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Synchrotron-radiation study of the satellites in Ni L_3-$M_{4,5}M_{4,5}$ Auger spectra

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The Ni L_3-$M_{4,5}M_{4,5}$ Auger spectrum is shown to be free of any satellite structure when the ionizing photon energy is close to the ionization threshold. Making use of this observation, we extract the exact line shape of the satellite features appearing with higher ionizing energies. The dependence of the intensities of different features in the satellite reveals two distinctly different kinds of satellite structure to be present. The origin of these satellites is discussed.

The L_2- and L_3-$M_{4,5}M_{4,5}$ Auger spectra of Ni, Cu, and Zn are by far the most studied and discussed ones over the last two decades.[1–25] This distinction stems from the fact that these spectra show evidence of some very interesting many-body effects that are fascinating both experimentally and theoretically. For example, a competition between the localizing effects of the Coulomb correlation strength, U_{dd}, within the $3d$ electrons and the delocalization via the $3d$ band formation in these late $3d$ transition metals give rise to partly bandlike and partly atomiclike features in the two $3d$-hole final states of L_2- and L_3-$M_{4,5}M_{4,5}$ Auger spectra of these elements, the extent of each type (atomic- or bandlike) depending on the ratio between U_{dd} and the bandwidth. Besides this, the L_2- and L_3-$M_{4,5}M_{4,5}$ Auger spectra of these elements also exhibit features that cannot be explained in terms of the two-hole final states of the normal Auger transitions.[1–21] These are, in general, referred to as the satellites, appearing on the lower kinetic energy side of the atomic two-hole final-state features. In the case of L_3-$M_{4,5}M_{4,5}$ spectra, the satellite has been primarily explained in the following manner. It is considered that besides the direct generation of an L_3 hole via ionization, L_3 holes can also be generated by the Coster-Kronig (CK) transition of an L_2 hole via an L_2-$L_3M_{4,5}$ decay channel. The thus-generated L_3 hole has an accompanying $M_{4,5}$ hole as well. Then, the decay of this double-hole $L_3M_{4,5}$ initial state via an $L_3M_{4,5}$-$M_{4,5}M_{4,5}M_{4,5}$ Auger decay will generate a three-hole final state that is theoretically expected[11,19] to be 6 eV lower kinetic energy compared to the two-hole final state arising from the normal L_3-$M_{4,5}M_{4,5}$ Auger transitions, as observed experimentally. In the case of Ni metal, the contributions from shakeup transitions in the Auger initial state (i.e., the final state of the photoemission) may also contribute to the satellite features.[20] Moreover, as shown[21] for Cu and Zn, the Auger satellite may also have a significant contribution from the shakeup transitions in the Auger final state. We have used synchrotron radiation to study in detail the satellite features in the L_3-$M_{4,5}M_{4,5}$ spectra of Ni metal. We have also investigated the dependences of the shape and intensity of the satellite on the ionizing photon energy. From these studies, we delineate the contribution to the satellite due to the L_2-$L_3M_{4,5}$ CK transition preceding the $L_3M_{4,5}$-$M_{4,5}M_{4,5}M_{4,5}$ transition and that due to the intrinsic shakeup process in the Auger final state. We do not find any strong evidence for the four-hole satellite discussed in Ref. 20, originating from the Auger initial state.

The most direct evidence for the interpretation of the satellite in the L_3-$M_{4,5}M_{4,5}$ Auger spectrum of Cu based on a preceding L_2-$L_3M_{4,5}$ CK transition was provided by coincidence experiments.[14] It should be noted that the satellite structure appearing in the vicinity of the L_2-$M_{4,5}M_{4,5}$ spectra of Cu and Zn, however, cannot be explained on the basis of the preceding L_2-$L_3M_{4,5}$ CK transition, since such a transition will transfer the hole to the L_3 level. Thus, the satellite in the L_2-$M_{4,5}M_{4,5}$ spectra of Cu and Zn has been attributed[6] to a $L_2M_{4,5}$-$M_{4,5}M_{4,5}M_{4,5}$ transition (with a three-hole final state) following the L_1-$L_2M_{4,5}$ CK transition. While the above interpretations for the satellite features in L_2- and L_3-$M_{4,5}M_{4,5}$ spectra of Cu and Zn have enjoyed nearly unanimous acceptance over the last two decades, one single study[9] had indicated the possible noninvolvement of the L_1-$L_2M_{4,5}$ CK transition in the origin of the satellites in the L_2-$M_{4,5}M_{4,5}$ Auger spectra of Cu and Zn. However, the arguments put forward in Ref. 9 were subsequently countered in Ref. 19. Very recently, we have established[21] by direct experimental observations that the satellite features in the L_2-$M_{4,5}M_{4,5}$ spectra of Cu and Zn indeed do not arise from a preceding L_1-$L_2M_{4,5}$ CK transition, this fact was made self-evident by the observation of the satellite feature in the photon-initiated Auger spectra with photon energy substantially lower than the L_1-ionization thresholds. We also established that the photon energy dependences of the satellite intensities are very similar for the satellites of the L_2- and L_3-$M_{4,5}M_{4,5}$ spectra of Cu and Zn, indicating a predominantly common origin of the satellites. Thus we suggested that while a portion of the L_3-$M_{4,5}M_{4,5}$ satellite spectra is due to a preceding L_2-$L_3M_{4,5}$ CK transition, the majority of the satellite signal, however, arises from an intrinsic shakeup process accompanying the L_3-$M_{4,5}M_{4,5}$ as well as L_2-$M_{4,5}M_{4,5}$ Auger transitions in Cu and Zn.

The L_3-$M_{4,5}M_{4,5}$ spectrum of Ni metal is considerably more complicated by several factors compared to those of Cu and Zn. Since the ratio of U_{dd} and the bandwidth is substantially smaller for Ni compared to Cu and Zn (Ref. 26), there is substantial intensity in the bandlike part of the Ni spectrum, while the spectra of Cu and Zn are dominated by the atomiclike structures. Moreover, the smaller value of U_{dd} in Ni leads to a considerable overlap between the bandlike and atomic parts of the spectrum. Besides, the smaller electron-electron (multiplet) interaction strength in Ni makes the various atomic multiplet components in the atomiclike part of the transition considerably less resolved. These three factors together make the spectrum of Ni much less structured and, therefore, more difficult to analyze. Added to these complications, one also has to consider the possibility of configuration interaction (CI) affecting the initial states of the Auger transitions and thereby leading to the presence of satellite structures. Such CI effects are clearly seen[27] in the $2p$ core-hole photoemission spectra of Ni metal. Since the final state of the $2p$ core-level spectra is closely related to the initial state of the L_2- and L_3-$M_{4,5}M_{4,5}$ Auger spectra, it is not unreasonable to expect CI effects in the Auger spectra. An early study[20] of the L_3-$M_{4,5}M_{4,5}$ Auger spectrum of Ni metal applied an elaborate fitting procedure to extract information concerning the satellite structures. However, in such an approach there are always several uncontrolled approximations that severely limit the reliability of the conclusions. On the other hand, we have recently shown[21] for Cu and Zn that the satellite structures in the L_2- and L_3-$M_{4,5}M_{4,5}$ Auger spectra can be entirely suppressed by choosing the ionizing photon energy just above the corresponding core-hole thresholds. It is interesting to note that similar effects of changing line shape and energy positions have been observed[28] in another near-threshold-spectroscopy (viz. x-ray emission) study of the valence bands in Ni, Cu, and Zn. Similar effects are also observed for Ni with photon energies near the $L_{2,3}$ thresholds (approximately 852.6 and 870 eV for L_3 and L_2, respectively). Using such a spectrum without any satellite contribution as a reference, we can then deduce the exact shape of the satellite structures accompanying the Auger spectra at higher photon energies.

The experiments were performed at the HE-TGM1 beam line in BESSY, Berlin. The photon energy available was between 400 and 1300 eV with a resolution of 0.8 eV at the lower end of the photon energies and 2.5 eV at the upper end.[29] The contribution from the second-order light in the beam line is negligible[29] and did not affect the results presented here. The resolution for the Auger spectra was between 0.3 and 0.5 eV, being essentially determined by the pass energy of the analyzer. The typical data collection time for a single spectrum was between 15 and 60 min, and the total count at the peak was in the range of $(1-10)\times 10^4$. The sample of Ni metal was cleaned by *in situ* scraping with a Al_2O_3 file in a vacuum of about 7×10^{-11} Torr.

In Fig. 1 we show the L_3-$M_{4,5}M_{4,5}$ Auger spectrum of Ni metal with a photon energy of 1112 eV. The spectral features are very similar to the previously reported[17,20] spectra with higher photon energies. In the same figure, we also give the L_3-$M_{4,5}M_{4,5}$ spectrum recorded with 865 eV photon energy (i.e., approximately 10 eV above the L_3 ionization energy). While the high kinetic energy features of the spectra with $h\nu=1112$ and 865 eV are the same, the broad satellite structure appearing between 835 and 845 eV kinetic energy in the spectrum with $h\nu=1112$ eV is totally absent in the spectrum with the lower photon energy. It should be noted here that the choice of the lower photon energy eliminates the possibility of L_1-$L_3M_{4,5}$ and L_2-$L_3M_{4,5}$ Coster-Kronig transitions. Thus, the reference spectrum free of satellite structures obtained with $h\nu=865$ eV allows us to extract the satellite structure appearing in the Auger spectra with higher ionization energies by taking the difference spectrum between these and this reference spectrum. The resulting satellite structure for $h\nu=1112$ eV is shown in Fig. 1. The satellite shows basically a two-peak feature, with one peak near 845 eV and the other broad one at $\sim$840 eV.

In order to understand the nature of these satellite features in detail, we have investigated the development of their spectral shape with photon energy starting from very near the threshold to considerably above it. In Fig. 2 we

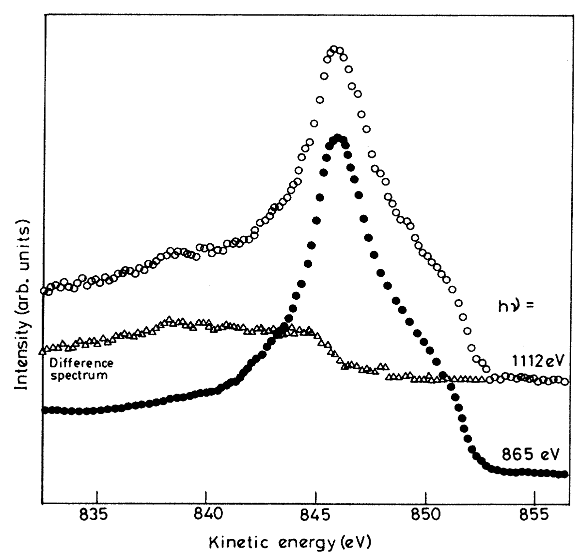

FIG. 1. The Ni L_3-$M_{4,5}M_{4,5}$ Auger spectra with $h\nu=1112$ eV (open circles) and 865 eV (filled circles). The difference spectrum (triangles) shows the satellite line shape.

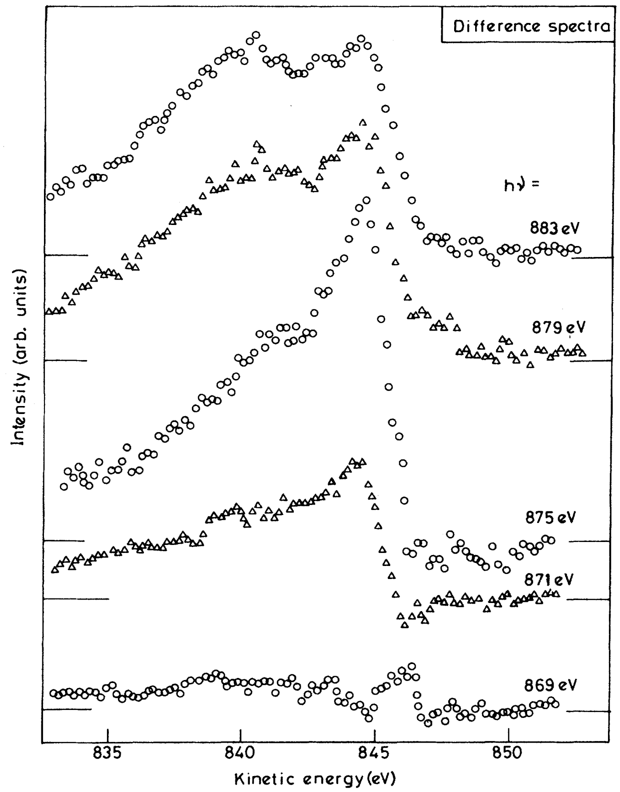

FIG. 2. The satellite line shapes (as obtained from difference spectra) in the Ni L_3-$M_{4,5}M_{4,5}$ Auger spectra at different photon energies.

show the difference spectra between a set of selected Auger spectra recorded with $h\nu > 865$ eV and the reference Auger spectrum with $h\nu = 865$ eV. With $h\nu = 869$ eV, the satellite feature is found to be very weak with the 845 eV peak being virtually absent. However, small intensity is seen between 835 and 842 eV kinetic energy in the difference spectrum with this photon energy. When the photon energy is increased by 2 to 871 eV, we see a dramatic increase in the 845 eV feature in the difference spectrum. It should be noted that the L_2-$L_3M_{4,5}$ CK decay channel opens up for $h\nu > 870$ eV. Thus the dramatic jump in the intensity of the 845 eV kinetic energy feature suggests that this feature is connected with the L_2-$L_3M_{4,5}$ CK decay channel. The intensity of this satellite feature continues to grow up to $h\nu = 875$ eV; over this photon energy range the cross section for L_2-hole creation is also expected to increase rapidly. For $h\nu > 875$ eV, the satellite feature at $\cong 840$ eV begins to gain in intensity relative to that at 845 eV. It should be noted here that strong modifications in the spectral shapes have also been noticed by varying the primary electron energy in electron-induced Auger spectra.[16] Several interesting conclusions can be drawn from these observations. The fact that the satellite features at 845 and 840 eV have different dependences on photon energy suggests different origins for these two features. The appearance of the 845 eV feature only for $h\nu \gtrsim 870$ eV and its rapid increase in intensity for small variations in photon energy above the L_2 threshold indicate that this feature is related to the L_2-$L_3M_{4,5}$ CK event preceding the $L_3M_{4,5}$-$M_{4,5}M_{4,5}M_{4,5}$ transition. The appearance of this feature close to the main L_3-$M_{4,5}M_{4,5}$ Auger peak is consistent with our earlier observations[21] in the case of L_3-$M_{4,5}M_{4,5}$ Auger spectra of Cu and Zn. This is also consistent with the findings of the coincidence experiment[14] on Cu, indicating that such a part of the satellite feature is indeed close in energy to the main peak. The broad satellite feature at ~ 840 eV that is present even for $h\nu < 870$ eV and exhibits a more gradual dependence of intensity on photon energy is attributed to a shakeup satellite. In this interpretation, it is suggested that the three-$M_{4,5}$-hole final state may be directly reached in an Auger transition starting with a fully screened L_3-hole initial state due to shakeup processes. Thus, the generation of the three-$M_{4,5}$-hole final state is coupled to the final state rather than the initial state.

The slow increase in the intensity of the satellite feature at about 840 eV is an indication of a gradual transition between the adiabatic and the sudden limits, contrary to earlier expectations,[30] but consistent with our observations on the Auger spectra of Cu and Zn. In Fig. 3, we plot the relative intensity of the satellites (measured as the total area under the difference spectra between 855 and 832 eV kinetic energy) compared to the main Auger signal as a function of photon energy. The rapid increase of this ratio at about $h\nu = 870$ eV is related to the growth of the satellite feature at ~ 845 eV kinetic energy, originating from a L_2-$L_3M_{4,5}$ CK transition preceding the $L_3M_{4,5}$-$M_{4,5}M_{4,5}M_{4,5}$ Auger transition and, therefore, the intensity of this satellite is expected to follow the variation of the photoionization cross section of the L_2 level. Figure 3 clearly shows that the total intensity of the satellite continues to grow for photon energies far above the threshold. This gradual increase of the satellite intensity is due to the satellite feature at ~ 840 eV (see Fig. 2), and signifies a breakdown of the sudden approximation even for energies far above the threshold.

In conclusion, we have shown that it is possible to ob-

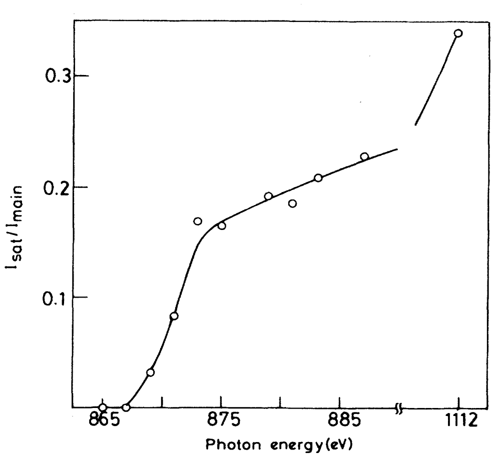

FIG. 3. The relative intensity of the satellite in the Ni L_3-$M_{4,5}M_{4,5}$ spectra as a function of the photon energy.

tain a satellite-free L_3-$M_{4,5}M_{4,5}$ Auger spectrum of Ni metal by tuning the photon energy close to the L_3-ionization threshold. Using such a spectrum as a reference, we have been able to extract for the first time the exact line shape of the satellite feature accompanying the Auger spectra at higher photon energies. This approach has made it possible to study the dependences of the line shape and the intensity of the satellite on photon energy and reveal that there are two separate contributions to the satellite. The satellite feature at ~845 eV kinetic energy is due to a L_2-$L_3M_{4,5}$ CK transition preceding the $L_3M_{4,5}$-$M_{4,5}M_{4,5}M_{4,5}$ transitions, whereas the broad satellite feature at 840 eV kinetic energy is a shakeup satellite leading to a three-$M_{4,5}$-hole final state. The intensity variation of this satellite feature indicates a possible breakdown of the sudden approximation for energies considerably above threshold and signifies a gradual transition from the adiabatic to the sudden limits.

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