Origin of Cu and Zn L_2- and L_3-$M_{45}M_{45}$ Auger Satellites: Breakdown of the Sudden Approximation

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Initiating Auger transitions using tunable monochromatic x rays from a synchrotron, we show that the satellite intensities in $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ spectra of Cu and Zn increase with increasing photon energies up to about 200 eV above the thresholds. This indicates a pronounced influence of the history of the core-hole generation on Auger spectra, in sharp contrast to the universally accepted belief, and suggests a breakdown of the sudden approximation. Details of the photon energy dependence of the satellite intensity provide a new interpretation for the origin of the satellite.

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While satellite structures in photoelectron spectroscopy have been extensively investigated in recent years, comparatively much less experimental work has been carried out in order to investigate the satellite structures appearing in the Auger spectra. The most well-known satellites in the Auger spectra are associated with the $L_3M_{45}M_{45}$ spectra of Cu and Zn. These were noticed[1] very early in the history of Auger spectroscopy, and attributed[2-10] to an Auger transition in the presence of a spectator vacancy in the M_{45} level generated via a preceding $L_2L_3M_{45}$ Auger process. This interpretation has been accepted in its entirety for more than a decade now and has in fact been extended to the cases of satellite structures observed in the Ni $L_3M_{45}M_{45}$ (Ref. 11) and Eu $N_{45}N_{67}N_{67}$ (Ref. 12) Auger spectra. In this context, we also point out that synchrotron radiation in the study of Auger spectra of solids has been sparingly used, unlike the case of photoemission studies. This presumably stems from the widely believed notion that Auger spectra are unaffected by the history of the generation of the initial hole state, as a consequence of the assumed validity of the sudden approximation for photon energies somewhat (≤ 20 eV) above the core threshold energies. In the course of our detailed investigations of Cu and Zn $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger spectra employing tunable monochromatic synchrotron radiation to excite the transitions we have conclusively established that, contrary to the universally accepted view, (i) the photoionized electron in the continuum is an integral part of the subsequent Auger process, violating the sudden approximation for photon energies up to about 200 eV above threshold, and (ii) the interpretation of the $L_{23}M_{45}M_{45}$ Auger satellite on the basis of a spectator hole is incorrect. On the basis of our observations, we suggest a possible alternative explanation for the origin of this satellite; however, our primary aim here is to provide motivation for reinvestigating the very concepts involved in Auger transitions. This is all the more necessary since our observations have far reaching consequences for the interpretation of electron-spectroscopic results to investigate the ground-state properties of materials.

The experiments were performed at the HE-TGM1 beam line of BESSY, Berlin. The photon energy range available was between 400 and 1300 eV with a resolution of $\simeq 0.8$ eV at the lower end of photon energies and 2.5 eV at the upper end.[13] However, the resolution for the Auger spectra was between 0.3 and 0.5 eV, being essentially determined by the pass energy of the analyzer. Most of the results presented here were obtained with 0.3-eV resolution. The samples of Cu and Zn were cleaned by *in situ* scraping with a Al_2O_3 file in a vacuum of $\simeq 7\times10^{-11}$ Torr.

Before we discuss the results of the present study, it is instructive to critically review the essential elements for the existing interpretation of the satellite structure in the $L_3M_{45}M_{45}$ Auger transitions of Cu and Zn. These satellite features were explained[2-10] in terms of a two-step Auger process. First, an L_2 hole decays via a Coster-Kronig transition, generating a two-hole initial state (L_3M_{45}) for an Auger decay of the thus produced L_3 hole. The final state of this Auger process (with a spectator M_{45} hole, hereafter referred to as the spectator Auger) has three M_{45} holes, in contrast to the two holes for a normal L_3-hole Auger decay. The three-hole final state is expected to be about 6 eV above the two-hole final state,[7] and the satellites in the case of Cu and Zn are indeed found in this energy range in relation to the main Auger peak. However, the main question here is whether the M_{45} hole is stable within the Auger-decay time scale of the L_3 hole in the L_3M_{45} initial state. Since the L_3 hole must decay via the non-Coster-Kronig transition and the screening of a M_{45} hole in transition metals should be considerably fast (particularly due to the L_3-hole–M_{45}-hole repulsion), one should expect the M_{45} hole to be first screened away from the L_3 hole before the decay of the L_3 hole. In such a case, the spectator Auger energy will be similar to the normal Auger energy. This scenario is in fact supported by the results of Ref. 8 which show the coincidence feature in the $L_3M_{45}M_{45}$ region with L_2 photoemission to be only 2.5 eV away from the normal Auger energy rather than 6 eV. The most convincing argument against the spectator-Auger interpretation is the little discussed observation that the $L_2M_{45}M_{45}$ transition is also accompanied by a very similar satellite feature. There has been an attempt to explain the satellite in the $L_2M_{45}M_{45}$ spectrum as a spectator Auger involving the $L_{\rm I}$ level.[3,14] However, our experimental observations conclusively refute such an interpretation.

The Cu $L_3M_{45}M_{45}$ and $L_2M_{45}M_{45}$ Auger spectra for various photon energies above the L_3 and L_2 thresholds are shown in Figs. 1(a) and 1(b). For photon energies close to the thresholds, there is no evidence of the satellite structure (D,E) in either spectrum, while these features grow in intensity with increasing photon energies. The growth of the satellite intensity with photon energy as well as the spectral shape can be better studied by taking the difference spectra, using spectra with $h\nu=941$ and 955 eV as reference spectra. These difference spectra are shown in Figs. 1(c) and 1(d).

The intensity ratios, $I_{\rm sat}/I_{\rm main}$, between the satellite and the main line for L_3- and L_2-hole Auger decays are plotted in

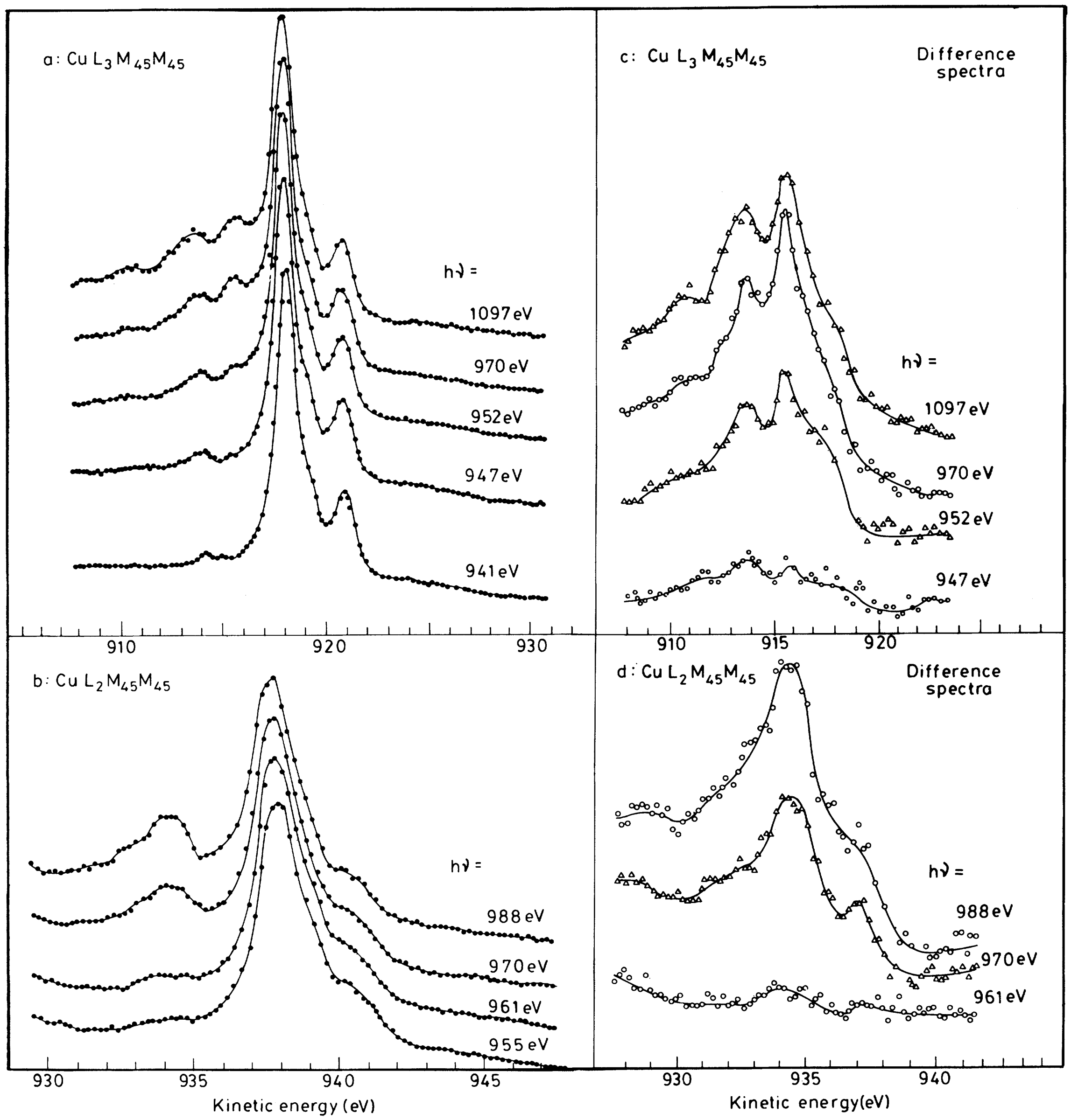

FIG. 1. The photon-initiated Auger spectra of Cu with photon energies are shown in the figure: (a) $L_3M_{45}M_{45}$ and (b) $L_2M_{45}M_{45}$; these spectra are normalized to the same height. (c) The difference after subtracting the $L_3M_{45}M_{45}$ spectrum with $h\nu=941$ eV from the other $L_3M_{45}M_{45}$ spectra with different photon energies. (d) The difference after subtracting the $L_2M_{45}M_{45}$ spectrum with $h\nu=955$ eV from the other $L_2M_{45}M_{45}$ spectra with different photon energies. The difference spectra in (c) and (d) are normalized in such a way as to indicate the development of the satellite intensity with photon energy.

Fig. 2 as a function of photon energy. For this purpose, the integrated intensities due to the satellites (the difference curves between 908 and 923 eV for L_3 and between 930 and 940 eV for L_2) were used without any background subtraction. I_{main} was similarly calculated between 908 and 929 eV for L_3 and between 930 and 948 eV for L_2. We find from Fig. 2 that the satellite intensity increases dramatically for photon energies up to 955 and 975 eV for L_3- and L_2-hole decays, respectively; however, the satellite intensity does not saturate even for photon energies up to $\simeq 200$ eV above the thresholds. It is important to notice that the satellite in the $L_2M_{45}M_{45}$ transition gains considerable intensity for photon energies far below the L_1 threshold ($\simeq 1095$ eV). This conclusively establishes that the satellite in the $L_2M_{45}M_{45}$ transition cannot be due to a spectator-Auger transition. The striking similarity between the photon energy dependences of the satellites in the L_3 and L_2 regions (Fig. 2) suggests primarily a common origin for both of these satellite features, other than the spectator-Auger interpretation.

There is an important difference between the satellite line shapes in the L_3- and L_2-$M_{45}M_{45}$ difference spectra of Cu [Figs. 1(c) and 1(d)]. While the $L_2M_{45}M_{45}$ spectra exhibit essentially a single-peak (E') structure at ~ 4 eV below the main peak, the $L_3M_{45}M_{45}$ spectra have a two-peak structure (D,E) with energy separations from the main peak of ~ 4 and 2 eV. This difference can be seen in the raw spectra [Figs. 1(a) and 1(b)] as well. A final-state satellite is not expected to have such differences in line shape between $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ transitions. Since the coincidence experiments in Ref. 14 showed the presence of the spectator-Auger signal ~ 2.5 eV away from the normal Auger peak, it is reasonable to associate the satellite feature (D) in $L_3M_{45}M_{45}$ with the spectator Auger. Thus the majority of the satellite feature in $L_3M_{45}M_{45}$ (peak E) and the entire satellite feature (E') in $L_2M_{45}M_{45}$ spectra are due to a mechanism different from the spectator-Auger transition.

In the case of Zn, the Auger spectra are very similar to those of Cu, both having a d^8 final state. The details of the Zn spectra will be presented elsewhere;[15] only the intensity variations of the satellites with photon energy in this case are summarized in Fig. 3. Here we find a smooth growth of satellite intensities with photon energy, in contrast to the case of Cu. However, similar to the case of Cu, here also $L_2M_{45}M_{45}$ spectra exhibit sizable satellite intensity for photon energies far below the L_1 threshold ($\simeq 1194$ eV) and the behavior of the satellites in the L_3 and L_2 regions are very similar (Fig. 3). This again proves that the satellites for Zn Auger L_2- and L_3-$M_{45}M_{45}$ spectra primarily have a common origin, and cannot be explained on the basis of spectator-Auger transitions.

We suggest that these are primarily configuration-interaction satellites in the Auger spectra of Cu and Zn; the strong perturbation in forming the two-M_{45}-hole final state may also take the system to a final state with a third M_{45} electron above the Fermi level, giving rise to the satellite. It should be noted here that in this interpretation we again have a three-hole final state leading to the expected[7] 6-eV separation between the main peak and the satellite in close conformity with the experiment (4 eV for Cu and 5 eV for Zn). However, unlike the interpretation based on the spectator-Auger transition, the formation of the satellite is coupled primarily to the final state rather than the initial state.[16] This explains the occurrence of the satellite in both the L_3 and L_2 regions. The present interpretation is also consistent with the observation that the intensity of the satellite decreases markedly with increasing atomic number in the series Cu, Zn, Ga, etc., due to the rapid increase in the binding energy of the M_{45} level.

The photon energy dependences of the satellite features (Figs. 2 and 3) are surprising, since the two-

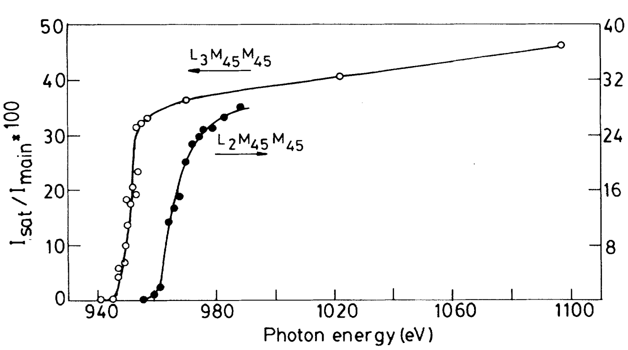

FIG. 2. The variations of the intensities I_{sat} of the Auger satellites in $L_3M_{45}M_{45}$ ($D+E$) and $L_2M_{45}M_{45}$ (E') transitions of Cu relative to the intensity I_{main} of the rest of the spectra ($A+B+C$) with photon energy.

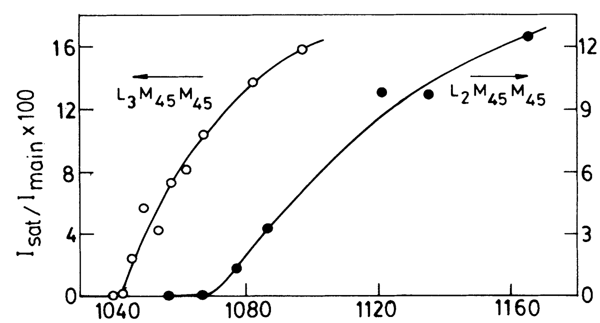

FIG. 3. The variations of the intensities I_{sat} of the Auger satellites in $L_3M_{45}M_{45}$ and $L_2M_{45}M_{45}$ transitions of Zn relative to the intensity I_{main} of the rest of the spectra (as in Fig. 2 for the case of Cu), with photon energy. I_{sat} was evaluated between 979 and 995 eV for L_3 and between 1003 and 1016 eV for L_2 from difference spectra without background subtraction.

hole final state of the Auger transition is independent of the photon energy. The only factor that does depend on it is the final state of the photoexcited L_3 or L_2 electron. Normally the accepted view of the Auger transition holds that the initial state of the Auger transition is the core-hole state, decoupled from the photoemitted electron, and the state of the photoexcited electron is assumed to be unimportant for the subsequent decay of the core hole. The data summarized in Figs. 2 and 3 clearly demonstrate that the presence of this photoexcited electron in the continuum has drastic effects on the Auger spectral shape. Thus, even for energies far ($\simeq$200 eV) above the thresholds, the presence of the photoelectron is found to affect the probability of the satellite formation in the Auger spectra. This observation implies that a detailed understanding of the Auger spectra must include consideration of the presence of the photoelectron in the initial and final states of the Auger process, in sharp contrast to the universally accepted belief. We hope that the present experimental observations, surprising as these are, will prompt theoreticians to reinvestigate the concepts involved in Auger transitions in order to achieve a deeper understanding in the future. This is all the more necessary since any analysis of the electron-spectroscopic results in terms of model Hamiltonians assumes the validity of the sudden approximation in describing the process of satellite formation. Within the validity of this approximation, the relative intensity of the satellite is independent of the photon energy. This is demonstrably contradicted by the data in Figs. 2 and 3. Under such a situation, an assumed validity of the sudden approximation will lead to erroneous conclusions concerning the ground-state electronic structure.

In conclusion, we have shown that the origin of the satellite features in the L_3- and L_2-$M_{45}M_{45}$ spectra of Cu and Zn is not primarily due to Auger transitions in the presence of a spectator hole in the initial states, as has been believed for more than a decade. We have suggested that these originate from a shakeup transition in the final state generating a three-hole configuration. The photon energy dependence of the relative intensities of the satellites has been used to point out the very complex nature of the Auger transitions; in particular, in contrast to the well-accepted present view, it has been shown that the photoelectron in the initial state of the Auger process has a pronounced effect on the subsequent Auger decay. The present results indicate that the sudden approximation is not a valid approach even for energies far ($\simeq$200 eV) above the threshold. Theoretical understandings and ramifications of our observations need urgent investigation through critical reexamination of the decade-old concepts involved.

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[16]Similar correlation effects in the initial photoemission step also could have generated the three-M_{45}-hole final state. However, we reject this interpretation, since such a satellite will also manifest itself in the core photoemission spectra. However, spectra recorded with standard Mg $K\alpha$ or Al $K\alpha$ radiation have virtually no satellite in the core-level spectra, but have intense satellites in the Auger spectra, clearly eliminating an initial-state interpretation.