RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 30, NUMBER 4 15 AUGUST 1984

Four-hole satellites in the L_3VV Auger and the valence-band spectra from nickel

Nils Mårtensson
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

Ralf Nyholm
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

Börje Johansson
Department of Physics, Aarhus University, DK-8000 Aarhus C, Denmark

(Received 29 February 1984)

A satellite in the L_3VV Auger spectrum in Ni is identified experimentally and interpreted as an $L_3M_{45}^2$-M_{45}^4 transition, i.e., an LMM Auger transition in the presence of two spectator vacancies. Previously published valence-electron spectra, recorded close to the $3p$ resonance energy, are reconsidered and besides the well-known d^8 double-hole satellite they are shown to reveal d^7 and d^6 multiple-hole states.

Recently, a lot of attention has been directed towards the observation of satellite features in photoelectron spectroscopy, both in valence-band spectra and core-level spectra. Most well known is perhaps the 6-eV satellite in the nickel valence band,[1] which is resonantly enhanced for photon energies close to the $3p$ ionization threshold.[2] Theoretical treatments by Penn,[3] Liebsch,[4] and Davis and Feldkamp[5] have greatly contributed to the understanding of this experimental finding. Related to this is the observation of so called quasiatomic CVV (C = core and V = valence) Auger spectra in nickel as well as in several other metals,[6,7] which in the case of filled band metals has been satisfactorily explained by Cini[8] and Sawatzky.[9] The appearance of core-level satellites in certain metallic systems[10] was treated by Kotani and Toyosawa,[11] who invoked two different final-state screening channels for the core hole. Also the Auger spectra from these metallic systems should be expected to show similar complex behavior.

It has previously been shown that the L_3VV Auger spectrum in Ni is dominated by the atomic multiplet levels of the d^8 configuration.[6,12] However, there are also other contributions to this spectrum. In Cu and Zn strong Auger satellites have been identified which originate from the decay of doubly ionized states into three-hole final states.[13–16] A major portion of these initial states is produced by the $L_2L_3M_{45}$ Coster-Kronig (CK) decay of the $2p_{1/2}$ hole. This decay channel is allowed also in Ni and the same type of satellite should, therefore, be present in its L_3VV spectrum. In this Rapid Communication the Ni Auger spectrum is analyzed in detail, and a *four-hole final-state satellite* is identified. Also the satellite region of a previously published Ni valence-band spectrum[17] is shown to be consistent with three- and four-hole states.

The $L_3M_{45}M_{45}$ Auger spectrum of Ni is displayed in Fig. 1.[18] A major complication in the analysis of the Ni Auger spectrum compared to the analysis of the corresponding spectra in Cu and Zn (Refs. 13–16) is that the Ni spectrum is broad and rather featureless and it is, therefore, not straightforwardly resolved into its various spectral components. To do this it is, therefore, necessary to have rather detailed information concerning their relative positions, shapes, and/or intensities. To obtain this we start out from an analysis of the Cu $L_3M_{45}M_{45}$ Auger spectrum shown in the inset in Fig. 2. Using optical data for the d^8 multiplet splittings[19] and adjusting the relative intensities and widths of the multiplet lines to obtain agreement with the experimental spectrum, the $L_3M_{45}M_{45}$ principal contribution can be identified. Subtracting the fitted principal Auger spectrum from the measured spectrum, we isolate in Cu a

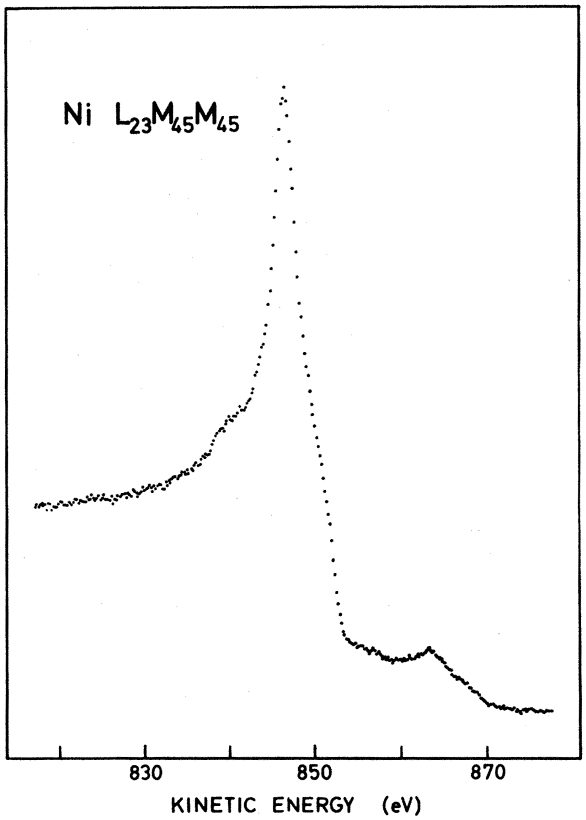

FIG. 1. Experimental Ni Auger spectrum.

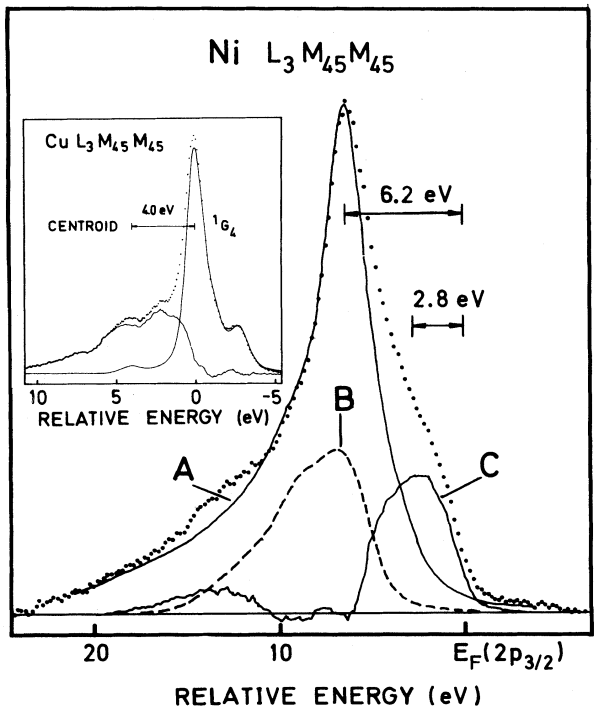

FIG. 2. Ni Auger spectrum (after background subtraction) is compared to the calculated sum (curve A) of the L_3-$M_{45}M_{45}$ and L_3M_{45}-M_{45}^3 (curve B) Auger structures. Curve C is the difference between the experimental spectrum and curve A. The inset shows the Cu L_3VV Auger spectrum from Ref. 16.

strong residual contribution (satellite) which is due to the L_3M_{45}-$M_{45}M_{45}M_{45}(=M_{45}^3)$ processes.

We will now determine what the shape would be of a Ni spectrum, containing the same type of spectral contributions as Cu. Again we utilize optical energies for the multiplet splittings in the d^8 configuration[19] and assign the same relative intensities as in Cu to these multiplet lines. For the satellite width we perform an energy contraction by 15% relative to the observed Cu satellite to account for the lower nuclear charge in Ni. Furthermore, the satellite–main-line separation will be different in Ni and Cu. A calculation of this separation (multiplet averages) shows that it is 2 eV smaller in Ni than in Cu.[20] This means that the satellite will have a considerable overlap with the $L_3M_{45}M_{45}$ principal transitions in Ni. With this information we can now subtract the $L_3M_{45}M_{45}$ and the $L_3M_{45}-M_{45}^3$ structures from the experimental Ni spectrum (Fig. 2).[21] Thereby we find that there are *two additional contributions:* one at higher and one at lower kinetic energies, relative to the subtracted part. The feature at high kinetic energies agrees well with the self-convoluted valence-band spectrum which has a peak position of 2.6 eV, and can thus be interpreted as a double-hole final state where the two $3d$ holes are bandlike.[12,22] However, the relatively intense contribution at lower kinetic energies remains to be explained. We propose that this structure is dominated by an Auger process starting with L_3MM triple-hole states (mainly $L_3M_{45}M_{45}$, for simplicity we will in the text only use this notation) which decays into $MMM_{45}M_{45}$ four times ionized states (in the following denoted M_{45}^4), i.e., an $L_3M_{45}M_{45}$ Auger process with two spectator vacancies in the M levels. We will, therefore, investigate whether the observed energy fits to such a process, as well as whether the intensity is consistent with this mechanism.

As concerns the intensity of the satellite we note from Fig. 1 that it is very difficult to make a detailed determination of this quantity from the experimental data. The satellite is broad and featureless and the determined intensity will, therefore, depend strongly on the background subtraction. However, considering the large width of the Auger satellite it is clear that its intensity must be rather substantial. We, therefore, have to consider what is reasonable to expect for the ratio of $L_3M_{45}^2$ three-hole states to the number of L_3 single vacancies. In this connection it is most instructive to study the $2p$ core-level spectrum of Ni which is shown in Fig. 3. In this spectrum we observe several satellites to the $2p$ core electron lines. First of all we note the strong "6-eV" satellite which has been extensively discussed in the literature before.[12,23] The experimental data are compared to a theoretical spectrum obtained by combining the calculated average configuration satellite separation from Ref. 12 with the calculated multiplet pattern using a Dirac-Fock program.[24] In addition to this satellite there are also significant satellite structures at 11 eV from the main lines. In Ref. 25 these were identified as double $3d$ shake-up processes. In Fig. 3 we have also included the calculated spectra for the $2p^53d^8$ configuration and again we note a very good agreement with the measured spectrum, thereby supporting the three-hole state interpretation. Although these shake-up structures are clearly seen in the spectra, their intensities alone cannot be sufficient to explain the intensity of the Auger satellite in Fig. 1. From the spectrum in Fig. 3 we now make the following observation: the L_2M_{45} satellite has a significantly higher binding energy than the $L_3M_{45}^2$ satellite. Thus, the L_2M_{45}-$L_3M_{45}^2$ CK decay channel is open for the L_2M_{45} satellite state. The L_2M_{45} intensity is a most significant fraction of the total L_2 intensity and, furthermore, when this type of CK decay is allowed it will be the dominating decay channel. In addition, there are also $L_3M_{45}^2$ states which are connected to the ionization of the L_1 level, either from the CK decay of the L_1M_{45} satellite

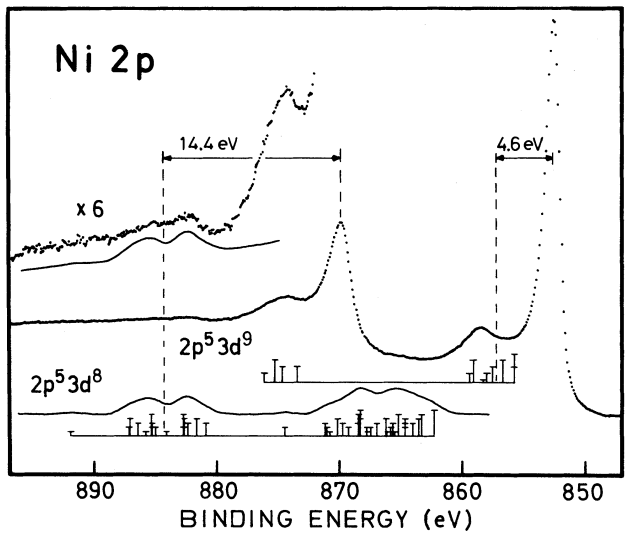

FIG. 3. Ni $2p$ satellite spectrum compared with calculated $2p^53d^9$ and $2p^53d^8$ shake-up satellites.

state or from the decay of L_1 single-hole states via the L_2M_{45} intermediate configuration. Summing up these contributions we find that the $L_3M_{45}^2$-M_{45}^4 satellite will have an intensity of the order of 20%–30% relative to the main $L_3M_{45}^2$ Auger lines.[26]

Concerning the energy of the $L_3M_{45}^2$-M_{45}^4 Auger satellite transition we first of all note that the initial-state energy can be obtained from Fig. 3. To obtain the energy of the four-times ionized state M_{45}^4 we investigate the Ni VB spectrum reported by Eberhardt and Plummer[17] (see Fig. 4). In this spectrum several satellite peaks (labeled A–F) are resolved. Peak A has been identified as due to the $d^8(^1G_4)$ state, and also peak C has been mentioned previously. However, no detailed interpretation of the complete satellite spectrum has been performed. In Fig. 4 we compare the measured spectrum to the calculated positions of d^8, d^7, and d^6 multiple hole satellites completely screened by sp electrons.[27] First we note that peak A corresponds closely to the calculated $^1G_4$ position and it is also known that this multiplet level dominates the spectrum at resonance.

When we compare the measured spectrum with calculated d^7 and d^6 satellites we have tentatively assigned satellite intensities to the various multiplet lines according to the multiplicities, and have then performed a Gaussian broadening [full-width at half maximum (FWHM) $=2.5$ eV] of the satellite pattern in order to get some impression of the satellite shape. That this approximation is not necessarily very good can, for instance, be seen from the d^8 satellite for which we know that the $^1G_4$ multiplet level contributes much more than what is its statistical weight. The broadening is, therefore, mainly a convenient way to illustrate the density of the multiplet levels. However, both in the d^7 and d^6 configurations the levels are displaced in relatively separated groups and, therefore, the positions of the broadened structures will be rather accurate, although the intensities can be off by a considerable amount. In this comparison we first of all note that satellite structure B in addition to the ^1S level of the d^8 configuration also coincides with the lowest multiplet levels (^4F) of the d^7 configuration. The main number of multiplet levels of the d^7 configuration are calculated to be located between 12 and 15 eV, i.e., corresponding to the position of peak C. Also at the high-energy side of the d^7 configuration there are two multiplet levels ($^2D_{5/2,3/2}$) which are split off from the remaining lines and their calculated position coincides with satellite D in the experimental spectrum. Also the d^6 satellite configuration is predicted to give rise to several isolated satellite peaks. First of all there is a calculated position of 22.5 eV (^5D), i.e., very close to the observed feature E. The main portion of the d^6 satellite is then predicted to start at 25.7 eV and contains a large number of multiplet lines which are spread over several electron volts. The appearance of two peaks in this range is not seen in the experimental spectrum, but rather only one comparatively broad feature F. However, since there is in this spectral region multiplet lines spread out rather evenly over as much as 5 eV, the predicted shape depends strongly on the assumed intensities of the various contributions. Furthermore, the analysis of the experimental spectrum in this region becomes also increasingly difficult due to the rapidly increasing background.

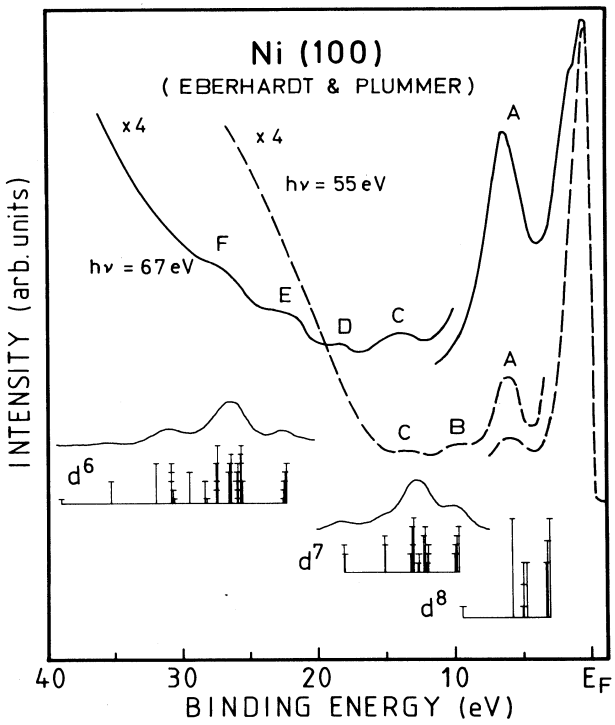

FIG. 4. Valence-band spectrum of Ni (100) (Ref. 17) compared with calculated d^8, d^7, and d^6 satellites.

Turning back to the Ni Auger spectrum we can now use the energy difference between the d^8 and d^6 valence-band satellites together with the three-hole-satellite–main-line separation in the Ni $2p$ spectrum to derive the position of the four-hole Auger satellite relative to the principal transition. Using the configuration average for the p^5d^8 and d^6 states we calculate a satellite separation of 7 eV from the $L_3M_{45}^2(^1G_4)$ Auger position. This is in close agreement with the position in Figs. 1 and 2, which strongly supports the given interpretation of the satellite.

These results show that both the Auger and the valence-band spectra of Ni contain satellite features of considerable complexity, where three and even four d holes form strongly bound states. For the valence-band satellites further work is needed to elucidate the occurrence of these very highly polar configurations.

[1]Y. Baer, P. F. Hedén, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, Phys. Scr. **1**, 55 (1970); S. Hüfner and G. K. Wertheim, Phys. Lett. **51A**, 299 (1975).

[2]C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétroff, and L. M. Falicov, Phys. Rev. Lett. **39**, 1632 (1977); J. Barth, G. Kalkoffen, and C. Kunz, Phys. Lett. **74A**, 360 (1979); M. Iwan, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. **43**, 1829 (1979).

[3]D. R. Penn, Phys. Rev. Lett. **42**, 921 (1979).

[4]A. Liebsch, Phys. Rev. Lett. **43**, 1431 (1979).

[5]L. C. Davis and L. A. Feldkamp, Phys. Rev. B **23**, 6239 (1981).

[6]A. B. Baró, M. Salmerón, and J. M. Rojo, J. Phys. F **5**, 826 (1975).

[7]S. P. Kowalczyk, R. A. Pollak, F. R. McFeely, L. Ley, and D. A. Shirley, Phys. Rev. B **8**, 2387 (1973); E. D. Roberts, P. Weight-

man, and C. E. Johnson, J. Phys. C **8**, L301 (1975).
[8]M. Cini, Solid State Commun. **20**, 605 (1976); **24**, 681 (1977).
[9]G. A. Sawatzky, Phys. Rev. Lett. **39**, 504 (1977).
[10]F. U. Hillebrecht, J. C. Fuggle, P. A. Bennett, Z. Zolnierek, and Ch. Freiburg, Phys. Rev. B **27**, 2179 (1983).
[11]A. Kotani and Y. Toyosawa, J. Phys. Soc. Jpn. **37**, 912 (1974).
[12]N. Mårtensson and B. Johansson, Phys. Rev. Lett. **45**, 482 (1980).
[13]P. Weightman and P. T. Andrews, J. Phys. C **12**, 943 (1979).
[14]E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B **15**, 1669 (1977).
[15]H. W. Haak, G. A. Sawatzky, and T. D. Thomas, Phys. Rev. Lett. **41**, 1825 (1978).
[16]N. Mårtensson and B. Johansson, Phys. Rev. B **28**, 3733 (1983).
[17]W. Eberhardt and E. W. Plummer, Phys. Rev. B **21**, 3245 (1980).
[18]The spectra have been recorded with an HP5950A ESCA spectrometer on mechanically cleaned samples, using Al $K\alpha$ excitation.
[19]C. E. Moore, Natl. Bur. Stand. (U.S.) Circ. 467 (1958).
[20]The position of the Auger satellite was calculated for Cu in Ref. 16 and the Ni position is calculated in an analogous manner.
[21]For simplicity it is assumed that the satellite intensity is the same in Ni as in Cu. It is also found that variation of the satellite intensity has very little effect on the residual peaks in Fig. 2.
[22]P. A. Bennet, J. C. Fuggle, F. U. Hillebrecht, A. Lenselink, and G. A. Sawatzky, Phys. Rev. B **27**, 2194 (1983).
[23]S. Hüfner and G. K. Wertheim, Phys. Lett. **51A**, 299 (1975).
[24]I. P. Grant *et al.*, Comput. Phys. Commun. **21**, 207 (1980).
[25]A. Bosch, H. Feil, G. A. Sawatzky, and N. Mårtensson, Solid State Commun. **41**, 355 (1982).
[26]Estimated from measured $2s$ and $2p$ satellite intensities, calculated Auger rates [E. J. McGuire, Phys. Rev. A **3**, 1801 (1971)] and calculated photoionization cross sections [J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8**, 129 (1976)]. The relative contributions to the satellite are approximately as follows: (i) 20% from the $2p^*_{3/2}3d^8$ shake-up satellite; (ii) 50% from the $2p^*_{1/2}3d^9$ satellite; (iii) 10% from the $2s^*$ state; and (iv) 20% from the $2s^*3d^9$ satellite. In addition there will also be a small contribution from an L_3-V^3 final-state shake-up process in the same energy region.
[27]The position of the d^8 satellite was calculated in Ref. 12 and the calculations for the d^7 and d^6 satellites are completely analogous to the calculations for Cu in Ref. 16.