Synchrotron-Radiation-Excited Soft-X-Ray-Fluorescence Studies of Cu and Zn: On the Validity of the Sudden Approximation

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The L_{23} x-ray-emission spectra of Cu and Zn have been recorded using tunable-synchrotron-radiation-excited fluorescence spectroscopy. The satellite structure was studied in detail by varying the excitation energy from threshold to several hundred eV above. Strong satellites are observed which can unambiguously be associated with the decay of multiply excited states. This disproves recent claims of a breakdown of the sudden approximation in this regime.

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Synchrotron radiation provides an important tool for investigating threshold phenemona in photoionization and different types of secondary decay processes. In connection with decay spectra different routes can be identified by investigating the spectra above and below different core-level thresholds. An important issue in this connection concerns the transition from the sudden to the adiabatic regime for the description of the spectra. This question has continuously attracted much attention since it determines when significant simplifications in the theoretical treatment can be made, in this case for instance, when the excitation and decay processes can be treated as separable events.

During the last decade much attention has been paid to the strong satellites observed in Auger spectra from certain 3*d* transition metals.[1-12] This was first observed by Roberts, Weightman, and Johnson[1] in the $L_3M_{45}M_{45}$ spectrum from Cu and was interpreted as due to an L_3M_{45}-$M_{45}M_{45}M_{45}$ decay, i.e., an $L_3M_{45}M_{45}$ process with a spectator vacancy in the M_{45} shell. It was proposed that the satellite is mainly due to the decay of double-hole states generated by the $L_2L_3M_{45}$ Coster-Kronig (CK) process. A direct link between the L_2 photoionization and the satellite in the $L_3M_{45}M_{45}$ Auger spectrum was demonstrated in a coincidence experiment by Haak, Sawatzky, and Thomas.[11] Similar conclusions concerning the origin of the satellite were reached by Weightman and Andrews, who compared the $L_3M_{45}M_{45}$ Auger spectrum excited by Al $K\alpha$, Mg $K\alpha$, and Cu L x rays.[9] They found that the intensity ratio between the satellite and the principal Auger line depends on the ratios of initially created L_1, L_2, and L_3 holes, which are significantly different for the three x-ray excitation energies. Similar conclusions were drawn by Jach and Powell,[12] who investigated the *LMM* Auger spectrum for different primary electron excitation energies.

This picture of the origin and character of the *LMM* Auger satellites in Cu and Zn has recently been questioned on the basis of an investigation of synchrotron-radiation-excited Auger spectra.[13] From these measurements it was concluded that the Auger satellites are mainly due to shakeup in the Auger emission process (final-state shakeup) and not to additional vacancies produced prior to the Auger emission. The crucial observations were mainly that the satellite intensities cannot be straightforwardly related to the number of excited deeper holes, which would be the case for CK-preceded vacancy satellites. Particular emphasis was put on the observation that the satellites in the L_2 decay spectra (for which there are no CK processes before the L_1 threshold is reached) are as intense as the satellites in the L_3 spectra. With the proposed interpretation, the observed large intensity variations of the satellite must be explained by a direct coupling between the photoexcitation and the decay steps. Since the intensity variations are observed over a considerable energy range, this would violate the present understanding of the applicability of the sudden approximation. It was concluded that the photoionization cannot be described as a sudden event even for photon energies a couple of hundred eV above the core ionization energy. If this is the case, it has far reaching consequences for a number of spectroscopies and for our understanding of core-level excitation processes in general.

We report a related study of synchrotron-radiation-excited x-ray-emission spectra for the same elements. These measurements have only recently become feasible due to experimental developments.[14-16] There are important differences between the two types of spectroscopies for investigating the core-hole decay: (i) The final states in x-ray emission are one step less ionized which leads to smaller multiplet splittings. (ii) The probability of shakeup in x-ray emission is much smaller than in Auger since it connects two equally charged states. (iii) The initial- and final-state shakeup satellites are more easily separated in x-ray emission. In particular, *for the present systems a spectator vacancy leads to a high-energy satellite while a final-state shakeup leads to a low-energy satellite.*

In our measurements we find the same trends in the satellite intensities as in the corresponding Auger emission studies. However, we show that the spectra can be described within the previously accepted picture of vacancy satellites. There are no alarming discrepancies which point to the proposed breakdown of the sudden approximation. From the gained insight an alternative and fully consistent explanation of the seemingly contradictory Auger results can be presented.

The spectra were excited by photons from the Flipper I monochromator[16] at the multipole wiggler beam line at HASYLAB in Hamburg. The resolution of the monochromator was set to 6 eV for the Cu spectra and to 9 eV for Zn. The spectra were recorded in a grazing incidence multigrating spectrometer constructed in our laboratory.[14,15] The instrument contains several fixed mounted gratings optimized for different energy regions. The detector, which is based on multichannel plates and a resistive anode, is oriented at the correct position on the relevant Rowland circle using computer-controlled translational stages. In the present experiment a 5-m spherical grating mounted at 88.1° angle of incidence was used. The grating had 1200 grooves/mm and all spectra were recorded in second order of diffraction. For Cu the entrance slit width was chosen to yield 1.9-eV resolution and for Zn a slit giving 0.8 eV was used.

Figure 1 shows the L_{23} fluorescence spectra for Cu measured for excitation energies starting just above the L_3 threshold (932.6 eV) to energies above the L_2 and L_1 thresholds at 952.4 and 1097.1 eV, respectively.[17] For excitation energies below the L_2 threshold only the L_3 emission feature is seen. As the photon energy is increased the shape of the L_3 spectrum changes continuously and a satellite appears. Especially a tail on the high-energy side is seen which grows in prominence. A line is drawn through all spectra at an energy for which there is practically no main line contribution on the high-energy side, i.e., all the intensity which appears on this side of the line belongs to the satellite. By direct inspection of the spectra it can be seen how the satellite contribution develops with photon energy. The satellite appears already below the L_2 threshold and it grows in such a way that it cannot only be connected to the excitation of deeper core holes.

The L_2 spectrum is considerably less intense than expected from the statistical ratio of $\frac{1}{2}$ for L_2/L_3 holes. The large deviation from this ratio directly indicates that there are additional decay channels for the L_2 holes. A high-energy satellite appears also in the L_2 spectrum for excitation energies well below the L_1 threshold which is as intense as the L_3 satellite when the satellites are compared to their respective main lines.

Figure 2 shows a similar series of L fluorescence spectra for Zn. In this case the L_2 and L_1 thresholds are located at 1044.8 and 1196.3 eV, respectively.[17] All the qualitative features of Fig. 1 are reproduced in the Zn spectra. The complete spectral behavior for both Cu and Zn is thus very similar to what was reported for the

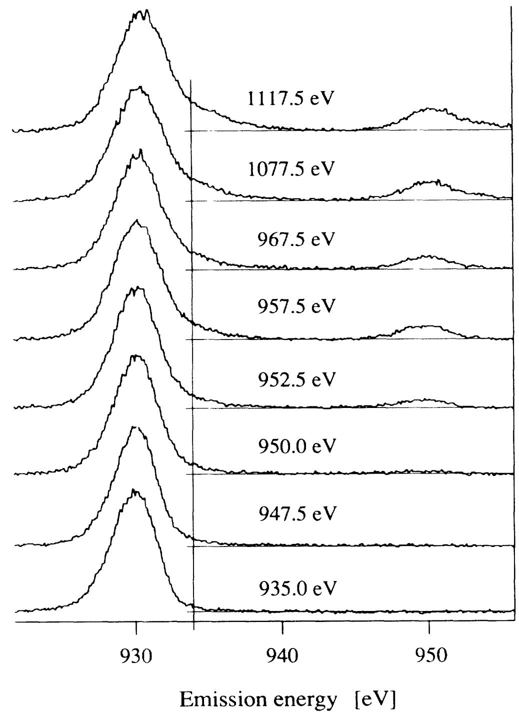

FIG. 1. $L_{2,3}$ emission spectra of Cu metal, excited at photon energies from just above the L_3 threshold (932.6 eV) to well above the L_1 threshold (1097.1 eV).

Auger satellites.[13]

For the interpretation of the L_3 x-ray-emission spectra we have in the present case to consider the following possible processes (the corresponding Auger transitions are given by the primed processes):

$$L_3\text{-}M_{45}\,, \tag{1}$$

$$L_3\text{-}M_{45}M_{45}\,, \tag{1'}$$

$$L_3M_{45}\text{-}M_{45}M_{45}\,, \tag{2}$$

$$L_3M_{45}\text{-}M_{45}M_{45}M_{45}\,, \tag{2'}$$

$$L_3\text{-}M_{45}M_{45}\,, \tag{3}$$

$$L_3\text{-}M_{45}M_{45}M_{45}\,. \tag{3'}$$

Process (1) is the main transition, (2) a vacancy satellite, and (3) a shakeup transition in the decay step.

In the following discussion we will concentrate on the results for Cu. The main x-ray transition (1) has an energy of about 930 eV which is the energy separation between the L_3 core hole at 932.6 and the Cu $3d$ band states at about 3 eV. In process (2) the initial state has a mean energy of $932.6+11.8=944.4$ eV with a multiplet spread of about 4 eV.[7] The final-state energies are 14.2 and 11.4 eV for the $^1G_4$ and $^3F_4$ states, respectively.[5] This gives estimated satellite energies of 930.2 and 933 eV with an additional multiplet spread originating

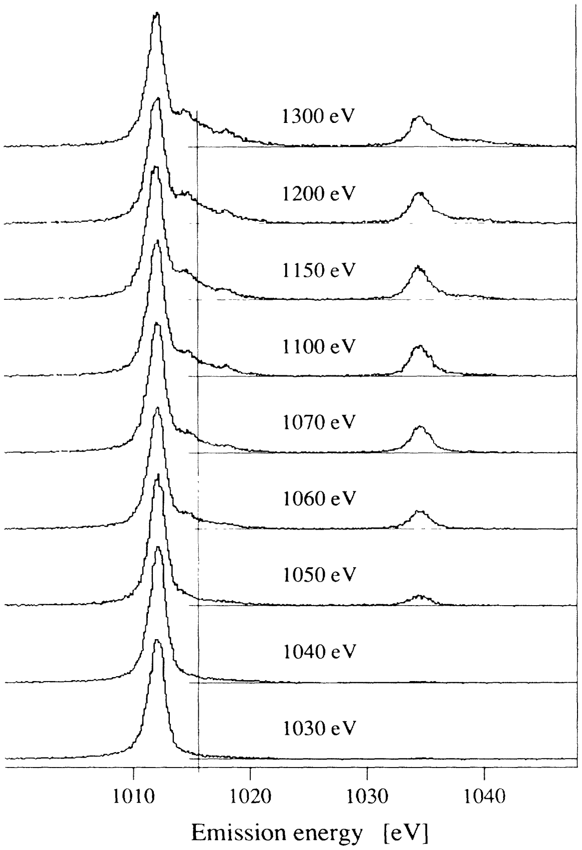

FIG. 2. $L_{2,3}$ emission spectra of Zn metal, excited at photon energies from just above the L_3 threshold (1021.8 eV) to well above the L_1 threshold (1196.3 eV).

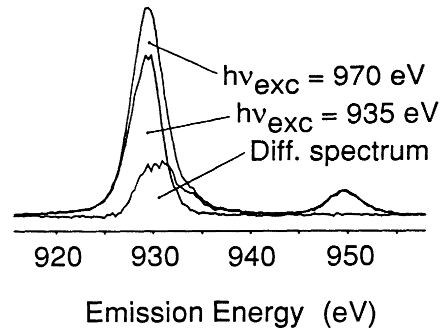

FIG. 3. L emission spectra of metallic copper excited with photons at energies above and below the L_2 threshold (952.4 eV).

from both the initial and final states. The x-ray vacancy satellite will thus appear mainly on the high-energy side of the main x-ray transition. Process (3) has the same final state but the initial state is an L_3 hole instead, leading to well separated *low-energy* satellites between 918 and 921 eV with some additional peaks originating from other final multiplet states. The observed satellites can therefore only be due to process (2). It should also be noted that there are no satellites at all at around 920 eV.

For the Auger process the main transition ($^1G_4$) has an energy of $932.6-14.2=918.4$ eV. The energetics of process (2′) has been considered previously,[6] and it is seen that this process will give rise to transitions mainly within 5 eV on the low-kinetic-energy side of the main Auger transition. Process (3′) will also give rise to satellites on the low-kinetic-energy side. The energy difference between the initial states of process (2′) and (3′) is 11.8 eV (Ref. 7) which would place the main part of this satellite at between 12 and 17 eV from the main Auger transition. These energies are larger than what was assumed in Ref. 13 which also contradicts the proposed interpretation of the Auger satellites.[18]

The fact that the observed photon-energy dependence of the satellites is not only related to the L_2 and L_1 thresholds shows that a substantial amount of L_3M_{45} states must be produced directly in the photoemission process. Contrary to the claims in Ref. 13 *such shakeup states have been seen in photoemission spectra*[7] *and, furthermore, there will be additional excitations in the form of shakeoff which will produce similar initial states for the decay* but which will not be easily seen in photoemission since they produce only broad continua.

Another observation which was used to disprove the CK interpretation was the fact that the L_2 and L_3 satellites show very similar intensities relative to the respective main lines. However, this is, in fact, a direct manifestation of the presence of the CK effect instead. Since the CK decay offers an alternative decay route for the L_2 holes, this reduces the main line intensity. The crucial point here is that the corresponding CK decay for the L_2M_{45} double-hole state is largely forbidden[19] which leads to an apparent increase of the L_2 satellite intensity. If the L_2 satellite intensity is related to the number of *originally* created L_2 holes, it is substantially lower than the L_3 satellite intensity. Roughly speaking the L_2 satellite intensity measures the importance of double-hole excitations by shakeup and shakeoff while the additional L_3 satellite intensity is largely due to the CK process.

Having established the origin of the main satellite contribution it is interesting to consider the various decay possibilities of the core-hole states in more detail. Figure 3 shows the Cu L emission spectrum excited below and above the L_2 threshold (935- and 970-eV photon energy, respectively). The 935-eV spectrum represents a pure L_3 decay while the 970-eV spectrum also contains the L_2 emission as well as the satellites. In Fig. 3 the 970–935-eV difference spectrum has also been constructed.[20] This represents the part of the 970-eV spectrum which is due to the excitation of L_2 holes. As can be seen from this difference spectrum most of the L_2 holes (66%) decay via the $L_2L_3M_{45}$ CK process before further decay and appear as satellites in the L_3 spectrum. This CK decay leads to a shorter lifetime of the L_2 holes which is seen as an additional $2p_{1/2}$ broadening of 0.68 eV in photoemission spectra.[21] Since 66% of the decay rate corresponds to a width of 0.68 eV the total L_2 width should be 1.03 eV.[22] Then, assuming equal non-CK decay rates for the L_2 and L_3 holes, one obtains an L_3 width of 0.35 eV.

In summary, we have shown that the strong satellites in the Cu and Zn $L_{2,3}$ x-ray-emission and Auger spectra are due to M vacancies produced before the decay. These additional vacancies are produced by CK processes but to a large extent also by shakeup and shakeoff. A fully consistent picture of the spectral intensities is obtained by considering the excitation and decay steps as separable events and no indications of the proposed breakdown of the sudden approximation are found.

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[18]Note, however, that shakeup and shakeoff should be of significance in the Auger process since it corresponds to an effective ionization. These satellites are probably too smeared out to be seen as distinct features.

[19]This can be seen using similar energy considerations as in Ref. 8.

[20]A consistent decomposition of the 970-eV spectrum is only obtained with a ratio close to 2 (the statistical ratio) between the pure L_3 spectrum and the difference spectrum.

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[22]One should correct for satellites produced by shakeup and shakeoff. A more detailed analysis shows that the effects of this almost completely cancel in the present case.