, separated by a significant energy splitting W_2 ($W_2 \approx 8.5$ eV for CuO), are present in the 2p x-ray photoelectron spectra, and one of these components has pronounced multiplet structure. In accordance with what we have said above, these two components correspond to the two possible forms of the hole state ($2p_{3/2}$ and $2p_{1/2}$).

We are not aware of any published data on the x-ray photoelectron spectra of the 1s level of copper. Since, however, from the energetic standpoint, the 2p and 1s holes have almost an identical effect on the valence shell (of course, neglecting, in particular, the multiplet effects), two analogous states should also be manifested in the 1s spectrum and should give the 1s x-ray photoelectron spectrum of copper a two-component structure. It follows that four corresponding components should be manifested in the $K\alpha_1$ ($K\alpha_2$) line, and in addition the extreme components should be split from the two central components by an amount close to W_1 in both the low- and high-energy regions (although, as follows from the subsequent analysis, the intensity of the extreme components is substantially suppressed).

It is of interest to compare next the $K\alpha$ lines of CuO and Cu_2O. The state of the valence shell of the copper atom in Cu_2O is described well by the state vector $|3d^{10}\rangle$ [subject to the same stipulations that were made regarding the formula (1)]. Accordingly, a single component is observed in the $2p_{3/2}(2p_{1/2})$ x-ray photoelectron spectrum of Cu_2O; likewise, the $K\alpha_1$ ($K\alpha_2$) line of Cu_2O consists of one component. The experiment shows that the form of the $K\alpha_1$ ($K\alpha_2$) line is virtually identical for both Cu_2O and CuO; in particular, the experimental linewidth hardly changes:[12] ($\Gamma_{K\alpha_1}(Cu_2O) = 2.29 \pm 0.10$ eV, $\Gamma_{K\alpha_1}(CuO) = 2.42 \pm 0.10$ eV, $\Gamma_{K\alpha_2}(Cu_2O) = 2.89 \pm 0.10$ eV, $\Gamma_{K\alpha_2}(CuO) = 2.77 \pm 0.10$ eV.[12] This is not consistent with the results of calculation [$\Gamma_{K\alpha_1}(Cu_2O) \approx 2.22$ eV, $\Gamma_{K\alpha_1}(CuO) \approx 3.90$ eV, $\Gamma_{K\alpha_2}(Cu_2O) \approx 2.56$ eV, $\Gamma_{K\alpha_2}(CuO) \approx 4.48$ eV (Ref. 12)] based on the idea that the $3d^9$ configuration plays the main role in CuO. If this were the case, then because of strong multiplet splitting, which plays an important role in the case of an open shell, the width of the $K\alpha_1$ ($K\alpha_2$) line would be significantly larger in the case of CuO than in the case Cu_2O.

3. APPLICATION OF LARSSON'S MODEL TO X-RAY SPECTROSCOPY

We now examine the $K\alpha$ process. We determine the matrix elements of the transition:

$$\langle\Psi_M^{(1s)}|r|\Psi_M^{(2p)}\rangle = \langle\Psi_S^{(1s)}|r|\Psi_S^{(2p)}\rangle = \langle 1s|r|2p\rangle \cos(\theta_2-\theta_1),$$

$$\langle\Psi_M^{(1s)}|r|\Psi_S^{(2p)}\rangle = -\langle\Psi_S^{(1s)}|r|\Psi_M^{(2p)}\rangle = \langle 1s|r|2p\rangle \sin(\theta_2-\theta_1).$$

In the sudden approximation[13] we obtain the following ratio of the intensities of the satellite and principal lines in the $K\alpha$ x-ray photoemission spectrum:

$$\frac{I_S}{I_M} = \frac{|\langle\Psi_G|\Psi_S^{(1s)}\rangle\langle\Psi_S^{(1s)}|r|\Psi_S^{(2p)}\rangle|^2}{|\langle\Psi_G|\Psi_M^{(1s)}\rangle\langle\Psi_M^{(1s)}|r|\Psi_M^{(2p)}\rangle|^2}$$

$$= \mathrm{tg}^2(\theta - \theta_1) = \frac{I_S^{(1s)}}{I_M^{(1s)}}$$

(compare with the analogous ratio in Ref. 14).

We now examine the energy of these components of the $K\alpha$ spectrum of copper in the compound CuO. Averaging the Hamiltonian over the corresponding states, we obtain the energy of the principal and satellite $K\alpha$ lines relative to the configuration $|3d^{10}\underline{L}\rangle$:

$$\Delta E_M = (\cos 2\theta_2 - \cos 2\theta_1)\Delta/2 + (\sin 2\theta_2 - \sin 2\theta_1)T + (Q_1\cos^2\theta_1 - Q_2\cos^2\theta_2),$$

$$\Delta E_S = (\cos 2\theta_1 - \cos 2\theta_2)\Delta/2 + (\sin 2\theta_1 - \sin 2\theta_2)T + (Q_1\sin^2\theta_1 - Q_2\sin^2\theta_2).$$

Therefore the splitting between the principal and satellite lines is determined by the relation

$$\Delta E=\Delta E_M-\Delta E_S=(\cos 2\theta_2-\cos 2\theta_1)\Delta+2(\sin 2\theta_2-\sin 2\theta_1)T+(Q_1\cos 2\theta_1-Q_2\cos 2\theta_2)=-\Delta Q\cos 2\theta_1+o(\Delta Q), \tag{5}$$

where $\Delta Q = Q_2 - Q_1$. We determine ΔQ by the effective-ion method.[10,11] In Ref. 15 it was shown with the help of this method that the shift of the $K\alpha$ line in copper compounds is determined primarily by the magnitude of the effective partial $3d$-charge on the copper atom. The dependence on $4s$ and $4p$ is somewhat weaker. In accordance with Ref. 15

$$\Delta E_{K\alpha}=-C_1\bar{q}_{3d}-C_2\bar{q}_{3d}^2,\quad C_1\approx 0{,}426\text{ eV},\quad C_2\approx 0{,}075\text{ eV},$$

where $\bar{q}_{3d} = 10 - q_{3d}$, q_{3d} is the partial $3d$-charge on the copper atom, and

$$\Delta E_{K\alpha}=E_{K\alpha}(3d^{q_{3d}})-E_{K\alpha}(3d^{10}).$$

Substituting $\bar{q}_{3d} = 1$ ($3d^9$ configuration) gives the required value $\Delta Q = E_{K\alpha}(3d^{10}) - E_{K\alpha}(3d^9) \approx 0.501$ eV; this confirms the assumption that Q_1 does not differ much from Q_2 [$\Delta Q/Q_2 < 0.1$ (see Table I)].

The position of the center of mass of the principal and satellite lines of the $K\alpha$ spectrum relative to the $|3d^{10}\mathrm{L}\rangle$ configuration is determined by the formula

$$\begin{aligned}\Delta\bar{E}&=(\Delta E_M I_M+\Delta E_S I_S)/(I_M+I_S)\\&=(\Delta E\cos[2(\theta-\theta_1)]-\Delta Q)/2\\&=-\Delta Q(\cos 2\theta_1\cos[2(\theta-\theta_1)]+1)/2+o(\Delta Q).\end{aligned}\tag{6}$$

The energy of the "cross" satellites, which correspond to the processes $\Psi_M^{(1s)}\rightarrow\Psi_S^{(2p)}$ and $\Psi_S^{(2s)}\rightarrow\Psi_M^{(2p)}$, is determined by the respective formulas

$$\Delta E_{MS}=W_2\quad\text{and}\quad\Delta E_{SM}=-W_1.$$

The intensity of these satellites, relative to the principal line, is equal to $\lambda = \tan^2(\theta_2 - \theta_1)$. The relative intensity of the "cross" satellites in the case of CuO is determined by the value $\lambda \approx 0.03\%$, and their energy splittings from the diagram line are equal to $\Delta E_{MS} = 8.97$ eV and $\Delta E_{SM} = -8.56$ eV (in accordance with the parameters given in Ref. 9). Finding these satellites could be an important confirmation of the correctness of the approach under study.

The magnitude of the $3d$-charge transfer in the case of the principal and satellite lines is determined with the help of the respective formulas

$$\Delta q_M=\cos^2\theta-\cos^2\theta_1\quad\text{and}\quad\Delta q_S=\cos^2\theta-\sin^2\theta_1$$

The numerical values for these formulas are given in Table I. Figure 1c shows the structure of the $K\alpha$ line in accordance with the approach under study. We note that Larsson's model gives the form of the $1s$ x-ray photoelectron spectrum shown in Fig. 1a (neglecting multiplet effects, which are insignificant in the $1s$-hole state).

In contrast to Ref. 14, the principal and satellite components of the $K\alpha$ spectrum are associated not to the $3d^{10}L$ and $3d^9$ configurations but rather the states Ψ_M and Ψ_S, respectively. This is the reason for the dependence (5) of the energy splitting between the principal and satellite components on the parameters θ_i (this dependence is in principle absent in Ref. 14) and why our computed value of this energy splitting (0.4 eV) is 20% less than the value 0.5 eV given in Ref. 14.

4. $X\alpha$-CALCULATION OF CuO_4^{6-} CLUSTER: X-RAY SPECTRA

We performed an $X\alpha$-PB calculation of the electronic structure of the ground state as well as the $1s$ and $2p$ hole states of the cluster CuO_4^{6-}, which approximates the first coordination sphere of a copper atom in CuO.[17] The valence levels form the following sequence in order of increasing energy: $1b1_g$, $2b_{1g}$, $2a_{1g}$, $1e_g$, $1a_{2u}$, $2e_u$, $3a_{1g}$, $1b_{2u}$, $3e_u$, $1a_{2g}$, $2e_g$, $2b_{2g}$, and $3b_{1g}$. The top valence level $3b_{1g}$ is partially filled. The bottom vacant level is $4a_{1g}^*$. The total d-charge in the sphere of the copper atom is equal to $8.62e$.

TABLE I. Values of the parameters in Larsson's model and results of calculations of the Cu$1s$ and $2p$ x-ray photoelectron spectra as well as the Cu$K\alpha$-line for copper (II) compounds.

parameters	CuO		La_2CuO_4	$La_{1,8}Sr_{0,2}CuO_4$	$YBa_2Cu_3O_7$
T, эВ	2,5 [9]	2,4 [16]	2,3 [16]	2,4 [16]	2,5 [16]
Δ, эВ	1,55 [9]	1,0 [16]	0,3 [16]	0,3 [16]	0,5 [16]
Q_1, эВ	8,5	7,9	6,9	7,3	7,3
Q_2, эВ	9,0 [9]	8,4 [16]	7,4 [16]	7,8 [16]	7,8 [16]
θ, °	36,39	39,12	43,13	43,21	42,14
θ_1, °	72,13	72,59	72,56	72,78	71,83
θ_2, °	73,07	73,52	73,53	73,69	72,80
$I_S^{(1s)}/I_M^{(1s)}$	0,52	0,44	0,32	0,32	0,33
$I_S^{(2p)}/I_M^{(2p)}$	0,55	0,47	0,34	0,35	0,35
λ	$2{,}66\cdot 10^{-4}$	$2{,}63\cdot 10^{-4}$	$2{,}87\cdot 10^{-4}$	$2{,}53\cdot 10^{-4}$	$2{,}81\cdot 10^{-4}$
ΔE_M, эВ	−0,045	−0,043	−0,043	−0,042	−0,046
ΔE_S, эВ	−0,456	−0,458	−0,458	−0,459	−0,455
ΔE, эВ	0,411	0,415	0,415	0,417	0,409
Δq_M	0,55	0,51	0,44	0,44	0,45
Δq_S	−0,26	−0,31	−0,38	−0,38	−0,35
W_1	8,56	8,40	8,04	8,49	8,44
W_2	8,97	8,82	8,46	8,90	8,85

Note. The results presented were obtained with the help of the parameters T, Δ, and Q_2, determined in Refs. 9 and 16 on the basis of spectral information.

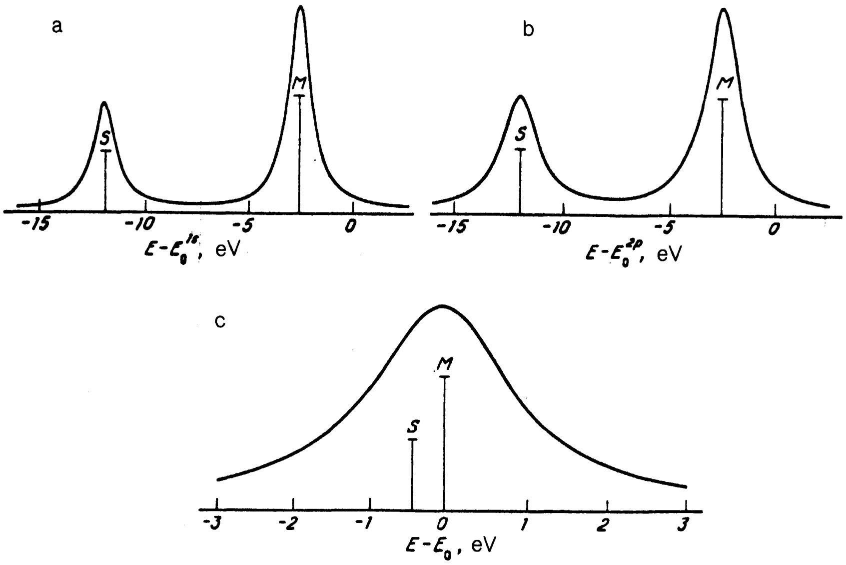

FIG. 1. Relationship between the structure of the Cu 1*s* (a) and 2*p* (b) x-ray photoelectron spectra and the structure of the Cu*Kα* line (c) in copper (II) compounds on the basis of the approach studied in the present paper. E_0^{1s} (E_0^{2p}) is the energy of the maximum of the 1*s* (2*p*) x-ray photoelectron spectrum, corresponding to the $3d^{10}$ configuration; E_0 is the energy of the maximum of the *Kα* x-ray emission spectrum, corresponding to the same configuration.

The 1*s* and 2*p* hole states are characterized by an ionic-type bond. When core-hole states are formed the electronic density flows from the ligands onto the central atom. As a result of relaxation the energy levels drop and in their structure changes. A strongly pronounced separation of levels into two widely separated groups occurs. The first group, which is deeper and energetically well localized, consists predominantly of the 3*d*-electrons of copper (the levels $1e_g$, $2a_{1g}$, $1b_{2g}$, and $2b_{1g}$). The second group lies significantly higher and covers a much wider energy range; it is formed predominantly by the 2*p*-electrons of oxygen (see Figs. 2 and 3). These levels form the following sequence in order of increasing energy: $3a_{1g}$, $1a_{2u}$, $2b_{2g}$, $2e_u$, $2e_g$, $1b_{2u}$, $3e_u$, $1a_{2g}$ and, finally, the partially filled level $3b_{1g}$. The bottom vacant level is $4a_{1g}^*$. The total *d*-charge in the sphere of the copper atom is equal to 9.38*e* for the case of a 1*s*-hole state (9.42*e* for the case of a 2*p*-hole state). Therefore when a hole is formed the *d*-charge increases by almost by 1 unit; this corresponds to transfer of an electron from the ligands onto the central atom.

The structure of the ground state indicates that shake-up processes with the participation of the partially filled $3b_{1g}$ level will play a significant role in the x-ray and x-ray photoelectron spectra, and in addition the highest intensity will correspond to transfer of an electron from the $2b_{1g}$ level to the $3b_{1g}$ level,[18] since this transition does not change the

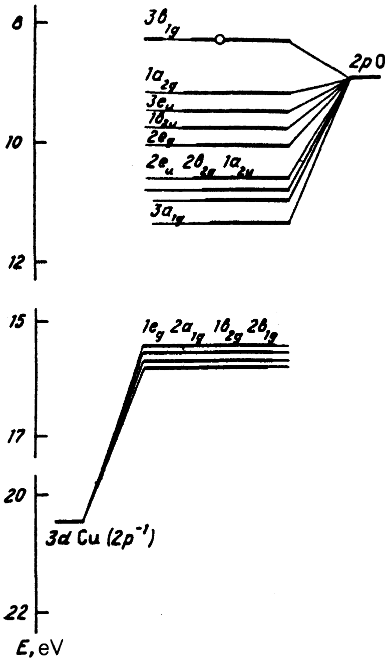

FIG. 2. Energy diagram of the valence levels of the state $\Psi_S^{(2p)}$. The length of the thick line, starting from the left, denotes the contribution of the 3*d* (Cu) state and the line starting from the right denotes the contribution of the 2*p*(0) state.

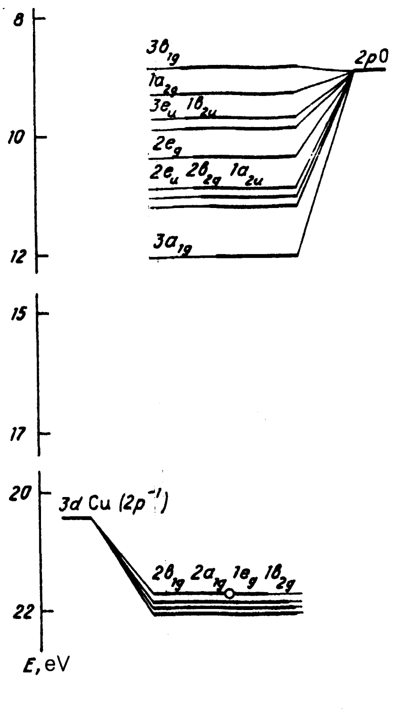

FIG. 3. Energy diagram of the valence levels of the state $\Psi_S^{(2p)}$ (see comments in Fig. 2).

symmetry of the wave function. Therefore, in contrast to other possible transitions, the indicated process is not suppressed in the sudden approximation. In addition, the composition of the $2b_{1g}$ level is close to that of the $3b_{1g}$ level, which cannot be said about the vacant levels.[17] The energy of this transition is equal to approximately 10 eV.

We now examine the electronic structure of the 1*s* and 2*p*-hole state of the cluster in the presence of the indicated excitation (transfer of an electron from the $2b_{1g}$ level to the $3b_{1g}$ level). This excitation does not change the type of chemical bond between the copper and oxygen atoms; moreover, the energetics of the MOs remains almost unchanged. However the shake-up process decreases the 3*d*-charge in the sphere of the copper atom to 8.54*e* in the case of the 1*s*-hole state and 8.48*e* in the case of the 2*p*-hole state. Thus in the presence of the shake-up process under study the 3*d*-charge in the sphere of the copper atom in the case of the hole states was found to be close to the 3*d*-charge in the sphere of the copper atom in the case of the ground state. This latter circumstance also favors the given satellite having a significant intensity.

We calculated the ionization potentials of the 1*s* and 2*p* levels of copper with the help of the transition-state method[19] for the shake-up process under study. The energy of the computed shake-up satellite agrees with experiment (see Table II). The discrepancies in the relative positions of the diagram and satellite lines in the 1*s* and 2*p* spectra are insignificant (the multiplet structur is neglected).

5. COMPARISON OF LARSSON'S MODEL WITH THE *Xα* RESULTS

Larsson's model and the *Xα*-method make it possible to obtain independently a number of important energy characteristics of the x-ray and x-ray photoelectron spectra. These are primarily data on the relative position of the diagram lines and the satellites.

On the basis of Larsson's model the energy splitting W_i between the diagram and satellite lines in the 1*s* ($i = 1$) and 2*p* ($i = 2$) x-ray photoelectron spectra is determined with the help of Eq. (4). In accordance with Table I for CuO $W_1 = 8.56$ eV and $W_2 = 8.97$ eV (the parameters from Ref. 9 were used). The *Xα* calculation gives $W_1 = 5.50$ eV and $W_2 = 5.54$ eV. In Ref. 20 the value 7.8 eV was obtained for W_2 with the help of the same *Xα*-PB method. It probably differs from our value because in Ref. 20 a nonstandard choice of the radius of Watson's sphere was made.

Our *Xα* value of W_2 is less than the experimental value. One reason for this is that in the *Xα* calculation the interaction of the configurations is neglected, and as is well known this interaction increases the energy splitting between the levels.

Larsson's model leads to the conclusion that the splitting between the diagram and satellite lines in the $K\alpha_1$ ($K\alpha_2$) spectrum is determined by the formula (5): In the case of CuO $\Delta E \approx 0.4$ eV (see Table I). The *Xα* calculation using the transition-state method gives the same value.

The energy of the "cross" satellites, which correspond to the processes $\Psi_M^{(1s)} \to \Psi_S^{(2p)}$ and $\Psi_S^{(1s)} \to \Psi_M^{(2p)}$, is determined, in accordance with the *Xα* calculation, by the values $\Delta E_{MS} = 9.75$ eV and $\Delta E_{SM} = -10.03$ eV, which are close to the corresponding values obtained on the basis of Larsson's model (see Sec. 3).

We note that the satellite structure is seemingly "smeared" in the emission spectrum, since the cross transitions $\Psi_M^{(1s)} \to \Psi_S^{(2p)}$ and $\Psi_S^{(1s)} \to \Psi_M^{(2p)}$ are suppressed (unique selection rules operate), while the transitions $\Psi_M^{(1s)} \to \Psi_M^{(2p)}$ and $\Psi_S^{(2s)} \to \Psi_S^{(2p)}$ have close energies (see Fig. 1).

TABLE II. Energies and composition molecular orbitals of the core-hole states of the cluster CuO_4^{6-}.

	1*s*-hole state						2*p*-hole state					
	$\Psi_M^{(1s)}$			$\Psi_S^{(1s)}$			$\Psi_M^{(2p)}$			$\Psi_S^{(2p)}$		
	E, eV	n_{3d}, %	n_{2p}, %	E, эВ	n_{3d}, %	n_{2p}, %	E, эВ	n_{3d}, %	n_{2p}, %	E, эВ	n_{3d}, %	n_{2p}, %
$2b_{1g}$	−15,45	83	10	−21,25	78	2	−15,76	83	9	−21,54	75	2
$1b_{2g}$	−15,38	89	4	−21,77	96	–	−15,72	90	3	−22,13	96	–
$2a_{1g}$	−15,28	90	4	−21,58	91	–	−15,62	91	3	−21,94	91	–
$1e_g$	−15,27	92	2	−21,74	96	–	−15,62	93	1	−22,10	96	–
$3a_{1g}$	−11,41	3	55	−12,18	1	54	−11,35	3	56	−12,08	–	54
$1a_{2u}$	−10,93	–	58	−11,25	–	55	−10,91	–	58	−11,23	–	56
$2b_{2g}$	−10,71	7	61	−11,17	1	63	−10,73	6	62	−11,17	1	63
$2e_u$	−10,66	–	69	−11,00	–	67	−10,62	–	68	−10,96	–	68
$2e_g$	−10,06	3	67	−10,41	1	67	−10,05	3	67	−10,41	1	67
$1b_{2u}$	−9,74	–	75	−9,96	–	74	−9,73	–	75	−9,95	–	74
$3e_u$	−9,50	–	74	−9,75	–	74	−9,47	–	74	−9,73	–	74
$1a_{2g}$	−9,14	–	77	−9,36	–	76	−9,13	–	77	−9,36	–	76
$3b_{1g}$	−8,19	13	68	−8,90	5	75	−8,24	12	69	−8,91	4	75
q_{3d}	9,38			8,54			9,42			8,48		
q_{2p}	16,04			16,28			15,95			16,34		

Note. n_{3d} is the contribution of the 2*p* (O) orbital and n_{2p} is the contribution of the 3*d* (Cu) orbital to molecular orbital.

Our analysis explains why a significant increase of the linewidth does not occur on transferring from Cu_2O to CuO. The point is that in CuO the configuration $3d^{10}\underline{L}$ plays a large role (the valence hole is localized on the oxygen atoms); in the hole states generated by this configuration the multiplet splitting is insignificant because the x-ray hole ($2p$ or $1s$) is located far from the valence hole. At the same time, the contribution of the $3d^9$ configuration, which leads to significant multiplet splitting, is largely suppressed.

We now consider the reasons why the two very different computational methods (Larsson's model and the $X\alpha$ method) agree with one another. The core hole states Ψ_M and Ψ_S primarily differ from one another only in the filling of the $2b_{1g}$ and $3b_{1g}$ molecular orbitals; the changes occurring in the energies of the molecular orbitals with a transition from one state to another are insignificant for the processes studied. This is why the interpretation of the process of formation of diagram and satellite lines in the x-ray and x-ray photoelectron spectra can be reduced to the interaction of two configurations in which the occupation numbers of these molecular orbitals are different; this is the essence of Larsson's model.

CONCLUSIONS

The three main conclusions of this work are as follows.

1. Larsson's model can be applied to copper (II) compounds because the wave functions of the core hole states Ψ_M and Ψ_S, which make the main contribution to the x-ray and x-ray photoelectron spectra, differing from one another by the occupation of the two molecular orbitals.

2. The separation of lines into "diagram" and "satellite" is very arbitrary in the case of copper (II) compounds, since the wave function of the core-hole state Ψ_M differs from the wave function of the ground state Ψ_G just as much as the state Ψ_S [since the difference $\theta_i - \theta$ ($i = 1,2$), determining the "similarity" of the wave functions of the core-hole and ground states, is equal to about 40° in the case of the compounds studied].

3. Systematic application of Larsson's model and the effective-ion method as well as the $X\alpha$ calculation indicate independently the existence of an intense shake-up satellite, split by ≈ 0.4 eV from the diagram line, in the Cu$K\alpha$ spectrum of copper (II) compounds; in the case of CuO this satellite results from the transition $2b_{1g} \rightarrow 3b_{1g}$.

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