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Resonance Interatomic Auger Transitions

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Abstract—The interatomic Auger transitions in compounds containing atomic components with core levels close in energy are studied theoretically and experimentally. The Coulomb transitions of holes between such levels lead to resonant enhancement of the Auger spectra (with respect to the energy difference between the levels). Interatomic Auger transitions involving higher levels are formed by shaking up electrons due to the dynamic field of photo-holes produced in the process of absorbing X-ray radiation and during the transition. These effects are observed experimentally in the XPS and Auger spectra of $CuInSe_2$-type materials.

Keywords: XPS spectra, Auger spectra, photohole effects, $CuInSe_2$

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INTRODUCTION

The investigation of interatomic Auger transitions is of significant importance for studying the evolution of excited stated in substances. It is of special importance to understand the Auger transitions in photoelectric transducers, because these transitions play a determining role in energy losses and limit the efficiency of transducer operation [1]. It was shown in [2, 3] that photoemission associated with the ground electronic level of a given atom "A" can be significantly altered in terms of its intensity when the photon energy overcomes the absorption edge of the core level of a neighboring atom "B". This effect is called multiatom resonant photoemission (MARPE). Its macroscopic description can be given in terms of a resonance optical dielectric model that considers a change in the complex permittivity in the process of passing the corresponding resonance [4–6].

In this work, Auger processes with no resonance photons are considered theoretically and experimentally. A photohole decays by means of a nonresonant Auger transition with the emission of an electron by a neighboring atom. It is shown that this process is significantly enhanced if the core levels of neighboring elements have nearly identical energies. From this point of view, it is possible to speak about a resonant interaction between the core levels involved in the Auger transition.

AUGER PROCESS IN A COMPOUND WITH TWO LEVELS CLOSE IN ENERGY

Let us consider the scheme (Fig. 1) of the interatomic Auger transition by the example of the $CuInSe_2$ compound. A Cu 2*p* hole that appears as a result of photoionization (the binding energy is 933 eV) due to the Coulomb interaction is filled by an electron from the upper Cu 3*p*-state (75 eV); the energy release in this process is spent on the emission of an electron of the neighboring atom of In 4*d* (17 eV) to the free state *f*. A detector measures the intensity of the emission of such electrons and their kinetic energy or the $CuL_3M_{2,3}$, $InN_{4,5}$ Auger spectra. Usually, the intensity of the interatomic transition is vanishingly small as compared with that of the intra-atomic transition, for example, Cu ($L_3M_{2,3}$V) (V designates the valence state), since the distances determining the Coulomb interaction energy $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ between electrons inside an atom is significantly smaller than the interatomic distance.

Let us show that the intensity of the interatomic Auger transition increases significantly, if the neighboring atom has a core level close in energy to the level of the central atom. In our example, it is the In 4*p* level with a binding energy of 73.5 eV, which is shifted by 1.5 eV only relative to the energy of the Cu 3*p* level. The probability of virtual hole transitions between levels increases (Fig. 1a); the real (in the final state) transition of a hole from one atom to another (Fig. 1b) also becomes possible. The rate of the transition from the

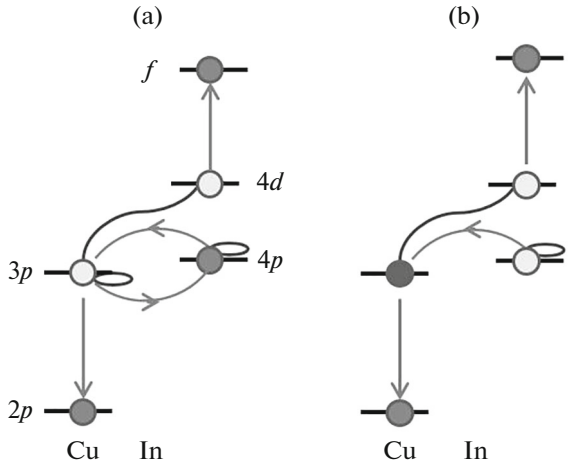

Fig. 1. Diagram of the multiatomic Auger processes Cu 2*p* Cu 3*p* In 4*d* (a) and Cu 2*p* In 4*p* In 4*d* (b) in $CuInSe_2$ taking into account the interaction between the Cu 3*p* and In 4*p* core levels.

initial state *i* to the final state *j* (generally speaking, decaying) is defined by the quantity

$$I_{ji} = \frac{1}{\hbar\pi}\operatorname{Im} G_{jj}(E_i)\left|A_{ji}(E_i)\right|^2. \quad (1)$$

Here,

$$A_{ji}(E) = \left(V + VG(E)V\right)_{ji}, \qquad G(E) = \left(E - H - V - i\gamma\right)^{-1} \quad (2)$$

is the total Green's function with the Coulomb interaction *V* leading to Auger transitions between the eigenstates *i* and *j* of the zero Hamiltonian *H*. The imaginary component in equation (1) reflects the energy conservation law (at $\gamma \to 0$) with consideration of the state decay (at a finite γ).

In the first order, the amplitude of the Auger transition is equal to the matrix element of the Coulomb interaction between the initial and final states:

$$A_{ji} = V_{ji} = \langle 1,3|V|c,f\rangle. \quad (3)$$

On the diagram (Fig. 1), the state *c* is a hole at the Cu 2*p* level; *f* is the Auger electron recorded by the detector; state *1* is the Cu 3*p* hole; state *3* is a hole at the In 4*d*-level. The amplitude (diagram *1*a) of the Auger transition with consideration of the interaction between states *1* and *2* (In 4*p*) can be written as follows:

$$A_{ji} = \frac{\langle 1,1'|V|2,1'\rangle}{E - E_2 - E_3 - i\gamma} \times \frac{\langle 2,2'|V|1,2'\rangle}{E - E_1 - E_3 - i\gamma}\langle 1,3|V|c,f\rangle. \quad (4)$$

In what follows, we will denote the matrix element of the Coulomb electron transfer between atomic levels *1* and *2* (the numerator in (4)) by symbol *W*; the matrix element (3), by symbol *V*. Calculating the first terms of the series with respect to interaction, we obtain the intensities of the Auger transitions in different orders of scattering theory.

The Auger-line intensity as a function of the electron kinetic energy and its integrated intensity (the line power) in the lowest order are given by the following equations:

$$I_0(e) = \frac{V^2}{\pi}\frac{\gamma}{e^2 + \gamma^2}; \quad S_0 = \int de I_0 = V^2. \quad (5)$$

The quantity $e = E_{\text{kin}} - (E_1 + E_3 - E_c)$ shows the deviation of the kinetic energy of the Auger electron from its nominal value.

The rise of the hole from level *1* to the level of the neighboring atom *2* (Fig. 1b) reduces the energy of the atom remnant by the value $E_{21} = E_2 - E_1$ and generates a spectral line of the following form:

$$I_1(e;E_{21}) = W^2V^2\frac{1}{\pi}\frac{1}{e^2 + \gamma^2}\frac{\gamma}{(e - E_{21})^2 + \gamma^2}; \qquad S_1 = \frac{2W^2V^2}{E_{21}^2 + 4d^2}. \quad (6)$$

The virtual hole transition between levels $1 \leftrightarrow 2$ gives the addition:

$$I_2(e;E_{21}) = W^4V^2\frac{1}{\pi}\frac{\gamma}{\left(e^2 + \gamma^2\right)^2}\frac{1}{(e - E_{21})^2 + \gamma^2}, \qquad S_2 = \frac{W^4V^2}{E_{21}^2 + 4\gamma^2}\left\{\frac{1}{2\gamma^2} + \frac{4}{E_{21}^2 + 4\gamma^2}\right\}. \quad (7)$$

The hole transition from level *1* to the neighboring level *2* taking into account the virtual $2 \leftrightarrow 1$ transition generates the line

$$\mathrm{I}_3(e;E_{21}) = \frac{W^6V^2}{\pi}\frac{1}{\left(e^2 + \gamma^2\right)^2}\frac{\gamma}{\left((e - E_{21})^2 + \gamma^2\right)^2}, \qquad S_3 = \frac{W^6V^2}{(E_{21}^2 + 4\gamma^2)^2}\left(\frac{1}{\gamma^2} + \frac{16}{(E_{21}^2 + 4\gamma^2)}\right). \quad (8)$$

Figure 2 shows the contributions to the Auger spectra from the above-considered scattering channels (formulas (5)–(8)) at an energy difference between levels equal to their width of $E_{21} = 2\gamma$. The thin solid line shows the intensity in the least order I_0 (5). The dotted lines are graphs of the functions $I_1(e)$, $I_2(e)$, and $I_3(e)$; the thick solid line shows the sum of all four contributions. Consideration for the contribution of neighboring atoms leads to a significant increase in the Auger-emission intensity in the case where $E_{21} = 2\gamma$. It should be noted that we summarize the intensities rather than the amplitudes of the transitions, since intensive scattering results in the chaotization of the phases of wave functions and in the attenuation of interference effects [7].

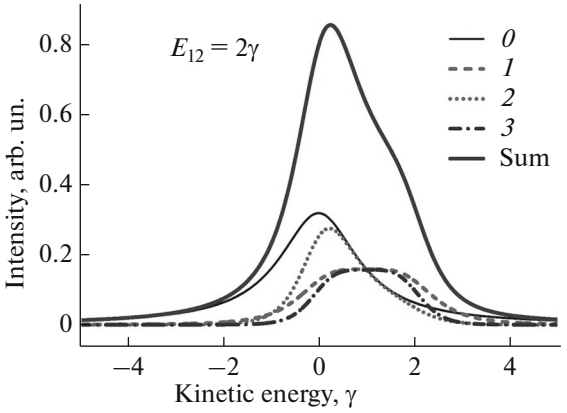

Fig. 2. Intensity of Auger emission (the thick solid line) and contributions of channels (5)–(8) at an energy difference equal to the level width $E_{12} = 2\gamma$.

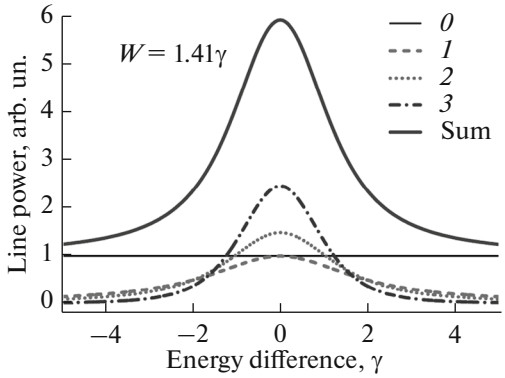

Fig. 3. Integrated intensity of the Auger line as a function of the energy difference between the levels E_{21} at $W = 1.41\gamma$: power of the S_0–S_3 processes and their sum (the thick solid line).

Figure 3 shows the dependence of the power of the $S_0 - S_3$ processes on the value of the energy difference between levels E_{21}/γ at a fixed value of the matrix element of the Coulomb transfer $W = 1.41\gamma$. The use of a finite series of the perturbation theory at zero energy difference between levels is not completely justified; however, even at $E_{21} = 2\gamma$, this series converges quickly and the increase in the Auger-emission power due to the interaction between core levels of neighboring atoms by two-three times is quite possible. The effect of an increase in the Auger-emission power quickly decreases as the energy difference grows and it becomes vanishingly small at $E_{21} > 5\gamma$.

The presence of a resonant (with a close value of energy) level at the neighboring atom significantly increases the Auger-transition probability. The contributions of the high-energy level deform the line towards increasing kinetic energy. The spectrum becomes narrower due to virtual excitations. It should be taken into account that the final states in real atoms are a level multiplet; therefore, several lines with different energies emerge instead of one line.

ANALYSIS OF EXPERIMENTAL AUGER SPECTRA

The experimental X-ray photoemission spectra (XPS) and Auger spectra of chalcopyrite $CuInSe_2$ at various excitation energies were obtained at the BESSY II Russian-German laboratory (Berlin). Figure 4 shows the Auger spectra of Cu in $CuInSe_2$ obtained at a photon energy of 1200 eV. For comparison, the Auger spectrum of metallic copper obtained for the case of MgK_α radiation with an energy of 1253.6 eV [8] is also presented. On both these curves, one can clearly see the CuL_3VV intra-atomic Auger transitions (the maximum of the kinetic energy is 918 eV) and a triple Auger-line formed by the Cu$L_3M_{2,3}V$ transition (the principal maximum is 838 eV, the multiplet splitting as a result of summation of the moments of two holes 3*p* and 3*d*). At the energy values located 20 eV above the main lines on the curves shown in Fig. 4, one can note their replicas originating from the CuL_2 hole. The formation of the CuL_3VV Auger line in the related compound Cu ($In_{0.9}Ga_{0.1}Se_2$) in the process of the photon-energy overcoming the excitation edge of the 2*p* level, the fine line structure, and the energy of the Hubbard repulsion of two holes in the valence band are studied in detail in [9].

It is seen in Fig. 4 that in $CuInSe_2$ at an energy of 14 eV below the Cu L_3VV peak, the interatomic CuL_3 In$N_{4,5}V$ Auger line with a width of 25 eV appears, while this line is absent in the spectrum of pure copper. A similar structure is also seen below the Cu$L_3M_{2,3}$V lines. This is a result of the second interatomic transition Cu$L_3M_{2,3}$ In$N_{4,5}$. Let us note that the Cu$M_{2,3}$ hole can be completed with the $N_{2,3}$ hole whose binding energy is lower only by 1.5 eV. Hence, in the XPS spec-

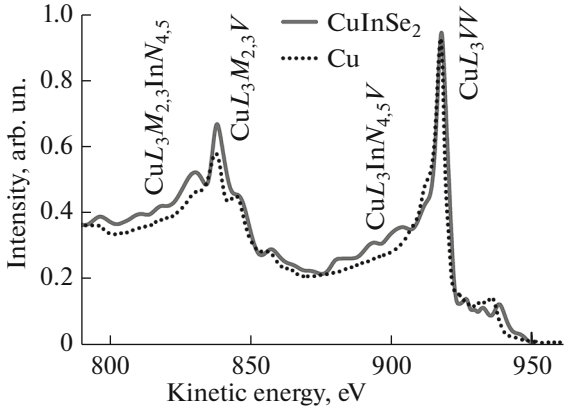

Fig. 4. Intra-atomic Cu*LMM* and interatomic Cu*LM* In*N* Auger lines in $CuInSe_2$ (the solid line) and the spectrum of pure copper [7] (the dotted line).

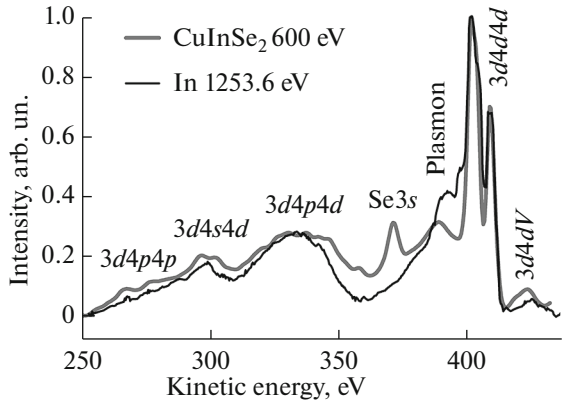

Fig. 5. Photoemission spectrum of $CuInSe_2$ obtained at a photon energy of 600 eV (the solid line) and the spectrum of pure indium at 1253.6 eV [7] (the dotted line).

tra of chalcopyrite $CuInSe_2$, interatomic Auger transitions are observed. Their intensity is enhanced due to resonant interaction between the Cu 3*p* and In 4*p* levels with close energies.

The model developed in the previous section is directly applicable to the interatomic Auger transitions $CuL_3M_{2,3}InN_{4,5}$ and $CuL_3InN_{2,3}InN_{4,5}$. But what is the mechanism of enhancement of the Cu L_3 In $N_{4,5}$ V transition? According to our opinion, it is highly likely that the scenario is as follows. First, a Cu 2*p*-hole is filled by a Cu 3*p*-electron with the emission of an Auger-electron from the valence state; next, the transition of the Cu 3*p*-hole to the In4*p* state of the atom of indium occurs; this process proceeds to completion by the intra-atomic electron transition at the indium atom In4*d* → In4*p* with the transfer of the energy excess to the Auger electron. As a result, we come from the initial Cu 2*p* hole state to the final In $N_{4,5}V$ hole state by means of two intra-atomic transitions and the resonant transfer of the hole between atoms, which have quite high probabilities.

Figure 5 shows a fragment of the photoelectron spectrum of $CuInSe_2$ in the region of Auger transitions that accompany the decay of the In $3d_{3/2,\,5/2}$ hole doublet (the binding energies are 451.4 and 443.9 eV) obtained at a photon energy of 600 eV, as well as the spectrum of pure indium for the case of MgK_α radiation of 1253.6 eV [8]. Both of these spectra have similar structures, except for the contribution of the direct photoemission from the Se 3*s* state (370 eV) in $CuInSe_2$. All the Auger transitions have an intra-atomic character. The most intensive line is the In 3*d*4*d*4*d* doublet with a kinetic energy of 401.5 and 408.5 eV. The line intensities in descending order are as follows: broad lines with two holes in the states 4*p*4*d* (with a center at 336 eV), 4*s*4*d* (296.5 and 301.5 eV), and 3*p*3*p* (267.5 and 278.5 eV). Apparently, a maximum with an energy of 13 eV below the principal peak occurs due to the energy loss spent on plasmon generation. A similar characteristic energy loss of 8.5 eV is also observed in metallic indium.

There is a small peak at an energy of 423 eV from the In 3*d*4*dV* Auger transition; the In 3*d VV* transition does not manifest itself at all. The In 4*p* hole that appears due to the decay process may move with considerable probability to the copper atom to the Cu 3*p* state; however, the probability of the transition of the valence electron *V* to the Cu 3*p* level is low (significantly lower than the probabilities of transitions $V \rightarrow$ Cu 2*p* and In 4*d* → In 4*p* initiated by Cu 2*p*-hole decay). As a result, the mixing of the Cu 3*p* and In 4*p* states does not manifest itself in the Auger spectra generated by In 3*d*-hole decay. Meanwhile, in the process of evolution of the excited state with a hole at Cu 2*p*, favorable conditions appear for the interatomic Auger processes.

CONCLUSIONS

Theoretical justification and experimental confirmation are given to the idea that the increase in the cross sections of the Auger processes due to interaction between the core levels of neighboring atoms with close energies makes it possible to observe the Auger transitions in the X-ray band. The experimental XPR spectra of compounds based on chalcopyrite $CuInSe_2$ show the intensive interatomic Auger transitions $CuL_3M_{2,3}$ $InN_{4,5}$ and CuL_3 $InN_{4,5}$. The resonant enhancement of the interatomic Auger-electron emission Cu $L_3M_{2,3}$ In $N_{4,5}$ is described by the theory of multiple scattering with consideration of the closeness in energy of the Cu 3*p* and In 4*p* levels. The sudden occurrence of photo- and Auger holes creates a dynamic field with a broad frequency spectrum, which initiates the shaking up of electrons of neighboring atoms. This process significantly increases the probability of the interatomic Auger transition CuL_3 $InN_{4,5}V$. In compounds with a narrow valence band (for example, in those of 3*d*-type) and a localized core level with a moderate binding energy (In 4*d*, 17 eV), strong Coulomb interaction between electrons and holes at neighboring atoms appears, which creates favorable conditions for the occurrence of intensive interatomic transitions in the soft X-ray band.

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REFERENCES

1. T. S. Navruz and M. Saritas, Sol. Energy Mater. Sol. Cells **93,** 1913 (2009).

2. A. Kay, E. Arenholz, B. S. Mun, F. J. Garcia de Abajo, C. S. Fadley, R. Denecke, Z. Hussain, and M. A. Van Hove, Science **281,** 679 (1998).
3. N. Mannella, S.-H. Yang, B. S. Mun, F. J. Garcia de Abajo, A. W. Kay, B. C. Sell, M. Watanabe, H. Ohldag, E. Arenholz, A. T. Young, Z. Hussain, M. A. Van Hove, and C. S. Fadley, Phys. Rev. B **74,** 165106 (2006).
4. F. J. Garcia de Abajo, C. S. Fadley, and M. A. Van Hove, Phys. Rev. Lett. **82,** 4126 (1999).
5. A. W. Kay, F. J. Garcia de Abajo, S.-H. Yang, E. Arenholz, B. S. Mun, N. Mannella, Z. Hussain, M. A. Van Hove and C. S. Fadley, Phys. Rev. B **63,** 115119 (2001).
6. H. Arai and T. Fujikawa, Phys. Rev. B **72,** 075102 (2005).
7. V. I. Grebennikov and T. V. Kuznetsova, Bull. Russ. Acad. Sci.: Phys. **82,** 591 (2018).
8. *Handbook on Electron Spectroscopy*, Ed. by J. Chastain (Perkin-Elmer Corporation, Eden Prairie, MN, 1995).
9. V. I. Grebennikov, T. V. Kuznetsova and M. V. Yakushev, Bull. Russ. Acad. Sci.: Phys. **77** (9), 1123 (2013).

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