

Valence-Band and Core-Level Satellites in Nickel and Related Elements

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The valence-band satellite in nickel (and in palladium) is described as due to a local excitation of a d electron. The calculated excitation energies show a good quantitative agreement with experiment. Also the core-level satellites are treated and, where possible, compared with appropriately selected Auger spectra.

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The 6-eV satellite structure observed in the 3d-band photoelectron spectrum from nickel metal has been frequently discussed in the literature, both from the experimental¹⁻⁶ and the theoretical⁷⁻⁹ point of view. Presently, this interest has been further stimulated by the observation of a resonant enhancement of the satellite for photon energies close to the binding energy of the 3p core electrons.⁴ In addition, and contrary to what was generally expected, a similar two-electron resonance has now also been observed in copper⁶ and zinc.¹⁰ In the case of nickel not only the valence band has a satellite but also the core-electron spectra show satellite structures^{1,2} and it has been suggested that all these satellites (valence and core) have the same origin.³ Palladium shows a similar behavior, namely a satellite both to the valence band and to the core levels. Two of the main aspects of these types of satellites are their intensities and energy positions. In a recent communication¹¹ we have shown that the core-electron binding energies in metals can be accurately determined from a complete screening picture of the final state. In the present Letter we will use a corresponding method to obtain the energy position of the satellites.

Following the suggested^{7,2} possibility of a two-hole exciton state in the nickel d band, Penn⁸ applied the Hubbard model in order to investigate the d -electron spectral density. Thereby he found a resonancelike state below the bottom of the d band. In a related treatment, Liebsch⁹ has recently shown that the spectral function of the d hole contains both band features and satellites due to remnant states of the d^8 multiplet. The picture that we will apply here to the photoemission spectrum of a d electron is that it contains two contributions: (a) The hole created in the ionization process is itinerant and reflects the

normal valence d -band density of states; (b) the created hole stays localized to a particular site. In the latter case the atomic site in question will be completely screened by s electrons giving a neutral-charge site. Thus the final state can be looked upon as a local bound state between two d holes and an attached screening charge of two s electrons. This localized excitation will be identified with the valence-band satellite. For the core levels and their satellites we use the following picture. The main core line corresponds to a d -electron final-state screening while the satellite is due to s -electron screening.¹²

We start with the valence-band satellite in nickel. With the complete screening picture given above the final localized state is a $d^8(X)s^2$ configuration (X stands for the spectroscopic assignment). Since the d^8 configuration is considered as a local magnetic configuration, these d electrons do not participate in the metallic bonding but only the 4s electrons. As far as the 4s valence electrons are concerned they will behave almost indistinguishably to those for a substitutional zinc impurity site in the nickel host metal. Thus the bonding of the original metallic nickel atom has been converted to a zinclike final-state bonding. Therefore the final state of the atomic site can be obtained from the original state by the following steps¹³:

$$[d^9s] \rightarrow d^8({}^3F_4)s^2 \rightarrow d^8(X)s^2 \rightarrow d^8(X)[s^2]. \quad (1)$$

The square brackets are here used to denote the metallic state of the valence electrons. The intermediate step is the excitation from the ground state of the free nickel atom to a higher level of the d^8s^2 configuration. The first step in Reaction (1) thus defines the cohesive energy of a nickel atom and the final step defines the cohesive energy of a $d^8(X)s^2$ atom (where the d electrons

remain nonbonding) as well as the heat of solution of such a metallic atom in the nickel host. For simplicity we will neglect this last impurity aspect of the "zinclike" final state and only consider this site as it would be in a zinc environment. [This is justified since the heat of solution of a metallic zinc atom in nickel is small in comparison with the other contributions in Eq. (1).] Thus for the last process in Eq. (1) we can to a high accuracy just use the cohesive energy of zinc. The calculated position of the $d^8(^3F_4)$ local configuration in the metal is then nothing but the cohesive-energy¹⁴ difference between nickel and zinc or $4.44 - 1.35 = 3.09$ eV. For the $d^8(^1G_4)$ multiplet level we only have to add the spectroscopic difference¹⁵ between the atomic $d^8(^1G_4)s^2$ and $d^8(^3F_4)s^2$ levels [compare Eq. (1)] and thereby we obtain $3.09 + 2.74 = 5.83$ eV. In metallic zinc the valence-band satellite spectrum has been shown¹⁰ to be dominated by the 1G and 3F multiplets of the d^8 configuration just as they dominate the $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum.¹⁶ From the most plausible assumption that the same will be true in nickel our calculated energies should be compared with the resonant satellite structures observed at about 6 eV and $\sim 2-3$ eV below the Fermi level.⁶ A further very weak satellite was observed at approximately 14 eV. This we interpret as due to a local d^7 configuration. A calculation of the same type as above shows that the multiplets of this configuration are situated 10 to 18 eV below the Fermi energy.

In Fig. 1 we show the L_3VV Auger spectrum relative to the L_3 line and compare with the self-convoluted valence-band spectrum $X(E)*X(E)$. The large discrepancy between these two spectra clearly indicates a dominating quasiatomic nature of the Auger final state.¹⁷ The main peak (identified as the 1G_4 level) is situated 6.2 eV below the Fermi level.¹⁸ This agrees well with the resonance experiment and our calculation above, which gives further support to the quasiatomic description of this Auger process. From Fig. 1 we notice, however, that there is a finite density of states of the convoluted spectrum at the main Auger peak. Therefore the decay of the $d^8(X)s^2$ state can be expected to be quite rapid, giving rise to a broadening of the d^8 multiplets. This will be especially effective for the 3F levels (compare Fig. 1) and explains why this peak could only partly be resolved in the resonance experiment. The $d^8(^1S)s^2$ level is estimated to be situated at about 9.5 eV below the Fermi level and should therefore decay much less readily than

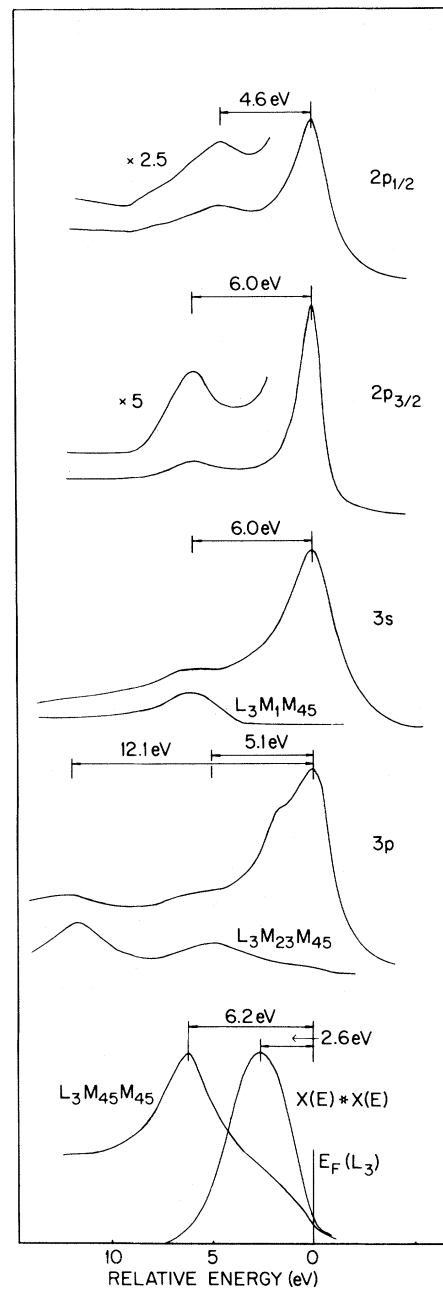


FIG. 1. Core-level satellite spectra for Ni recorded with an HP-5950A ESCA (electron spectroscopy for chemical analysis) spectrometer. The $3s$ and $3p$ satellite spectra are compared with the M_1M_{45} and $M_{23}M_{45}$ double-hole energies obtained from L_3MM Auger spectra. The $L_3M_{45}M_{45}$ final-state energy distribution is also included and is compared with the energy spectrum of two independent $3d$ holes.

the other d^8 multiplet levels. Unfortunately, its intensity is somewhat too low to be clearly seen in the spectrum.

Assuming complete screening the final valence state for an ionized core site will be $d^{10}s$. However, for the core-level satellite we assume that the core-electron ionization is accompanied by a shakeup process of this $d^{10}s$ state giving a d^9s^2 final state. In the presence of the core hole the d^9 state will be of localized type and thus non-bonding. As for the valence-band satellite this "core-hole" d^9 state is fully screened by the $4s^2$ valence state. Here we will first discuss the $2p_{1/2,3/2}$ holes for which the multiplet splitting between the p and d hole is relatively small. The method we will use is essentially the same as in Eq. (1) except that we now compare two different processes, one for the main line and one for the satellite:

$$[d^9s] - d^9s - 2p^{-1}d^{10}s - 2p^{-1}[d^{10}s], \quad (2a)$$

$$[d^9s] - d^9s - 2p^{-1}d^{10}s - 2p^{-1}d^9s^2 - 2p^{-1}d^9[s^2]. \quad (2b)$$

The difference between these two processes gives the satellite position relative to the parent $2p_{1/2}$ and $2p_{3/2}$ lines, respectively. For the intermediate atomic process in Eq. (2b) we compare with the corresponding excitation in copper, namely $d^{10}s - d^9s^2$, which is 1.49 eV (averaged over the two spin-orbit components). However, in the presence of a p hole in nickel the corresponding excitation energy is calculated¹¹ (neglecting the multiplets) to be nearly 1 eV higher, or 2.42 eV. Since the final state in Eq. (2a) is essentially a metallic copper atom dissolved in nickel and in Eq. (2b) a corresponding zinc atom, we at once discover that the difference between Eqs. (2b) and (2a) is equal to $2.42 - 1.35 + 3.49 = 4.6$ eV. This is our calculated position of the $2p$ core-hole satellite. However in practice the multiplet splitting is not negligible and is furthermore different for the $2p_{1/2}$ and $2p_{3/2}$ holes.¹⁹ Thus experimentally (Fig. 1) the satellites to the $2p_{1/2}$ and $2p_{3/2}$ levels are found at about 4.6 eV and 6.0 eV from their parent lines, respectively, which is in reasonable agreement with our calculated value. This experimental difference in the satellite positions is in fact a demonstration of the localized character of the d^9 configuration in the presence of the p hole. For the $3p_{1/2,3/2}$ core holes the multiplet splitting with the d^9 configuration will be very large which makes a direct comparison like the one above more difficult. However, in this case we can compare with the experimental $L_3M_{23}M_{45}$ Auger process, where the final state is of the same type as postulated

for the satellite. This comparison is shown in Fig. 1. The two satellite features to the $3p_{1/2,3/2}$ lines are seen to be well reproduced by the Auger spectrum. In the same way the $3s$ satellite is well reproduced by the $L_3M_1M_{45}$ Auger spectrum when the appropriate energies are compared (Fig. 1).

For the valence-band satellite in palladium we apply the same reasoning as for nickel. From Eq. (1), we then obtain for the $d^8(^3F_4)s^2$ final state in the metal a binding energy of $3.90 + 3.112 - 1.16 = 5.85$ eV. Here the numbers 3.90 and 1.16 eV are the cohesive energies of palladium and cadmium, respectively, and 3.112 eV is the energy position of the atomic $d^8(^3F_4)s^2$ level above the d^{10} ground state. For the $d^8(^1G_4)s^2$ we calculate a position of 8.0 eV below the Fermi level.²⁰ This is in good agreement with the value of 7.6 eV obtained from the M_5VV Auger spectrum,²¹ which also lies within the range of the rather broad valence-band satellite feature observed in palladium. Very recently this satellite structure has been seen to undergo a resonant enhancement.²² The energy position for the enhancement is at about 8 eV, which is in excellent agreement with our calculated value. For the satellites to the $3d_{3/2,5/2}$ core levels we use the same method as described in the Eqs. (2a) and (2b) for nickel and calculate a separation of 6.2 eV. This should

TABLE I. Calculated and experimental data (in electron volts) of the $d^8(X)$ configuration relative to the Fermi level. The Auger data references are Ni (present work), Cu and Zn (Ref. 16), Pd (Ref. 21), and Ag (Ref. 23). The resonance data references are Ni and Cu (Ref. 6), Zn (Ref. 10), and Pd (Ref. 22).

	Calculated	Experimental	
		Auger	Resonance
Ni 1G_4	5.8	6.2	6
Ni 3F_4	3.1		2-3
Cu 1G_4	14.3	14.2	14.6
Cu 3F_4	11.2	11.4	11.8
Zn 1G_4	29.4	29.4	30.0
Zn 3F_4	25.6	26.1	26.6
Pd 1G_4	8.0	7.6	8
Pd 3F_4	5.8		
Ag 1G_4	16.3	16.3	
Ag 3F_4	13.9	14.0	

be compared with the experimental value of 6.0 eV.²¹

The same model as above can also be applied for the excitation to a two- d -hole bound state in copper. In this case the final-state screening around the excited site is of a s^2p type. Thus these screening electrons behave essentially like the valence electrons for a metallic gallium atom impurity in the copper host. In Table I, we compare the calculated values with experiments (as obtained directly in the resonant experiment or as derived from the L_3VV Auger spectrum) and the agreement is found to be good. In Table I, we also include our calculated values for zinc and silver and compare with experiments. Again the agreement is good.

The presented pictures for the various satellites have been shown to give a good numerical agreement with experiment. The proposal in Ref. 3 that all the nickel satellites have the same origin agrees with our description of the core-level satellites. This similarity between the satellites can be extended to hold also for the valence-band satellite, provided that the $d^8(X)$ final state is looked upon as reached by a d -electron excitation in the presence of a local d hole. Since in the presence of a core hole the d^9 configuration is localized (as is clear from the multiplets), the same would then appear to be true also for the d^8 configuration (without core hole). This would *a posteriori* justify our local picture for the valence-band satellite.

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