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Two-electron resonances in transition metals

D. Chandesris and J. Lecante
*Service de Physique des Atomes et des Surfaces, Centre d'Etudes Nucleaires Saclay, 91190 Gif-Sur-Yvette, France
and Laboratoire d'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, Bâtiment 209 C,
91405 Orsay, France*

Y. Petroff
*Laboratoire d'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, Bâtiment 209 C,
91405 Orsay, France*

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We have studied experimentally the photoelectron spectra of Cr, Fe, and Co near the 3*p* excitation threshold. Comparison with earlier results in Ni and Cu yields a consistent picture for the behavior of the two-electron satellites. We show that resonance effects are observed in all materials with unfilled 3*d* bands, that the intensity of the resonance depends strongly on the number of 3*d* holes, and that the persistence of the satellite above the resonant energy in nickel, but not in the other transition metals, can be explained by a higher localization of the 3*d* electrons.

We report the observation in photoemission experiments of valence-band and satellite resonances at the 3*p* edge of magnetic transition metals, chromium, iron, and cobalt, and we discuss how these results can be compared with earlier ones.

Guillot *et al.*[1] reported the observation in photoemission of a strong resonance effect on a structure located below the *d* band of nickel, and explained this in an atomic picture, considering the autoionization of an excited quasidiscrete atomic configuration ($3d^9 4s$) into a continuum of excitations with two holes in the 3*d* shell. This interpretation of the satellite and the resonance was based on the existence of 3*d* holes.

Penn[2] confirmed the assumption of the main role of the empty *d* states: Owing to the width of the *s-p* band, the scattering of an electron into an empty *s-p* state has low probability and would not lead to a sharp satellite. Using perturbation theory within the Hubbard model, Treglia *et al.*[3,4] have shown that the correlations induce a deformation of the one-particle spectrum, creating the experimentally observed satellite in nickel,[3] iron, and cobalt,[4] and reducing the width of the *d* bands.

However, Iwan *et al.*[5] obtained a similar but much weaker two-electron resonance on copper, showing that these effects can also be obtained in metals with filled *d* bands. Davis and Feldkamp[6] explained this effect, based on the strong interaction between the 4*s*-4*p* conduction electron and the two-bound holes. We confirmed the atomic origin of the resonance, and we showed that it exists also on copper vapor.[7]

Clauberg *et al.*[8] obtained a high spin polarization of the satellite in nickel, at resonance, confirming the main role of the 3*d* holes. As predicted by Feldkamp and Davis[9] the polarization of the satellite can be understood in the following way: At the 3*p* threshold, only $3p\downarrow$ (minority spin) electrons can be excited to the empty part of the 3*d* band, the majority spin band being occupied.

We confirm the main role of the 3*d* holes in the resonance phenomenon and we compare the intensity of the satellite at resonance in different elements of the 3*d* transition series: chromium, iron, cobalt, nickel, and copper. We discuss also the position of the satellite in these materials and compare it with Auger spectroscopy results.[10,11]

The measurements were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) with the setup already used for angle-resolved photoemission.[12] The overall resolution (monochromator plus analyzer) was 200 meV.

The crystals were prepared by argon bombardment and annealing, and checked by low-energy electron diffraction (LEED) and Auger spectroscopy. Chromium was a (110) surface of a well-oriented single crystal. The main contaminants after several cycles were carbon and nitrogen. The best surface was obtained by heating the sample at 500 °C during a 10-h bombardment with argon ions of 1 keV (typical current on the sample was 4 μA). Carbon contamination was less than 3% of a monolayer; there was no nitrogen at all, and the sample

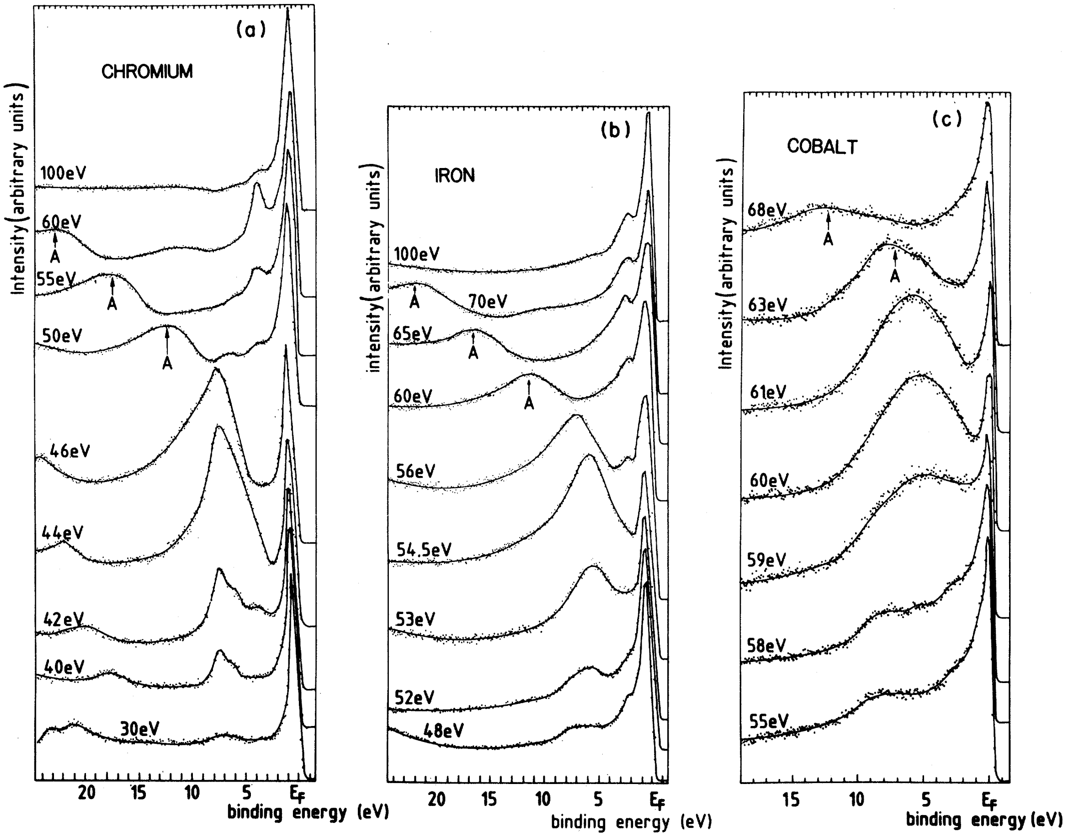

FIG. 1. (a) Photoelectron spectra in the valence-band region, with photons from 30 to 100 eV on a (110) face of chromium. The angle of incidence of the light is 30°. (b) Photoelectron spectra in the valence-band region, with photons from 48 to 100 eV on a (110) face of iron. The angle of incidence of the light is 70°. (c) Photoelectron spectra in the valence-band region, with photons from 55 to 68 eV on a (000,1) face of cobalt. The angle of incidence of the light is 30°.

was well reconstructed. For iron, (110) surface, and cobalt, (000,1) surface, the cleaning procedure was the same. The last contaminant was also carbon, but we did not obtain well-reconstructed surfaces (the LEED spots were not very sharp) because we never heated the sample at more than 600 °C to prevent phase transitions.

We have performed experiments with photons whose energy was tuned between 30 to 100 eV. Typical spectra are shown in Fig. 1. The peaks just below the Fermi level E_F (0—3 eV) correspond to electrons directly emitted from the valence band (mainly $3d$ electrons); the peak at fixed kinetic energy (A) is due to electrons emitted from the $M_{23}VV$ Auger transition; the last peak, at fixed binding energy (5—7 eV from E_F, depending on the element), is the satellite corresponding to a final state with two correlated d holes on the same atom. The intensity of this satellite shows great enhancement when the photon energy reaches the energy of excitation of $3p$ electrons to states above E_F.

To obtain an absolute value of the intensity of each peak as a function of photon energy, we measured, for every spectrum of chromium and iron, the intensity of the incident light. We draw the cross section of the different structures as a function of the incident photon energy (Fig. 2). We see that all the structures show strong resonances near the $3p$ edge. To avoid the problem of background substraction, we measured the height of a peak at constant binding energy (0.5 eV from the Fermi level for the $3d$ cross section, 7.3 eV for the chromium satellite, 5.5 eV for iron satellite), or at constant kinetic energy for the Auger electrons. Then, at resonance, we have the same value for the Auger peak and the satellite, which are indistinguishable. The position of the satellites is determined before resonance, where they are not mixed with the nonexisting Auger peak.

TABLE I. Measured distances (in eV) between the satellite and the main peak for different transition metals.

	Cr	Fe	Co	Ni	Cu
U_{sat}	6.5±0.5	5.0±0.5	5.5±0.5	5.3±0.5	11±0.5

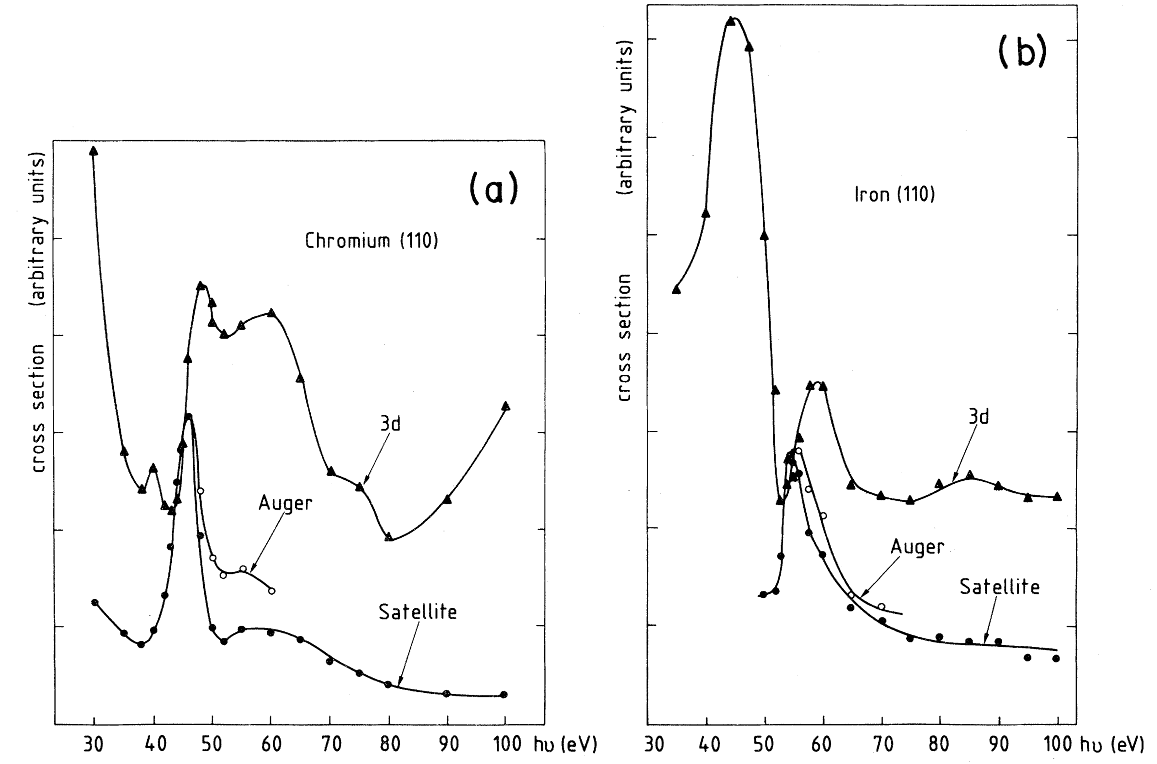

FIG. 2. Cross section of the different structures in the photoelectron spectra of chromium (a) and iron (b) normalized to the incident photon intensity. The curve labeled "3*d*" (▲) represents the heights of the peak just below the Fermi level for different photon energies. The curve labeled "Auger" (○) represents the height of the Auger peak, at constant kinetic energy (it is pointed "*A*" on Fig. 1). The curve labeled "satellite" (●) represents the height of the satellite at constant binding energy (7.5 eV from the Fermi level on chromium and 5.5 eV on iron).

Owing to the angular definition of our measurement, we may have some final-state effects on the cross section of the 3*d* levels, but these effects must be small compared to the strong structure observed at 42 eV in chromium and 52 eV in iron, which show the strong coupling between 3*p* and 3*d* electrons.

First of all, we discuss the position of the satellite relative to the main line. Using an atomic picture, the main line corresponds to electrons emitted directly from the 3*d* band:

$$3p^6 3d^n 4s + h\nu \rightarrow 3p^6 3d^{n-1} 4s + e^-$$

and the satellite corresponds to electrons emitted from atoms which are left with two correlated 3*d* holes below the Fermi level plus a low-lying excited (*nl*) electron

$$3p^6 3d^n 4s + h\nu \rightarrow 3p^6 3d^{n-2} 4snl + e^- \ .$$

The excited (*nl*) electron is mainly 3*d* or 4*s*. In this limit, the distance between the satellite and the main peak (U_{sat}) measures the main interaction energy between two 3*d* holes screened by the (*nl*) electron. The measured values of U_{sat} are listed in Table I.

The U_{sat} values are similar in the metals with unfilled *d* bands (Cr, Fe, Co, and Ni), but quite different in copper. This can be explained by a qualitative difference between these metals: In copper, the excited (*nl*) electron must be 4*s* but in the other metals it would be mainly a high-energy 3*d* state. In addition, there is a difference in the screening of the hole between nickel on one side and chromium, iron, and cobalt on the other. In nickel there is less than one 3*d* hole per atom (0.6 hole); then the screening of a deep hole by 3*d* electrons must be interatomic, whereas in the other metals, there is more than one 3*d* hole per atom and the screening could be accomplished in a single site. Nevertheless, these results

TABLE II. Binding energies of the 3*p* levels compared to the photon energies of the resonances.

	Cr	Fe	Ni
$3p^{3/2}$	42.3±0.5 eV	52.1±0.5 eV	66.2±0.5 eV
$3p^{1/2}$		53.0±0.5 eV	67.4±0.5 eV
$h\nu_{\text{res}}$	45.5±0.5 eV	54.5±0.5 eV	66.5±0.5 eV

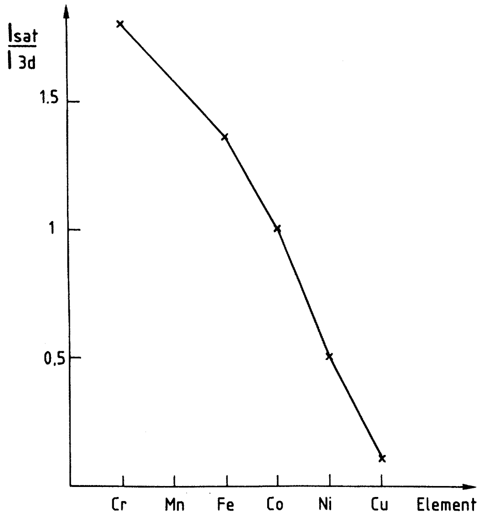

FIG. 3. The ratio between the intensity of the satellite and the intensity of the 3*d* peak, at resonance, with *s* polarized light on the (110) faces of chromium, iron, nickel, and copper and on the (000,1) face of cobalt.

suggest that the correlation energy between two 3*d* holes and the screening effects are quite similar in metals with unfilled *d* bands, but this similarity stops when the *d* band is filled.

Another fact which shows the importance of the empty 3*d* states in the satellite and resonance phenomena is the intensity of the satellite at resonance, compared to the intensity of the main line. In Fig. 3 we report the results obtained with *p*-polarized light on the (110) surfaces of copper, nickel, iron, and chromium and on the (000,1) surface of cobalt. The abscissa is the atomic number of the element. A general trend is obvious. The intensity of the satellite at resonance increases with the number of 3*d* holes.[13] It is experimental evidence of the main role of the *d* holes in the resonance phenomenon.

To compare the photon energy corresponding to the resonance of the satellite with the excitation energy of the 3*p* levels, we measured directly the binding energy and the width of the 3*p* levels, working at higher photon energy ($h\nu = 100$ eV).

The spectra are shown in Fig. 4. For iron, as for nickel, the spin-orbit splitting is resolved, but that is not the case for chromium. A satellite is clearly seen at about 6 eV from the 3*p* levels in nickel, but neither in iron nor in chromium. The results, a little different from those obtained by Bearden and Burr,[14] are summarized in Table II. Contrary to what happens in nickel, for chromium and iron the resonance occurs at an energy higher than the excitation of the 3*p* electrons to the Fermi level. We can understand these results in the atomic limit.

At resonance, there is a coupling between the two

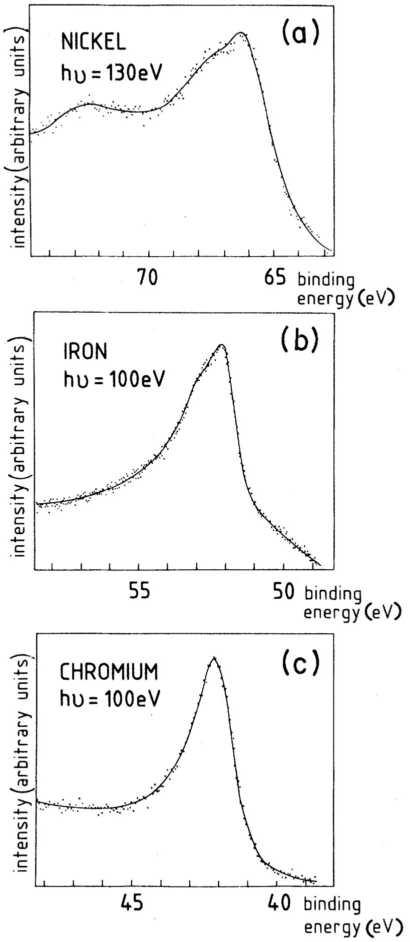

FIG. 4. The 3*p* levels of (a) nickel, excited with photons of 130 eV, (b) iron, excited with photons of 100 eV, and (c) chromium, excited with photons of 100 eV.

processes

$$3p^63d^n4s + h\nu \rightarrow 3p^63d^{n-2}4snl + e^-$$

and the other involving a 3*p* electron and a super Coster-Kronig decay

$$3p^63d^n4s + h\nu \rightarrow 3p^53d^n4snl$$
$$\rightarrow 3p^63d^{n-2}4snl + e^- .$$

As mentioned before, in metals with unfilled *d* bands, the excited (nl) electron is mainly 3*d*. In nickel, the empty 3*d* states are located just at E_F. In chromium, the 3*d* band is half filled and the empty 3*d* states extend well above the Fermi level. According to Moruzzi *et al.*[13] a paramagnetic calculation of the density of states gives the top of the *d* bands at 2 eV above E_F chromium, and a ferromagnetic calculation shows for iron a maximum of empty *d* states at 1.75 eV above E_F. The resonance occurs at a photon energy which corresponds to the excitation

TABLE III. Correlation parameters experimentally obtained in this work ($\Delta E_A = E_{3p} - 2E_{3d} - E_{\text{Auger}}$) and by $L_{23}M_{45}M_{45}$ Auger spectroscopy by Antonides *et al.* (Ref. 10) or Yin *et al.* (Ref. 11).

	Cr	Fe	Co	Ni	Cu
E_{Auger}	38.0±1 eV	48.5±1 eV	54.0±1 eV	60.0±1 eV	63.5±0.5 eV 61.5±0.5 eV
E_{3p}	42.3 eV	52.1 eV 53.0 eV	59.0 eV	66.2 eV 67.4 eV	75.0 eV 77.0 eV
E_{3d}	1.5 eV	1.5 eV	1.5 eV	1.5 eV	3.0 eV
ΔE_A	1.3±1 eV	1.0±1 eV	2.0±1 eV	4.0±1 eV	7.5±0.5 eV
U_{eff} (Ref. 10)		1 eV	1 eV	4 eV	8 eV
$\Delta\epsilon$ (Ref. 11)	1.3±0.8 eV	2.6±0.8 eV	3.7±0.8 eV	5.3±0.8 eV	8.6±0.3 eV

energy of a 3*p* electron to the maximum of the density of empty 3*d* states, and therefore at E_F for Ni and above E_F for the other transition metals. We thus corroborate the assumption of Penn[2] that in metals with unfilled *d* bands, the resonance of the satellite is related to photoexcitation of a 3*p* core electron to an empty *d* state.

For a photon energy greater than the resonance value the 3*p* core electron is photoemitted and this creation of a 3*p* hole is followed by Auger emission. In this case, we see (Fig. 1) that the Auger electrons (A) are emitted at a fixed kinetic energy which is the kinetic energy of the satellite at resonance. This indicates that the screening in the Auger process is mainly due to 3*d* excited electrons.

We can define ΔE_A as the difference between the measured kinetic energy of the Auger peak and the kinetic energy of a hypothetical Auger process with a final state with two noninteracting holes:

$$\Delta E_A = E_{3p} - 2E_{3d} - E_{\text{Auger}} \ .$$

These ΔE_A values are similar to those obtained by $L_{23}M_{45}M_{45}$ Auger spectroscopy by Antonides *et al.*[10] or by Yin *et al.*,[11] indicating that the relaxation effects are quite similar. The results are summarized in Table III.

These values obtained by Auger spectroscopy are different in nickel ($\sim$4 eV) and in iron and chromium ($\sim$1 eV), when the U_{sat} values, listed in Table I, are quite constant from chromium to nickel, indicating that the correlation energy between two 3*d* holes created below the Fermi level on the same site is similar in all these metals. Then we can suggest that the difference observed in Auger spectroscopy between nickel and iron (in this work, as well as in Refs. 10 and 11) is not mainly due to a difference in the correlation energy.

We have shown that there is a great similarity between the results obtained on metals with unfilled *d* bands with regard to the position of the satellite and its resonance. There are two further points to discuss: the difference between nickel and the other studied transition metals of the 3*d* series (persistence of the satellite above resonance, existence of a second satellite) and the comparison between the results obtained earlier on palladium[15] with all these results.

In nickel, the first satellite (at 6 eV from E_F) is observed for any photon energy, whereas for the other transition metals, it vanishes above resonance. At resonance, in nickel there is a second satellite at 13 eV from the Fermi level which we assigned to a $3d^7$ final state (three holes on the same atom). This second satellite is never observed in other metals. We can understand the persistence of the satellite above the resonance, considering the higher localization of the 3*d* orbitals of nickel. The process

$$3p^63d^n4s + h\nu \rightarrow 3p^63d^{n-2}4snl + e^-$$

is still possible above resonance. Actually, in the other metals where the behavior of the 3*d* electrons is more bandlike (the width of the *d* band increases when the number of *d* electrons decreases), the lifetime of such an atomic excitation is shortened. Therefore, the probability of this process vanishes above resonance, and only the Auger effect exists.

This difference was pointed out by Davis and Feldkamp[6] and by Parlebas *et al.*[16] who showed that different relaxation and screening effects of the conduction electrons can highly favor the Auger peak to the detriment of the satellite above resonance. In the same manner, the localization of the 3*d* electrons can favor at resonance the creation of a 3*d* hole simultaneously with the creation of the 3*p* hole, which leads to a final state with three correlated holes:

$$3p^63d^n4s + h\nu \rightarrow 3p^53d^{n-1}4s(2nl)$$
$$\rightarrow 3p^63d^{n-3}4s(2nl) + e^- \ .$$

This process corresponds to the second satellite observed at resonance in nickel. In the same manner, Eastman *et al.*[17] observed a smaller band narrowing in cobalt compared to nickel. They explained this effect by involving the more diffuse free-electron-like behavior of the *d* orbitals and the presence of more empty *d* levels in cobalt which make the two-hole one-electron state more short lived.

The last remark is about the results on palladium. The distance between the satellite and the *d* band is of the same order of magnitude as those obtained in the 3*d* transition metals (~ 6 eV). But this satellite is observable only at resonance, and even at resonance, it is small (about 10% of the *d* band peak). Moreover, the Auger peak, at fixed kinetic energy, is never observed. These results are in agreement with our previous arguments.

(i) The position of the satellite indicates a similar kind of two-*d*-hole interaction and screening for 4*d* electrons as for 3*d* electrons.

(ii) The absence of an Auger peak can be explained by the width of the 4*p* levels (which are broader than the 3*p*) because of interconfiguration interaction.

(iii) The low intensity of the satellite at resonance can have two origins: Firstly, the small number of *d* holes (about 0.3) and secondly, the absence of an Auger peak at any photon energy, and consequently at resonance.

For chromium we should mention the earlier results obtained by Barth *et al.*[18] They claimed that they observed no resonance of the satellite when scanning the photon energy through the 3*p* threshold. We disagree with them. Let us just notice that the satellite and Auger peak that we obtained seem to be narrower than theirs, and that our background is very smooth, maybe because of the use of a single crystal.

In conclusion, these experiments show clearly the importance of the empty 3*d* states on the resonance of the valence-band satellite at the 3*p* excitation threshold of transition metals with unfilled *d* bands. We also suggest that the correlation energy between two 3*d* holes must be quite constant for all these metals. The main difference between nickel and the other metals with unfilled 3*d* bands (second satellite at resonance, persistence of the first satellite above the resonance) may be related to the delocalization of the 3*d* electrons and the different screening mechanisms.

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