Energy dependence of Cu $L_{2,3}$ satellites using synchrotron excited x-ray-emission spectroscopy

M. Magnuson, N. Wassdahl, and J. Nordgren

Department of Physics, Uppsala University, P.O. Box 530, S-751 21 Uppsala, Sweden

The $L_{2,3}$ x-ray emission of Cu metal has been measured using monochromatic synchrotron radiation. The self-absorption effect in the spectra is shown to be very small in our experimental geometry. From the quantitative analysis of spectra recorded at different excitation energies, the L_3/L_2 emission intensity ratio and the partial Auger width are extracted. High-energy satellite features on the L_3 emission line are separated by a subtraction procedure. The satellite intensity is found to be slowly increasing for excitation energies between the L_3, L_2, and L_1 core-level thresholds due to shake-up and shake-off transitions. As the excitation energy passes the L_2 threshold, a step of rapidly increasing satellite intensity of the L_3 emission is found due to additional Coster-Kronig processes. [S0163-1829(97)05743-3]

I. INTRODUCTION

During recent decades, much interest has been focussed on multiple vacancy satellites in Auger spectra of the $3d$ transition metals.[1-5] In particular, the existence of Auger satellites originating from the decay of $L_{2,3}$ core holes in the presence of additional $3d$ vacancies have been studied. The $3d$ vacancies can be produced either as shake-up excitation or shake-off ionization due to relaxation in connection with the core excitation process or as a result of Coster-Kronig (CK) processes preceeding the Auger decay. The corresponding x-ray decay processes can be studied with x-ray-emission (XE) spectroscopy. XE spectroscopy is a powerful technique for studying the electronic structure in terms of the partial density of states (pDOS), since the decay from the core-excited state with a localized core hole can be described according to the dipole selection rules. In XE, the vacancy satellites are traditionally referred to as Wentzel-Druyvesteyn (WD) satellites[6] and typically end up on the high-energy side of the main line. Relaxation and screening effects are essential for the evaluation of the intensity and energy shift involved in the satellite transitions, which is an important reason for studies of satellites.

XE spectra of metal Cu excited with monochromatic synchrotron radiation were presented in a publication by Wassdahl *et al.*[7] and discussed in terms of shake-up/-off and CK processes. The results of this publication were discussed and compared with those of different Cu compounds by Kawai *et al.*[8] It was assumed that the CK contribution was too small to significantly contribute to the high-energy XE satellites and could not be discriminated from the solid-state process (charge transfer from the neighboring atoms). In a comment by Ohno,[9] it was concluded, based on the interpretation of Auger spectra, that the dominant part of the high-energy satellite intensity is indeed due to CK decay. To support their interpretation, Kawai *et al.*[10] then further assumed that the XE spectra of Wassdahl *et al.*[7] had been severely affected by the self-absorption effects and needed to be corrected for this.

As will be shown from our new high-resolution XE measurements of pure Cu metal, the self-absorption effect is indeed very small in the grazing-incidence experimental geom-

etry used. As the excitation energy is increased above the L_2 core level, a large enhancement of the L_3 satellite intensity is found, indicating $L_2 \rightarrow L_3M$ CK decay preceeding the x-ray emission. For excitation energies between the L edges, the satellite intensity is slowly increasing with energy, interpreted as due to additional shake transitions. As will be shown, our results indicate that the origin of the high-energy XE satellite should be interpreted as due to vacancies produced either by shake-up/shake-off upon primary excitation or, above the L_2 excitation threshold, mainly due to CK decay preceeding the XE process.

II. EXPERIMENTAL DETAILS

The experiments were performed at beamline 8.0 at the *Advanced Light Source*, Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5-cm period undulator and a spherical-grating monochromator. The end station built at Uppsala University includes a rotatable grazing-incidence grating XE spectrometer[11] and a Scienta SES200 photoelectron spectrometer.[12] The base pressure was lower than 2×10^{-10} Torr during preparations and measurements. The Cu(100) single-crystal sample was of high purity and crystal quality, and cleaned by means of cyclic argon-ion sputtering and annealing to remove surface contaminants.

In order to determine the excitation energies, x-ray-absorption (XA) spectra in the threshold region were measured by total electron-yield measurements. In order to normalize the XE spectra, the incident photon current was continuosly monitored using a gold mesh in front of the sample. During the XA and XE measurements the resolution of the monochromator of the beamline was 0.3 eV and 0.5 eV, respectively. The sample was oriented so that the photons were incident at an angle of 7° and with the polarization vector parallel to the surface plane. The emitted photons were recorded at an angle near normal to the sample surface, perpendicular to the incoming photons, with a resolution slightly better than 0.8 eV. The grazing-in normal-out setup was chosen to minimize self-absorption effects.

III. RESULTS AND DISCUSSION

Figure 1 shows $L_{2,3}$ XE spectra of Cu normalized to the integrated photon flux, excited at various energies indicated
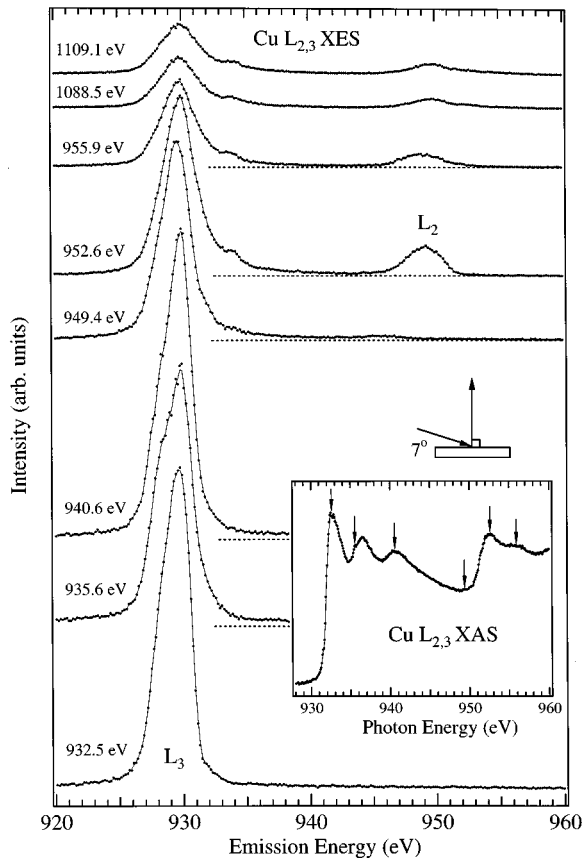
FIG. 1. A series of XE spectra of Cu measured for excitation energies 932.5 eV to 1109.1 eV. The excitation photon energies are indicated by arrows in the XA spectrum in the inset.

FIG. 2. Separation of CK preceeded satellite contribution between the spectra excited at 1088.5 and 932.5 eV photon energies. The dashed area represents the difference spectrum.

by the arrows in the XA spectrum shown in the inset. The spectra were measured from excitation energies from 932.5 eV, at the L_3 threshold, up to energies as high as 1109.1 eV, above both the L_2 ($E_B=952.3$ eV) and L_1 ($E_B=1096.7$ eV) thresholds. For excitation energies above the L_3 threshold ($E_B=932.5$ eV), a growing satellite tail extending towards higher energies on the high-energy side of the main line is clearly observed in the spectra. It should be noted that we do not observe any elastic emission peak due to recombination, even though our experimental geometry with the polarization vector parallel to the surface plane would enhance the probability for such a process to occur.

Self-absorption is known to affect the shape of XE spectra on the high-energy flank of the main peak, where the satellites occur, since there is an overlap in energy between the XE and XA spectra. The corrected observed XE intensity can be written as $I=I_o[1+(\mu_{out}/\mu_{in})\times\tan(\Theta)]^{-1}$, where I_o is the unperturbed decay intensity, and μ_{in} and μ_{out} are the absorption coefficients for the incident and outgoing radiation, and Θ is the incident angle of the photon beam relative to the sample surface (and between outgoing photon and surface normal). We derived the values of these coefficients at the $L_{2,3}$ thresholds by normalizing the XA spectrum to known atomic values ($\mu_{in}=2.20$ and 16.97 cm^2/g) well below and above the absorption edges.[13] Based on this procedure the maximum self-absorption at the most severe emission energy (932.5 eV) was found to reduce the emitted intensity between 9 and 10% for all spectra except for the
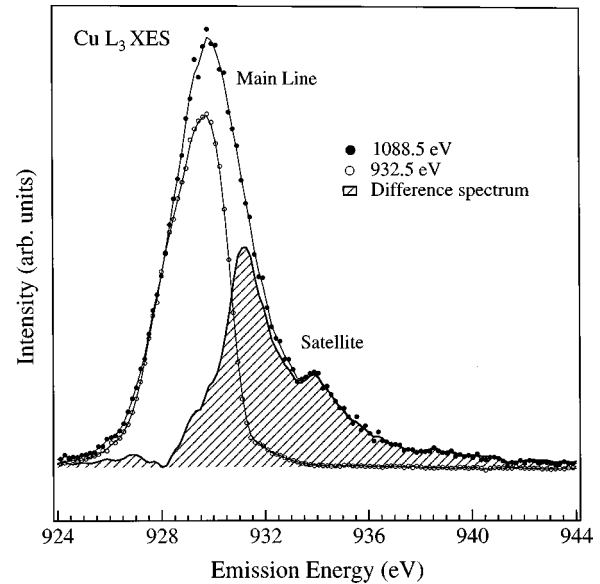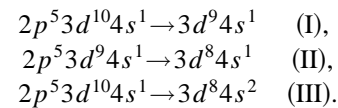
spectrum excited at 949.4 eV just below the L_2 threshold where it was 14% since the penetration depth is higher at this excitation energy. Since the self-absorption effect is small, the spectra shown in the figures were not corrected for this effect.

We consider the transitions from the core-excited states to the final states and will mainly discuss the following processes:

$$2p^5 3d^{10} 4s^1 \rightarrow 3d^9 4s^1 \quad \text{(I)},$$
$$2p^5 3d^9 4s^1 \rightarrow 3d^8 4s^1 \quad \text{(II)},$$
$$2p^5 3d^{10} 4s^1 \rightarrow 3d^8 4s^2 \quad \text{(III)}.$$

Process (I) is the main line, (II) an initial-state $3d$ vacancy satellite, and (III) a final-state satellite due to shake up in the decay step. The main line (I) has an energy of about 930 eV, which is the energy difference between the $2p_{3/2}$ core-level binding energy at 932.5 eV and the $3d$ band at about 3 eV. In process (II), the initial state has a mean energy of 944.4 eV with a multiplet spread of about 4 eV and the final state has a mean energy of 12.8 eV with a multiplet spread of about 2.8 eV. This gives estimated satellite energies between 928.2 and 935 eV, which thus overlap with the main line (I) but are slightly shifted towards the high-energy side.[14]

For excitation energies above threshold, the spectra can be treated as produced by an incoherent nonresonant "two-step" process, with separate excitation and emission steps, and the satellite contribution can, therefore, be separated from the main line by a subtraction procedure.[7,15] This is illustrated in Fig. 2, where the satellite difference spectrum (I_S, dashed area) has been constructed with the 1088.5 eV spectrum subtracted by the resonantly excited 932.5 eV spectrum (I_R) by normalizing the spectra so that the low-energy flanks coincide. The difference spectrum represents the part of the 1088.5 eV spectrum, which is mainly produced by excitation via the L_2 CK preceeded decay. As can be seen in Fig. 2, the peak position of the XE satellite is shifted by about 1 eV to higher energy and is broader than the main line due to multiplet effects in the initial and final states of the

TABLE I. Experimental L_3 and L_2 XE intensities in Cu metal for the main-line (R) and satellite (S) contributions at 1088.5 eV excitation energy. The values are normalized to the L_3 main line.

$I_R^{(3/2)}$	$I_R^{(1/2)}$	$I_S^{(3/2)}$	$I_S^{(1/2)}$
1.00	0.22	0.69	0.14

TABLE II. A comparison between the experimental and calculated values of the Auger width (in eV) obtained from the CK width of Refs. 18 and 17. The calculated values are atomic (Ref. 1) and solid (Ref. 19).

Γ_{tot}	Γ_{CK}	Γ_A^{expt}	Γ_A^{calc}
1.1 (Ref. 18)	0.68 (Ref. 18)	0.55	0.53 (Ref. 1)
0.90 (Ref. 19)	0.56 (Ref. 19)	0.45	0.43 (Ref. 19)

process. Process (III) has the same final state as process (II) but the initial state is solely an L_3 core hole leading to low-energy satellites between 918 and 921 eV. However, although process (III) is possible we do not observe any satellite peaks in the spectra due to this transition.

The direct observation of the x-ray-emission satellites makes it possible to obtain the relative inherent widths of the L_3 and L_2 hole states. Thus, the partial atomic-level widths can be quantitatively extracted by comparing the integrated intensities between the L_3 and L_2 XE peaks excluding their satellite contributions. From a statistical point of view, the $2p_{3/2}$ and $2p_{1/2}$ core-level ionization ratio is 2:1 for excitation energies between the L_2 and L_1 thresholds. When using excitation energies above the L_1 threshold, the L_1 CK decay will also affect the initial core hole population. This may change the subsequent XE L_3/L_2 intensity ratio (I_X^{ratio}) for the spectrum excited above the L_1 threshold. To avoid this problem, we used the XE spectrum excited at 1088.5 eV, i.e., the excitation energy is just below the L_1 threshold, and the two threshold spectra excited at 932.5 and 952.6 eV to extract the satellite contributions. Including the satellites, I_X^{ratio} was found to be 4.64 using the values given in Table I for the main line (I_R) and the satellite (I_S) contributions of the L_3 and L_2 levels. Excluding the satellites, the I_X^{ratio} is found to be 4.48.

Apart from the pDOS spectral distribution, the widths of the XE peaks include Lorentzian lifetime contributions from the core and final states, also convoluted with the Gaussian instrumental resolution profile. The natural lifetime energy width Γ of a state is related to its lifetime τ by the Heisenberg uncertainty principle, $\Gamma\tau=\hbar$, where $\hbar$ is Planck's constant. We consider the decay from one core hole with characteristic exponential decay times corresponding to the partial energy widths for the Auger (Γ_A), radiative (Γ_X), and Coster-Kronig (Γ_{CK}) decays, respectively. From this, the L_3/L_2 XE intensity ratio can be written as

$$I_X^{ratio} = \frac{2\Gamma_X^{(3/2)}}{\Gamma_X^{(3/2)}+\Gamma_A^{(3/2)}} \bigg/ \frac{\Gamma_X^{(1/2)}}{\Gamma_X^{(1/2)}+\Gamma_A^{(1/2)}+\Gamma_{CK}^{(1/2)}}. \quad (1)$$

The L shell fluorescence yields are small for Cu, and furthermore the Auger width, XE width, and photoionization cross section are approximately the same at the L_3, respectively, the L_2 thresholds.[16] The x-ray width Γ_X is expected to be in the range of a few meV. We try to obtain the Auger width Γ_A using experimental values[17,18] of Cu metal, yielding CK and total widths shown in Table II. The value of Γ_A is difficult to obtain explicitly with x-ray photoemission spectroscopy (XPS) since the measured total linewidths of the L_3 and L_2 levels contain contributions from the instrumental broadening, the width of excitation, electron-phonon interactions, many-electron effects etc. Γ_{CK} can be determined from the

difference in linewidths between the L_3 and L_2 XPS levels. If we neglect Γ_X (since $\Gamma_X \ll \Gamma_A$, Γ_{CK}) and assume that $\Gamma_A^{(1/2)}=\Gamma_A^{(3/2)}$, the Auger width can be derived from Eq. (1) as

$$\Gamma_A = \frac{2\Gamma_{CK}^{(1/2)}}{I_X^{ratio}-2}. \quad (2)$$

We find the Auger decay width Γ_A, for pure Cu to be between 0.45 and 0.55 eV by using $I_X^{ratio}=4.48$ and the values of Γ_{CK} given in Table II. The theoretical prediction of the Auger width for Cu atoms (gas phase) by Yin et al.[1] (0.53 eV) and a many-body Green's function calculation by Ohno, Mariot, and Hague[19] (0.43 eV) are in good agreement with our experimental results. The extracted I_X^{ratio} value (4.48) is also in fairly good agreement with the $[2p_{3/2}\rightarrow d^2(^1G_4)]/[2p_{1/2}\rightarrow d^2(^1G_4)]$ Auger main-line intensity ratio of 5.3 obtained by Antonides, Janse, and Sawatsky[17]

The difference between the statistical ratio (2:1) and the derived intensity ratio ($\sim$4.5/1) indicates that part of the high-energy shoulder of the L_3 XE line is related to the L_2 ionization through the CK process providing the dominating decay channel for the L_2 hole state, leading to a decrease of the fluorescence yield for the L_2 state compared to the L_3 state. The CK decay from the L_2 core level leads to a shorter lifetime and a larger Lorenzian width for this core state than for the L_3 state. The CK process furthermore explains the modified shape of the XE spectra as the L_2 hole state is excited.

Measurements of the relative L_3 and L_2 XPS intensities and linewidths $\Gamma^{(3/2)}$ and $\Gamma^{(1/2)}$ give an indication of the initial vacancy distribution in the L_3 and L_2 shells immediately after photoionization. For Cu such XPS experiments indicate that the initial $2p_{3/2}/2p_{1/2}$-shell vacancy ratio is approximately 2:1, whereas $2s$ photoionization is about six times weaker than for the $2p_{3/2}$ photoionization[17] at photon energies close above the $2s$ threshold. The I_X^{ratio} value essentially reflects the L_3/L_2 vacancy ratio at the time of the x-ray emission. Thus, the large ratio in the spectra indicates that considerable reorganization of vacancies takes place after the excitation of the L_2 shell and before the emission of an x-ray photon.

Figure 3 shows the relative $I_S/(I_R+I_S)$ XE satellite intensity ratio (in percent), normalized to the satellite-free L_3 threshold spectrum excited at 932.5 eV (I_R). The difference spectra have been constructed by normalizing the spectra to the low-energy flanks as described above, using the satellite free threshold spectrum. The error bars of the satellite intensity have been constructed from varying the fit parameters.
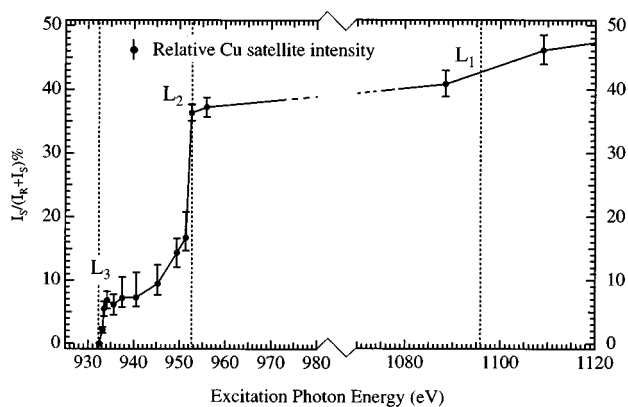
FIG. 3. The relative XE satellite vs the main line intensity ratio (in %) shown close to the L_3, L_2, and L_1 thresholds.

For excitation energies below the L_2 threshold, the satellite has a slowly increasing intensity to less than 10% of the total intensity, whereas for excitation energies closer to the L_2 threshold, a step of very rapid intensity increase is observed up to a new plateau at about 40%. The satellite intensity is related to the XA cross section which has a peak at the L_2 threshold. Above the L_2 threshold, the intensity is again slowly increasing due to additional shake processes up towards the L_1 level, where additional L_1 CK processes are enabled, leading to a new intensity step of about 6%. This increase of the satellite intensity as the excitation energy passes the L_1 threshold is thus much lower than at the L_2 threshold. This is mainly due to two things; the difference in photoemission cross section in the excitation process mentioned previously but, also due to the fact that the L_1 CK decay is distributed to several decay channels, mainly the $L_1 \rightarrow L_2 M$, $L_1 \rightarrow L_3 M$ and $L_1 \rightarrow L_3 MM$. The intensity steps show that the CK process plays a very important role for the origin of the energy shift and the satellite intensity by the production of extra $3d$ vacancies, preceding the XE decay.

In the description of the satellite phenomena we focus on the relative importance of excitations in the initial state. When the absorbed photon excites or ionizes an electron and a core hole is created, the surrounding electron cloud will contract in order to screen the positive charge created, causing shake-up excitations or shake-off ionizations in the valence band. The shake intensity depends on the relative configuration coupling due to relaxation. This can be understood with the aid of the Manne-Åberg theorem for inner-shell ionization.[20] The relaxation energy with respect to the unrelaxed Koopmans' energy gives rise to a shake cross section implying WD satellites in the XE spectra.

IV. CONCLUSIONS

X-ray emission spectra of Cu metal have been measured close to the L_3, L_2, and L_1 excitation thresholds with monochromatic synchrotron radiation. Due to the grazing-incidence sample orientation, the spectra are found to be almost free of self-absorption effects. From the quantitative analysis of the spectra, the L_3/L_2 intensity ratio and the $L_{2,3}$ Auger width are extracted. For excitation energies passing the L_2 threshold, a sharp step of increasing satellite intensity is found at the L_3 emission line, proving the importance of Coster-Kronig decay to the satellite contribution. Thus, we interpret the spectra in the previously accepted picture of initial-state satellites, produced either by shake-up/shake-off during the excitation or as a result of Coster-Kronig decay of inner hole states.

[1] L. I. Yin, I. Adler, M. H. Chen, and B. Crasemann, Phys. Rev. A **7**, 897 (1973).

[2] E. D. Roberts, P. Weightman, and C. E. Johnson, J. Phys. C **8**, L301 (1975).

[3] J. A. D. Matthew, J. D. Nuttall, and T. E. Gallon, J. Phys. C **9**, 883 (1976).

[4] E. Antonides and G. A. Sawatzky, J. Phys. C **9**, L547 (1976).

[5] P. Weightman, J. F. McGlip, and C. E. Johnson, J. Phys. C **9**, L585 (1976).

[6] G. Wentzel, Z. Phys. **31**, 445 (1925), M. J. Druyvesteyn, *ibid.* **43**, 707 (1927).

[7] N. Wassdahl, J.-E. Rubensson, G. Bray, P. Glans, P. Bleckert, R. Nyholm, S. Cramm, N. Mårtensson, and J. Nordgren, Phys. Rev. Lett. **64**, 2807 (1990).

[8] J. Kawai, K. Maeda, K. Nakajima, and Y. Gohshi, Phys. Rev. B **48**, 8560 (1993).

[9] M. Ohno, Phys. Rev. B **52**, 6127 (1995).

[10] J. Kawai, K. Maeda, K. Nakajima, and Y. Gohshi, Phys. Rev. B **52**, 6129 (1995).

[11] J. Nordgren and R. Nyholm, Nucl. Instrum. Methods Phys. Res. A **246**, 242 (1986); J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.-E. Rubensson, and N. Wassdahl, Rev. Sci. Instrum. **60**, 1690 (1989).

[12] N. Mårtensson, P. Baltzer, P. A. Brühwiler, J.-O. Forsell, A. Nilsson, A. Stenborg, and B. Wannberg, J. Electron. Spectrosc. Relat. Phenom. **70**, 117 (1994).

[13] B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, At. Data Nucl. Data Tables **27**, 1 (1982).

[14] I. R. Holton, P. Weightman, and P. T. Andrews, J. Phys. C **16**, 3607 (1983).

[15] N. Wassdahl, Ph.D. thesis (Uppsala University, Uppsala, Sweden, 1987).

[16] M. O. Krause and J. H. Oliver, J. Phys. Chem. Ref. Data **8**, 329 (1979).

[17] E. Antonides, E. C. Janse, and G. A. Sawatsky, Phys. Rev. B **15**, 4596 (1977); **15**, 1669 (1977).

[18] R. Nyholm, N. Mårtensson, A. Lebugle, and U. Axelsson, J. Phys. F **11**, 1727 (1981).

[19] M. Ohno, J. M. Mariot, and C. F. Hague, J. Electron. Spectrosc. Relat. Phenom. **36**, 17 (1985).

[20] R. Manne and T. Åberg; Chem. Phys. Lett. **7**, 282 (1970).