Resonant photoemission at core-level shake-up thresholds: Valence-band satellites in nickel

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

J. N. Andersen and C. Wigren
MAX-lab, Lund University, P.O. Box 118, S-221 00 Lund, Sweden

A. Nilsson
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

R. Nyholm
MAX-lab, Lund University, P.O. Box 118, S-221 00 Lund, Sweden

N. Mårtensson
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden
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Three-hole satellites ($3d^7$ final-state configuration) in the nickel valence-band photoelectron spectrum have been identified at 13 and 18 eV binding energy with use of synchrotron radiation from the MAX storage ring. The three-hole satellites show resonances at photon energies close to the threshold for excitation of $3p^5 3d^9$ core-hole shake-up states. The 13-eV satellite also shows a resonance directly at the $3p$ threshold. This is interpreted as an interference between the direct three-hole ionization and a shake-up transition in the Auger decay of the $3p$ hole. This shake-up process is also identified directly in the $M_{2,3}M_{4,5}M_{4,5}$ Auger spectrum.

INTRODUCTION

Photoelectron spectra of both valence-band and core levels of nickel show satellite structures that have attracted much attention during the past decade.[1-12] These satellites are intimately connected to the narrow-band properties of the nickel $3d$ level, which retains some of its atomiclike properties in the metallic state.[13] The satellites give important information on the correlation effects in the metal. (In fact, the term satellite may be somewhat misleading, since these states are as fundamental parts of the electronic structure as the "regular" valence-band states; we will, however, continue to use this terminology.)

Satellites have been observed in the nickel valence-band spectrum up to 30 eV binding energy. These satellites have been interpreted as due to multiple-hole final states.[7] The observed satellite energies are consistent with calculated energies for localized two-hole ($3d^8$), three-hole ($3d^7$) and possibly four-hole ($3d^6$) final-state configurations.[11] Most work has dealt with the well-known "6-eV" satellite in the valence-band spectrum. This satellite corresponds to a two-hole ($3d^8$) final state, and exhibits a strong resonance at the $3p$ threshold at 66 eV.[2] The resonance is understood as an interference between two different channels leading to identical final states (see, e.g., Refs. 3,4, and 9). These two channels are the direct photoionization of the $3d$ valence band resulting in a $3d^8$ shake-up final state and the $M_{2,3}M_{4,5}M_{4,5}$ Auger decay of the screened $3p^5 3d^{10}$ core-hole excited state. When the photon energy is such that the outgoing electrons from the two channels have the same kinetic energy, i.e., at the $3p$ threshold, the two processes are indistinguishable, resulting in a resonance phenomenon.

At somewhat higher photon energies, $3p^5 3d^9$ localized core-level shake-up states can be created. These excited states undergo Auger decay in a similar way as the $3p^5 3d^{10}$ states, resulting in a localized $3d^7$ final-state configuration. The satellites corresponding to this configuration can therefore be expected to exhibit resonances at the $3p^5 3d^9$ shake-up threshold. In this paper we will present a quantitative study of such resonances in these satellites, both directly at the $3p$ threshold and at the $3p$ shake-up threshold. Possible processes causing these resonances will also be suggested.

EXPERIMENTAL

To study possible resonances in the nickel valence-band satellites, photoelectron spectra of the valence-band region up to a binding energy of 35 eV were recorded using photon energies between 60 and 110 eV. The measurements were performed at the toroidal grating monochromator beamline of the MAX synchrotron radiation facility in Lund, using a commercial, angle-integrating double-pass cylindrical mirror analyzer to energy analyze the photoelectrons. The accuracy of the absolute photon energies is better than 0.5 eV. The relative photon energy determination is, however, much more precise. Since the studied satellites are neither very sharp nor very intense

features in the spectra, good statistics was more important than high resolution. The overall resolution (including both the monochromator and analyzer) as measured on the Ni Fermi edge was approximately 0.5 eV.

Sample preparation and measurements took place in a standard UHV chamber with a base pressure of 2×10^{-10} Torr. Clean nickel samples were obtained by *in situ* evaporation from a high-purity nickel wire, wound around a tungsten filament, onto a Mo(110) single crystal. During evaporation the pressure rose to 5×10^{-10} torr. The amount of contaminating C and O, checked with Auger-electron spectroscopy (AES), was less than 2%. The nickel films were approximately five monolayers thick, which was checked by the I(Ni)/I(Mo) AES intensity ratio.

The Ni $3p$ x-ray photoelectron spectroscopy (XPS) spectrum was recorded with a high-resolution XPS instrument in Uppsala, with a total resolution of 0.35 eV. The sample was a Ni(100) single crystal, which was cleaned by cycles of annealing and Ar^+ sputtering. The amount of C and O contamination was less than 2%.

RESULTS AND DISCUSSION

In Fig. 1 the satellite region of the Ni valence electron spectrum is shown for different photon energies. At this Ni coverage the Mo $4p$, which at the photon energies used has a higher cross section than the Mo $4d$ valence band, could not be seen in photoemission. The spectra are thus not influenced by the Mo substrate, but are representative of pure nickel. The spectra have been normalized to constant intensity of the main $3d$ band. Two different types of spectral features can be distinguished, valence-band satellite at constant binding energies and Auger lines at constant kinetic energies. The main Auger peak in Fig. 1 is due to the $M_{2,3}M_{4,5}M_{4,5}$ process.

The main constant binding-energy feature in Fig. 1 is the peak at about 6 eV binding energy. At photon energies below 66 eV only this satellite ($3d^8$ final-state configuration) is seen. Its intensity increases dramatically at the $3p$ threshold, as illustrated by the 66 eV spectrum. The satellite has been observed to display a Fano-like intensity variation[4,5] and shift in the centroid position from 6.0 eV off resonance to 6.8 eV on resonance,[4] behavior that is well reproduced in the present study.

A more careful inspection of Fig. 1 shows that there also exist a number of structures at other binding energies that seem to undergo resonances. The most prominent ones are located at 10, 13 and 18 eV binding energy, of which the first two are clearly seen also off resonance in the 90 eV spectrum. In order to assign these spectral features, the calculated two-hole ($3d^8$) and three-hole ($3d^7$) multiplet patterns from Ref. 11 have been inserted in Fig. 1. The multiplets from the two different configurations are well separated, except for a partial overlap around 10 eV binding energy. The accuracy of the calculated energy positions should be sufficient to allow an identification of the 13 and 18 eV structures as being due to multiplets of the $3d^7$ final-state configuration. This interpretation of the satellites is further supported by an analysis of their resonance properties. In order to make such a more detailed investigation of the satellites it is necessary to remove the Auger intensity from the spectra, which is done by subtracting an off-resonance Auger spectrum. The reference Auger spectrum used for this subtraction was obtained at 110 eV photon energy, where there is no overlap with any photoemission lines.

The subtraction procedure is illustrated in Fig. 2. The basic assumption is that the shape of the $M_{2,3}M_{4,5}M_{4,5}$ Auger line does not depend on the photon energy. To be strict this is only an approximation. When the photon energy is well above the $3p$ threshold, shake-up and shake-off states can be reached. The decay of these states may lead to Auger energies that are slightly shifted relative to the main transitions starting out from the $3p$ initial core-hole state. This implies that the 110 eV spectrum could be slightly affected by such satellites. However, since this would only lead to a slight broadening of the Auger spectrum,[11] these effects should only be of minor

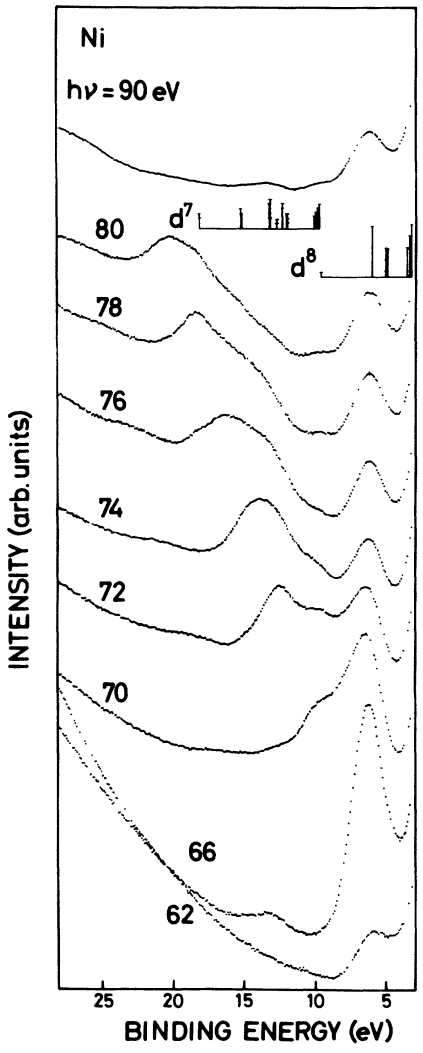

FIG. 1. Photoelectron spectra of the Ni valence-band satellite region. The spectra are normalized to the valence-band intensity. The multiplet pattern was taken from Ref. 11.

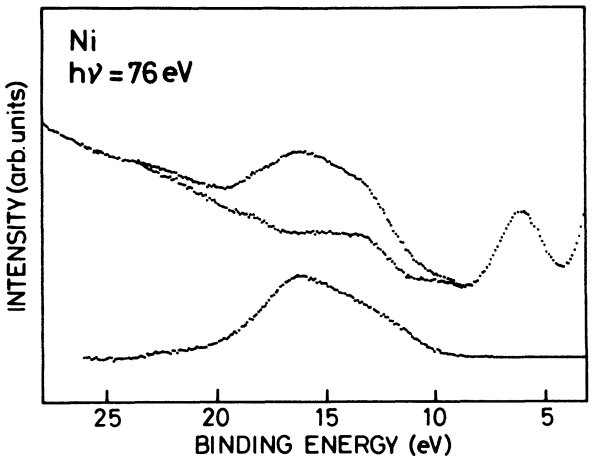

FIG. 2. A schematic illustration of the subtraction procedure. The upper spectrum is the experimental spectrum, the lower is the Auger peak as obtained from a 110-eV spectrum. In between is shown the resulting subtracted spectrum.

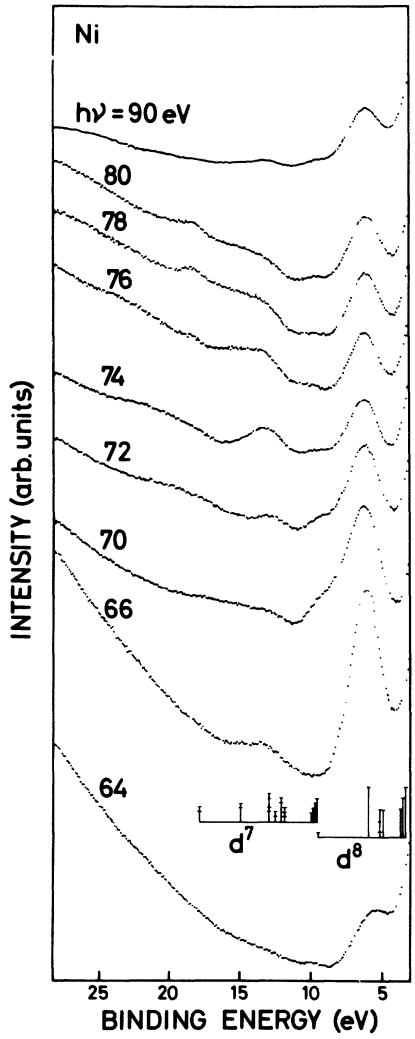

FIG. 3. Subtracted spectra, normalized to the valence-band intensity.

importance. Furthermore, this type of error in the subtraction procedure should mainly lead to structures in the spectra moving with the Auger peak, and not to constant binding-energy peaks.

The main difficulty is the subtraction procedure is to establish the intensity of the Auger peak relative to the other features in the spectra. Assuming a constant ratio between radiative and nonradiative decay of the $3p$ core hole, the intensity of the Auger peak will vary as the $3p$ cross section, while the intensity of the valence band and the background in the satellite region will vary as the $3d$ cross section. Unfortunately, the $3p/3d$ cross section ratio is neither theoretically nor experimentally sufficiently well known to base the subtraction procedure on. The relative intensity of the subtracted Auger peak was therefore estimated by a visual comparison of the experimental and subtracted spectra. The intensity of the subtracted Auger peak was varied until all extra intensity at the kinetic energy corresponding to the maximum intensity of the Auger peak was removed and a smooth background was left. As an additional criterion, any structures remaining after the subtraction should not move with the Auger peak, but appear at constant binding energies. In this way reasonably consistent subtracted spectra were obtained. In may be added that the photon energy dependence of the subtracted intensity is consistent with existing $3p/3d$ cross section ratio data.[14] We are therefore confident that the subtracted spectra can be used to identify and characterize the satellite features in the spectra.

The subtracted spectra are shown in Fig. 3. The constant binding energy features discussed earlier are now more clearly seen. The 13-eV satellite is quite strong at 66 eV photon energy (note that this is already seen in the unsubtracted spectra), very weak at 70 eV, and then once more increases in intensity at 72 eV. It passes through a maximum between 74 and 76 eV, after which it gradually decreases in intensity. The satellite at 18 eV is mainly seen in the 76, 78, and 80 eV spectra. The satellite is, however, not visible in the 90 eV spectrum. Although the 18-eV satellite is very weak it is clearly seen due to its rather small width. This satellite is most prominent in the 80 eV spectrum. The satellite at 10 eV is mainly seen at about 70 eV photon energy. As mentioned above, this satellite probably consists of multiplets from both the $3d^7$ and $3d^8$ configurations. This complicates the analysis of its resonance properties, and the 10-eV satellite will therefore not be discussed any further in this paper.

The 13-eV satellite exhibits such a strong intensity variation that some quantitative information on the photon energy dependence can be extracted. Figure 4 shows the intensity of this satellite as function of photon energy. The intensity is measured as peak height after subtraction of a reasonable background function. It is seen that the 13-eV satellite has two intensity maxima, the first one at 67 eV and the second one at 75 eV. The exact positions of the onsets and magnitudes of these maxima are somewhat uncertain, but the existence of two well-separated maxima is clearly established.

The intensity variations of the 13-eV satellite can be understood in terms of resonance phenomena caused by

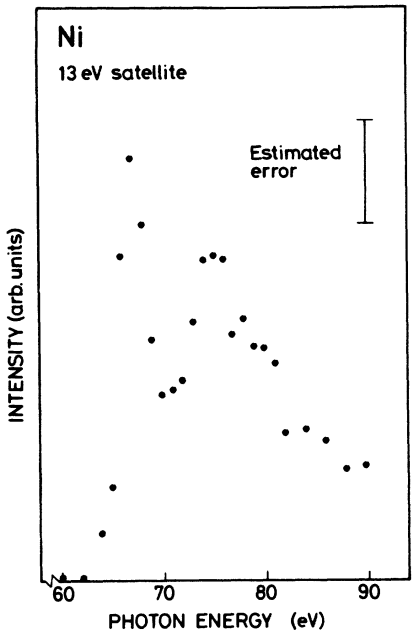

FIG. 4. The intensity of the 13-eV satellite relative to the valence band as function of photon energy. These values are based on the subtraction procedure, and the error is estimated as the difference in intensity after the maximal and the minimal reasonable Auger subtractions.

interference between different channels leading to the same final state. Resonance is possible when the final states are indistinguishable, i.e., when the outgoing electrons have the same kinetic energy. This is similar to the resonance in the 6-eV $3d^8$ final-state satellite at the $3p$ threshold. The present resonances, however, must involve other channels. The 13-eV satellite was assigned to a group of multiplets of the $3d^7$ final-state configuration, i.e., the photoemission channel is the $3d$ photoemission accompanied by $3d$ shake up to produce a localized $3d^7$ state. This final state can be reached by two different Auger decays, one of which is responsible for the resonance at 75 eV, the other one for the resonance at 67 eV.

One possible Auger decay ending up in a $3d^7$ final-state configuration is the decay of a $3p^5 3d^9$ shake-up satellite state produced in the $3p$ photoionization. This channel should resonate with the photoemission channel at the threshold for producing such $3p^5 3d^9$ shake-up states. This threshold can be estimated from the XPS $3p$ spectrum in Fig. 5. Two satellites are observed in the spectrum, one at about 7 eV and one at about 13 eV higher binding energy than the main line. The main line is due to the $3p^5 3d^{10}$ final-state configuration and the satelites have been identified as $3p^5 3d^9$ shake-up states.[15] The

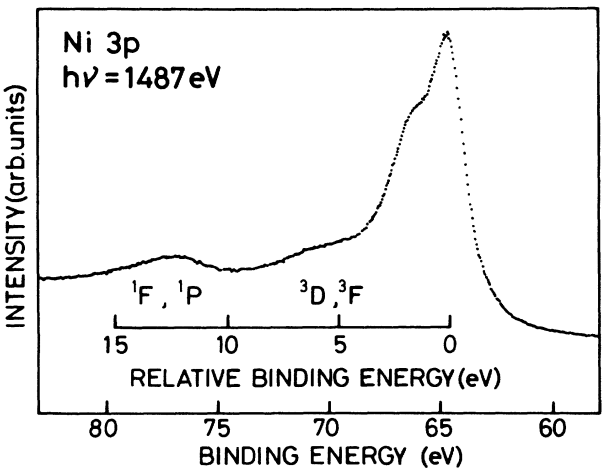

FIG. 5. XPS spectrum of nickel $3p$. The approximate energy positions of some multiplets of the $3p^5 3d^9$ final-state configuration relative to the $3p^5 3d^{10}$ main line are indicated.

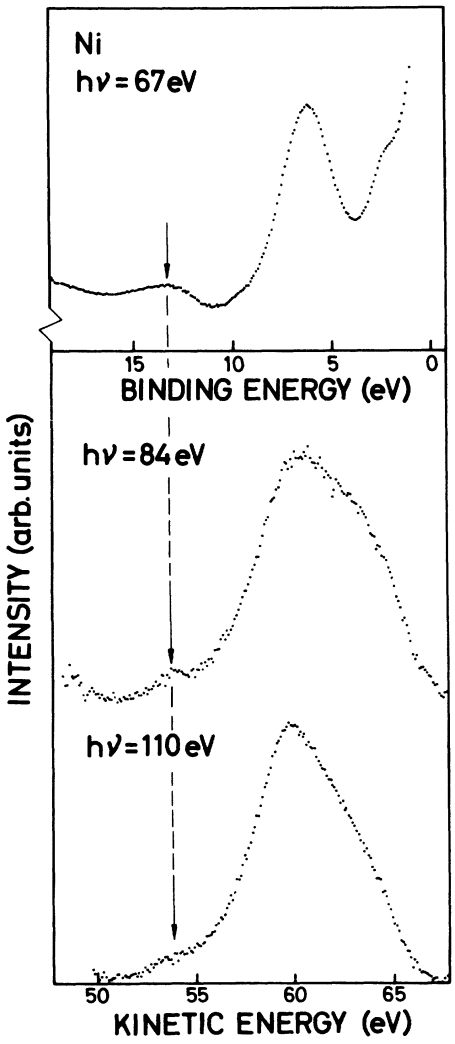

FIG. 6. The nickel $M_{2,3}M_{4,5}M_{4,5}$ Auger spectrum at different photon energies. The upper spectrum shows the same kinetic energy region at the low-energy resonance of the 13-eV satellite. The extra structure in the Auger spectra coinciding energetically with the 13-eV satellite is interpreted as due to a shake-up process in the Auger decay.

splitting into two satellites is due to the large multiplet splittings within the $3p^5 3d^9$ configuration. Resonance in the $3d^7$ final-state configuration can therefore be expected at about 7 and 13 eV higher photon energy than the resonance in the $3d^8$ final-state configuration at 66 eV, i.e., at 73 and 79 eV. This is in good agreement with the observed intensity maximum in the 13-eV satellite around 75 eV. Furthermore it can be noted that the 18-eV satellite, which also corresponds to multiplets of the $3d^7$ configuration, is mainly seen around 80 eV photon energy. The two $3d^7$ satellites are thus seen to have their main resonances at different photon energies, corresponding to the creation of different $3p^5 3d^9$ shake-up states.

To explain the intensity maximum of the 13-eV satellite around 67 eV photon energy, another Auger channel has to be involved. This photon energy corresponds to the $3p$ threshold and is too low for the creation of $3p^5 3d^9$ localized shake-up states. If the intensity maximum is due to the interaction with an Auger process, this has to start with a $3p^5 3d^{10}$ single-hole state. This implies a $3p^5 3d^{10}$ to $3p^6 3d^7$ transition i.e., a regular Auger process with a shake-up of an additional $3d$ electron. To the extent that this process is of any significant importance, this should give an enhancement of the $3d^7$ satellites at the $3p$ threshold.

The existence of a shake-up satellite in the Auger spectrum is supported by the following considerations. The shake-up energy in the Auger process corresponds to the energy separation between the $3d^7$ and $3d^8$ states. The energy separation between these two states can be directly obtained from, e.g., the 67 eV spectrum. This spectrum is shown at the top of Fig. 6 and the main $3d^8$ and $3d^7$ structures are seen. It is now interesting to plot the Auger spectra on the same energy scale. The spectra recorded at 84 and 110 eV are both included in the figure. They are aligned according to the position of the main $3d^8$ final state. As can be seen both Auger spectra show a satellite feature that coincides directly with the 13-eV satellite in the valence-band photoemission spectrum and is due to a shake up. This agreement further supports the interpretation that there is a shake-up satellite in the Auger spectrum.

SUMMARY AND CONCLUSIONS

The photoemission valence-band satellites of nickel have been studied around the $3p$ threshold. Intensity enhancement of the 13- and 18-eV satellites corresponding to the $3d^7$ final-state configuration have been observed at photon energies coincident with the threshold for $3p^5 3d^9$ states. These resonances have been interpreted as due to interference between photoemission and Auger channels having the same final states. The 13-eV satellite also has increased intensity directly at the $3p$ threshold. This resonance is interpreted as an interference between the direct photoemission and a $3d$ shake up accompanying the regular Auger transition. This shake up is also seen as a satellite in the $M_{2,3}M_{4,5}M_{4,5}$ Auger spectrum.

A similar Auger satellite originating from a shake up in the Auger transition may also be present in the nickel L_3VV spectrum. A structure is seen that is centered at approximately 7 eV lower kinetic energy that the main $L_3M_{4,5}M_{4,5}$ peak. The emission at this energy is mainly due to LMM Auger transitions in the presence of two spectator vacancies.[11] Part of the intensity may, however, be due to a shake-up process in the Auger decay. A study similar to the present one at the $2p$ threshold might clarify this.

ACKNOWLEDGMENTS

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