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$L_{2,3}M_{4,5}M_{4,5}$ principal and satellite Auger spectra of free copper atoms

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The atomic $L_{2,3}M_{4,5}M_{4,5}$ Auger electron spectrum of Cu has been measured and analyzed in detail. Besides determination of the kinetic energies and relative intensities of the lines in the Auger spectrum, the free-atom binding energies $E_B(2p_{3/2}) = 939.85 \pm 0.15$ eV and $E_B(2p_{1/2}) = 959.45 \pm 0.15$ eV are also obtained. The comparison with corresponding solid-state results gives 2.5 eV for the solid-state binding-energy shift of $2p$ levels and 13.2 eV for the $L_{2,3}M_{4,5}M_{4,5}$ Auger shift. L_3M-$M_{4,5}M_{4,5}M$ satellite Auger lines arising from primary ionization in L_1 shell are seen clearly in the measured spectrum. They have been discussed and compared with the corresponding solid-state spectra. After correction for the L_2M-$M_{4,5}M_{4,5}M$ satellite spectrum, which overlaps the $L_3M_{4,5}M_{4,5}$ spectrum, the intensity ratio between L_3 and L_2 Auger groups was found to obey the statistical ratio quite well in contradiction to solid-state measurements, where $L_2L_3M_{4,5}$ Coster-Kronig transitions are energetically possible and modify this intensity ratio.

The experimental photo- and Auger electron spectra of free atoms are still rather rare in spite of their importance both for theoretical free-atom calculations and for investigations of solid-state effects, like free-atom-solid Auger and binding-energy shifts. The solid-state Auger spectra of Cu have been studied by several authors (see, e.g., Refs. 1–7), but this is to our knowledge the first vapor-phase Auger investigation of free copper atoms. The solid-state $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum has been found to be atomiclike even though the final-state holes are in the valence band. The anomalously low relative intensity of $L_2M_{4,5}M_{4,5}$ group in solid Cu and the strong satellite structure on the low-energy side of $L_3M_{4,5}M_{4,5}$ group have been the other most striking features in the solid-state spectra. They have been studied recently by applying new methods incorporating the use of photoelectron-Auger electron coincidence measurements (Haak *et al.*[6]) and the use of near-threshold excitation (Jach and Powell[7]). Free-atom experiments were considered interesting also in order to justify their results. For the studies of free-atom-solid shifts, copper is of special interest because it is just on the edge where the solid-state shifts are expected to drop drastically.

The Auger spectrum of Cu was measured by means of a cylindrical-mirror-type electron spectrometer[8] making use of the resistance-heated high-temperature oven. The Cu atoms were ionized by an electron beam with 4-keV voltage and 0.5-mA beam current. By means of the microcomputer controlled spectrometer, the experimental spectrum shown in Fig. 1 was collected. The energy calibration of the spectrum with respect to the vacuum level was achieved by measuring the well-known Auger lines[8] of Ar and Ne simultaneously with the spectrum of Cu. The absolute kinetic energy of the strongest (^2G) peak in the $L_3M_{4,5}M_{4,5}$ group was recorded as 900.80 ± 0.15 eV and for the same line in L_2 group 920.40 ± 0.15 eV. For copper the energies of the double hole ($3d^{-2}$) final states are known from the optical measurements.[9] Thus the $L_{2,3}$-binding energies can be simply obtained by adding the corresponding double-hole final-state binding energies to the measured Auger energies of the line components. The values 939.85 ± 0.15 and 959.45 ± 0.15 eV are thus obtained for binding energies of L_3 and L_2 levels in free copper atoms, respectively. The relativistic ΔSCF (self-consistent field) Dirac-Fock calculations applying the program of Grant *et al.*[10,11] give 938.88

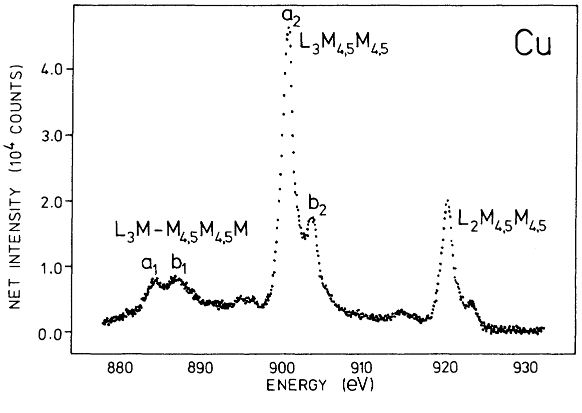

FIG. 1. $L_{2,3}M_{4,5}M_{4,5}$ Auger electron spectrum of free copper atoms excited by a 4-keV electron beam. The structures indicated by a_1 and b_1 are identified as L_3M-$M_{4,5}M_{4,5}M$ satellite lines arising from L_1L_3M Coster-Kronig process following the ionization in L_1 level.

and 958.90 eV for L_3 and L_2 binding energies. The agreement between calculated and experimental values is in itself very good but the deviations 1.0 and 0.6 eV are, however, too large, e.g., for the use of calculated values instead of experimental free-atom values as reference values for free-atom-solid binding-energy shifts.

The comparison of the obtained free-atom binding energies with the published values[12] in metallic Cu indicates a 2.5-eV free-atom—metal binding-energy shift. The corresponding solid-state shift in the kinetic energies of the Auger lines is found to be 13.2 eV. These values agree well with the simple thermochemical model calculated[13] estimates 2.6 and 14.0 eV.

In solid-state experiments very low intensity is obtained[5] for the $L_2M_{4,5}M_{4,5}$ Auger group, the intensity ratio between the $L_3M_{4,5}M_{4,5}$ and $L_2M_{4,5}M_{4,5}$ groups being ≥ 5. This arises from intensive $L_2L_3M_{4,5}$ Coster-Kronig transitions which are energetically possible in the metal; these transitions convert a great part from the initial L_2 holes to $L_3M_{4,5}$ double holes which then decay by satellite Auger transitions. The rather intensive structure in our vapor-phase spectrum (Fig. 1) about 16 eV to lower kinetic energies from the $L_3M_{4,5}M_{4,5}$ group can be identified also as the L_3M-$M_{4,5}M_{4,5}M$ satellite Auger transitions, but are preceded by L_1L_3M Coster-Kronig processes. By using high-energy (4-keV) electrons for the excitation of the Auger spectra, ionizations in the L_1 shell are obtained almost as frequently as ionizations in the L_2 shell, in addition, almost all L_1 holes decay by $L_1L_{2,3}M$ Coster-Kronig process. The analogous L_2M-$M_{4,5}M_{4,5}M$ satellite spectrum is associated with the $L_2M_{4,5}M_{4,5}$ Auger group, but it overlaps the $L_3M_{4,5}M_{4,5}$ group. In order to determine the intensity ratio between $L_3M_{4,5}M_{4,5}$ and $L_2M_{4,5}M_{4,5}$ groups as well as decompose the $L_3M_{4,5}M_{4,5}$ group into the line components, we have subtracted as background the satellite spectrum associated with the $L_2M_{4,5}M_{4,5}$ spectrum supposing that it has the same shape but half of the intensity of the corresponding L_3-satellite spectrum. After this background correction the value 2.3 is obtained for the intensity ratio between L_3 and L_2 groups. This value is in good agreement with the statistical ionization probability in the L_3 and L_2 shells. The same value was observed[14] for atomic Zn, verifying that L_2L_3M Coster-Kronig transitions are not possible in Cu atoms. It should be noted that there still remains the $L_2L_3N_1$ Coster-Kronig process which affects the L_3 to L_2 intensity ratio. However, its calculated[15] probability is rather low, about 8% from the $L_2M_{4,5}M_{4,5}$ transition probability.

The present L_3M-$M_{4,5}M_{4,5}M$ satellite Auger spectrum is very interesting because it is well separated from the diagram Auger lines and it is caused by the single L_1-L_3M-$M_{4,5}M_{4,5}M$ decay channel. In solid copper also L_2 ionization via L_2L_3M Coster-Kronig transitions contribute to the observed satellite spectrum. Both satellite spectra overlap energetically but they have different intensity distributions. This is done by the different transition probabilities of the primary L_1L_3M and L_2L_3M Coster-Kronig processes, causing different two hole distributions in the initial states of the satellite Auger transitions. These satellite spectra arising from both mentioned primary processes have been studied theoretically by McGuire.[16] Also his calculated profile from L_1 decay shows two larger peaks separated by about 3 eV in good agreement with our experimental profile. The satellite spectrum contains many line components and also the peaks indicated by a_1 and b_1 are superpositions from several line components. This was clearly shown by the fact that the peaks a_1 and b_1 were adequately fitted by 2.5-eV-wide full width at half maximum (FWHM) standard lines located 16.5 and 13.5 eV to lower energies from the main peak a_2, whereas the corresponding experimental line width (including the inherent linewidth and the spectrometer broadening) in the $L_{2,3}M_{4,5}M_{4,5}$ groups was 1.0 eV.

In the solid-state spectra, the satellite Auger groups are much closer to the corresponding principal Auger line groups than in the atomic spectra due to the extra-atomic relaxation effects. For principal Auger lines the shift between free atom and solid is mainly done by difference in the extra-atomic relaxation energies for single-hole initial and double-hole final states. In the case of satellite Auger lines, the solid-state shift is given by the difference in extra-atomic relaxation energies between double-hole initial and triple-hole final states. When the extra-atomic relaxation energies in each hole state can be assumed in first approximation to be proportional to the square of the number of holes, this qualitatively explains the decrease of energy distance, between the satellite peak a_1 and the main peak a_2, from 16.5 eV in free atom to 5.0 eV in solid copper.[3]

The Auger spectra have been decomposed into the line components with the aid of optical values[9] for the relative line positions and combined overlapping line components. The results are shown in Figs. 2 and 3 and in Table I where they are compared to the calculated energies and intensities[14] of Zn. The energies are calculated as the differences between the total energies of the relevant initial and final states. The total energies are computed with the Dirac-Fock method[10, 11] applying the intermediate coupling scheme. The obtained kinetic energies for ^2G components are 4.5 and 4.9 eV too high for L_3 and L_2 groups, respectively. Combining the intensities of the "daughter" lines, which result from the coupling between the two $3d$ final-state holes of Auger process with the unpaired $4s$ electron a correspondence to the "parent" line in closed-shell Zn atom is found. The intensities calculated for the closed-shell atoms have

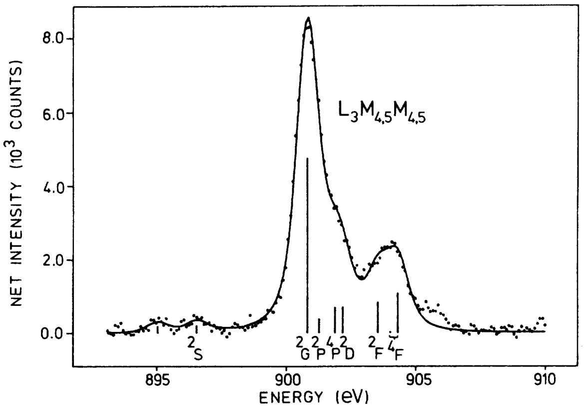

FIG. 2. $L_3M_{4,5}M_{4,5}$ spectrum of Cu decomposed into line components after the subtraction of a linear background and L_2M-$L_2M_{4,5}M_{4,5}M$ satellite structure. The points represent experimental results and the solid curve the sum of the line components shown by vertical bars.

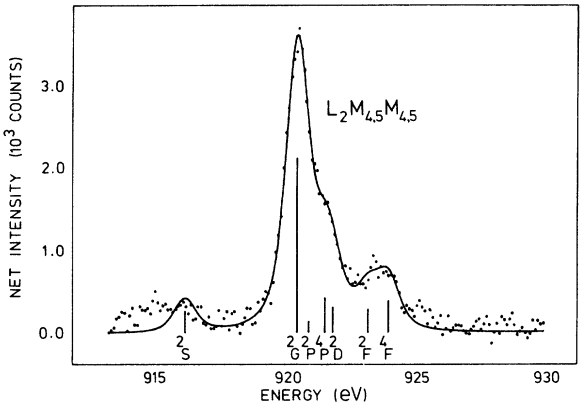

FIG. 3. The decomposition of $L_2M_{4,5}M_{4,5}$ spectrum of Cu into line components.

TABLE I. Calculated and experimental relative energies and intensities of the line components in $L_{2,3}M_{4,5}M_{4,5}$ Auger spectra of Cu.

	Energies			Intensities (%)			
				$L_3M_{4,5}M_{4,5}$		$L_2M_{4,5}M_{4,5}$	
Component	MCDF[a]	Opt. (Ref. 9)	Expt.	Expt.	Calc. (Zn) (Ref. 14)	Expt.	Calc. (Zn) (Ref. 14)
$^2S_{1/2}$	−5.25	. . .	−4.28	2.3	2.1 ($^1S_0$)	6.7	2.4
$^2G_{7/2}$	0.00 (905.33; L_3)[b]	0.00	0.00 (900.80; L_3)[b]	55.3	62.0 ($^1G_4$)	54.4	64.1
$^2G_{9/2}$	0.00 (925.35; L_2)[b]	0.01	0.00 (920.40; L_2)[b]				
$^2P_{1/2}$	0.18	0.36	0.44	4.3		3.4	
$^2P_{3/2}$	0.27	0.45					
$^4P_{1/2}$	0.99	1.07	1.07	} 12.2	3.1 ($^3P_{0,1,2}$)	} 14.1	4.2
$^4P_{3/2}$	1.02	1.09		7.9		10.8	
$^4P_{5/2}$	1.03	1.06					
$^2D_{3/2}$	1.30	1.27	1.37	8.0	9.6 ($^1D_2$)	7.8	10.3
$^2D_{5/2}$	1.37	1.38					
$^2F_{7/2}$	2.87	2.49	2.73	9.6		7.1	
$^2F_{5/2}$	3.11	2.73					
$^4F_{3/2}$	3.62	3.12	3.50	} 22.2	23.1 ($^3F_{2,3,4}$)	} 17.0	19.0
$^4F_{5/2}$	3.71	3.21		12.6		9.8	
$^4F_{7/2}$	3.83	3.35					
$^4F_{9/2}$	3.99	3.50					

[a] ΔSCF Dirac-Fock values.

[b] Calculated and experimental Auger energies.

been found to agree well with the grouped intensities also in the cases of potassium[17] and silver.[18] Because the intensities vary very slowly with Z, the comparison can well be done with the calculated values of Zn. The experimental results are also here found to be in reasonable agreement with the calculated intensity values.

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