

Comments on the electronic structure of nickel

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We comment on some recent theoretical discussions concerning the electronic structure of nickel and more particularly the position and the weight of the satellite observed in ultraviolet-photoemission spectra (UPS) and x-ray-photoemission spectra (XPS) experiments. We argue that there is no fully satisfactory quantitative theory at the moment for dealing with correlation effects within the d band. The ratio U/W (U is the Coulomb integral, W is the d -band width) is shown to be most probably in the range 0.5–1. The observed narrowing of the d band and Auger spectra are also briefly discussed.

I. INTRODUCTION

The interpretation of some features of the electronic structure of nickel as determined from photoemission experiments remains quite controversial; the width of the observed d bands is narrower than that obtained from self-consistent band calculations¹ and a satellite is observed about 6 eV below the Fermi energy.² Several recent theoretical studies^{3,5} agree in relating both these features to correlation effects within the d band, and the Hubbard model is usually considered to be an appropriate model for describing these effects. Our purpose here is to comment on these works, with special emphasis on a recent letter by Penn.³ In particular we want to discuss the relationships between the characteristics of the satellite (position, intensity) and the assumed value of the Coulomb interaction U . Although we agree that the states in the satellite are to be related to rather localized two-hole excitations, we will argue that there is no satisfactory theory from a quantitative point of view. We do not intend to discuss the resonant behavior of the satellite as seen in ultraviolet-photoemission spectra (UPS) for phonon energies near 67 eV,² and therefore confine ourselves to a discussion of x-ray-photoemission (XPS) spectra.^{6,7}

A simple and convenient extension of the Hubbard model is that used by Penn:

$$H = \sum_{k,n,\sigma} \epsilon_{k,n} a_{k,n,\sigma}^\dagger a_{k,n,\sigma} + \frac{1}{2} U \sum_{n,\sigma,n',\sigma',l} (1 - \delta_{nn'} \delta_{\sigma\sigma'}) n_{l,n,\sigma} n_{l,n',\sigma'} \quad (1)$$

The notations are identical to Penn's; let us just recall that k , l , n , and σ are band, site, degeneracy, and spin indices, respectively. Note that exchange integrals have been neglected so that this

model cannot consistently be used for discussing the occurrence of ferromagnetism. The characteristics of the satellite will be shown to be not very dependent on nickel being ferromagnetic or paramagnetic (in XPS at least or in UPS far from resonance⁵), and in the following we will only consider paramagnetic nickel.

II. VALIDITY OF THE t -MATRIX APPROXIMATION

The photoemission current is directly related to the hole excitation spectrum, i.e., to the total one-particle spectrum for energies below the Fermi energy. Then this spectrum is obtained from the knowledge of the single-particle retarded Green's function. This Green's function, or equivalently, the corresponding self-energy is not known in general for the Hubbard model. Only in some limiting cases can exact results be obtained. In particular Penn has used an expression that is exact when the number of holes (or electrons) in the d band is very small.⁸ We completely agree with his formulation and even with his further simplification of performing intermediate averages over \vec{k} vectors; this amounts to neglecting selection rules, or equivalently when going back in real space, to only including repeated scatterings on a single site. This local approximation is perfectly justified in general.⁹

Our main argument is that the hole concentration in nickel cannot be considered as being small. Let N_h be the number of holes per atom; it might seem that the hole concentration to be used is N_h divided by ten, the total number of atomic states, in which case the concentration would be actually very small, in nickel ($N_h = 0.6$), but this is not the case. Consider, for example, the atomic limit $U/W \rightarrow \infty$. Then the ground state is known. Considering only the d population, we are left with only d^9 and d^{10} atoms (this is the minimum

polarity model of Van Vleck¹⁰) whose concentrations are $N_h = 60\%$ and $1 - N_h = 40\%$, respectively. Single-particle excited states are also easily obtained and correspond to atomic transitions that may be analyzed as follows: first we find $9N_h$ possible $d^9 \rightarrow d^8$ transitions that involve the excitation energy $8U = 36U - 28U$, then $N_h d^9 \rightarrow d^{10}$ and $10(1 - N_h) d^{10} \rightarrow d^9$ transitions, each one involving the energy $9U = 45U - 36U$; therefore the weights of $d^9 \rightarrow d^8$ and $d^{10} \rightarrow d^9$ atomic transitions, with energies $8U$ and $9U$, are respectively $9N_h/10$ and $1 - 9N_h/10$. If only hole excitations are considered, the weights become $9N_h/N_e$ and $1 - 9N_h/N_e$, where $N_e = 10 - N_h$ is the number of electrons. Even if this limit does not correspond to a realistic situation (the relative population of d and sp electrons should vary as a function of U), this argument shows that for large U the relevant hole concentration is $9N_h/10 \approx N_h$ and not $N_h/10$.

Another more or less equivalent argument is based on the alloy analogy of the Hubbard model.¹¹ Note first that the alloy analogy applied to the degenerate model (1) requires some caution. If the motion of all electrons but one is frozen, we are reduced to the problem of a ten-constituent alloy, but the concentrations of the alloy constituents have to be determined in a self-consistent way.¹² Anyway for low hole concentrations, a binary alloy is recovered, and we have the problem of an electron scattered by d^8 and d^9 atoms, with effective potentials $8U$ and $9U$, respectively, and the relevant concentration involved in the formation of the satellite (scattering by d^8 atoms) is again $9N_h/10$. The numerical factor 9 is easily understood since it corresponds to the number of scattering channels of a given electron. This argument still holds in the ferromagnetic case. The number of scattering channels is then four or five depending on the spin, but since the number of states per spin direction is five, the relevant hole concentration becomes $\frac{4}{5}N_h$ or N_h . Thus, when using the alloy analogy for nickel, all configurations d^n , $n = 0, \dots, 9$ must be taken into account. As a result for large but finite values of U several peaks located at nU will appear.

On the other hand, it should be pointed out that the t -matrix approximation cannot properly describe the position and the weight of the satellite, even when the hole concentration is very low. For large values of U the self-energy has a pole (in principle several poles corresponding to different values of the two-hole momentum, but the local approximation is equivalent to neglecting the dispersion of the two-hole bound states), and in the strict dilute limit, this yields a pole at the same position in the Green's function. But inserting the approximate self-energy in the Green's func-

tion at finite concentration leads to a narrow satellite whose mean position and weight are not correct. Here again, using the alloy analogy is quite instructive. In alloy theory there is also a well known t matrix approximation, but in this case we have a better self-consistent approximation, the coherent-potential approximation.¹³ It is rather easy to show that for any small but finite value of the concentration, the coherent-potential approximation (CPA) does not reduce to the t -matrix approximation, as far as the impurity band (corresponding to the satellite) is concerned, at least. The CPA does yield an impurity band centered on $-U$ (the origin of energies is taken at the center of the main band), whereas the t -matrix approximation leads to an impurity band below $-U$. In particular in the atomic limit both the exact and the alloy t -matrix approximations yield bound states at $-(1 + \frac{9}{10}N_h)U$ instead of $-U$. From a mathematical point of view, the problem is that near the pole, the self-energy is finite even if the concentration is very small so that the expansion in successive powers of the concentration is no longer convergent. Thus, using the t -matrix approximation leads to an overestimate of the splitting of the satellite. This is apparent in Fig. 2 of Penn³ where it can be seen that the satellite is already well marked and is 8 eV below the Fermi energy for a moderate value of U , $U = 2$ eV. We have performed similar calculations and have found similar results.

III. PERTURBATION METHOD

Another possible approach is to use standard perturbation theory and calculate the self-energy up to U^2 terms. This may be realistic for reasonably small values of U/W , where W is the d -band width obtained from band calculations (about 4.5 eV for nickel). The linear Hartree-Fock term is assumed to be included in the initial energy levels; then making again a local approximation,⁹ the self-energy is independent of k , n , and σ and is given by

$$\begin{aligned} \Sigma(E) = 9U^2 \int dE_1 dE_2 dE_3 \{ & f(E_1)[1 - f(E_2)][1 - f(E_3)] \\ & + [1 - f(E_1)]f(E_2)f(E_3) \} \\ & \times \frac{n(E_1)n(E_2)n(E_3)}{E + E_1 - E_2 - E_3}, \end{aligned} \quad (2)$$

where $f(E)$ is the usual step Fermi-Dirac function, and $n(E)$ the unperturbed density of states. Kleinman has recently performed a similar calculation,¹⁴ but has apparently missed the second term. Actually this is the most important term. As a result, the real part of Σ is positive at the top

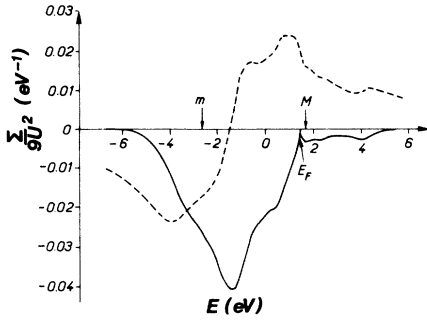


FIG. 1. Second-order self-energy for nickel, calculated within the local approximation: —, $\text{Im}\Sigma/9U^2$ (eV^{-1}); ----, $\text{Re}\Sigma/9U^2$ (eV^{-1}). For $U = W/2$ ($W = 4.5$ eV) the maximum value of $|\text{Im}\Sigma|$ is about 1.5 eV; m and M are the unperturbed band edges.

of the band, whereas Kleinman found a negative contribution (Fig. 1). In the dilute limit, the first term is negligible compared to the second one, and the second-order term of Penn's expression is recovered. On the other hand Eq. (2) is valid for any hole concentration. The behavior of $\Sigma(E)$ and of the one-particle spectrum for various fillings of the d band is described elsewhere.⁹ We shall just comment here on the results obtained for paramagnetic nickel. In Fig. 2 are shown the bare density of states calculated within a tight-binding scheme, and the one-particle spectrum obtained from the previous second-order perturbation theory. It may be seen that the agreement with the experimental XPS results is rather good for $U/W = 0.5$, $W = 4.5$ eV. At the present time we have no precise idea of the rate of convergence of the perturbation series, so that

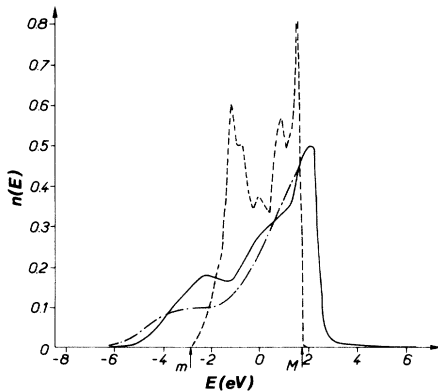


FIG. 2. Deformation of the one-particle spectrum of nickel induced by correlations [$n(E)$ in arbitrary units]: —, one-particle spectrum for $U/W = 0.5$, $W = 4.5$ eV; ----, unperturbed density of states of nickel; - · - · -, experimental XPS curve.⁷

we do not argue that these results are basically better than Penn's (perturbation theory probably underestimates the splitting of the satellite), but we have shown that from a semiquantitative point of view, a simple perturbation theory gives comparable results. Obviously it is no more possible within perturbation theory to describe the states of the satellite as being true quasibound states, but the physical effect is the same. The coupling of single hole to two-hole excitations induced by correlations produces a low energy weak satellite in the one-hole spectrum. We have checked that this effect is not very sensitive to the choice of the bare density of states.

IV. GENERAL DISCUSSION

As argued before, the dilute limit of the Hubbard model is not very appropriate to nickel. On the other hand for U values of a sizeable fraction of the band width, perturbation theory is probably not accurate enough. So we are faced with the problem of obtaining a reliable solution of the Hubbard model for intermediate couplings. Recently Davis and Feldkamp⁴ have given a numerical exact solution of the nondegenerate Hubbard model in the strong ferromagnetic case. Unfortunately, the basic feature that allows this calculation is that there is no scattering channel for an electron in the minority band, and it is difficult to extrapolate their results in the present case where scattering within the minority band is allowed. Finally the simplest theory that provides one-particle spectra is probably Hubbard's original theory¹¹ which is equivalent to the CPA when only the so-called scattering corrections are included. Unfortunately here again, the alloy analogy that completely neglects dynamical effects is not very good when studying the satellite for intermediate values of U/W . As explained before these dynamical effects (coupling of one-hole to two-hole excitations) are responsible for the diffuse nature of the satellite. As a result, within the CPA, states that are below the main band contribute to a separate and narrow impurity band. Including the so-called broadening corrections¹¹ would probably improve the situation, but from this discussion it can be concluded that the position of the satellite for intermediate values of U/W is very dependent on the approximations that are made, and it is very difficult to deduce U from experimental data.

Despite this, it is almost certain that U/W is of the order of 0.5–1; for very small values of U , no satellite at all is expected. For larger values of U , the satellite should occur, but with a very large amplitude: about 50% of the total spectral

weight in the atomic limit. Another argument is that an additional satellite has been observed (in UPS, at resonance, at least¹⁵). Within the present scheme this satellite should correspond to three-hole final states and would be at distance $2U$ below the main band for large values of U . But the corresponding two-hole initial states would not be allowed for very large values of U : large fluctuations in effective atomic configurations are suppressed when the intra-atomic correlations are important,^{10,16,17} which means that the weight of this second satellite and, *a fortiori*, of possible other ones vanishes in the atomic limit. On the other hand, it should be kept in mind that the Hamiltonian (1) is oversimplified; introducing exchange terms would reduce the scattering in some channels, and larger values of U should be used in order to reproduce the experimental data.

Let us now briefly comment on correlation effects in the main band. From the knowledge of the self-energy as obtained by perturbation theory [Fig. 1, but the overall shape of $\Sigma(E)$ is quite general¹⁸] we may draw some conclusions. First of all and in agreement with Landau theory, the spectral width, related to $\text{Im}\Sigma$ increases away from the Fermi level. Since the width due to correlation effects vanishes in copper (filled d band) but not for nickel or other transition metals,³ we have an appealing explanation for the corresponding observed widths.¹⁹ As far as the narrowing of the d bands is concerned, the situation is less clear. Having used a local second-order self-energy, the shift of the states, related to its real part only depends on the energy, provided that differences in $t_{2\sigma}$ and e_{σ} bare densities of states are neglected (this may be a poor approximation for states close to the Fermi level that are mainly $t_{2\sigma}$). Then, looking at Fig. 1, it is realized that the upper bands will tend to narrow because the real part of Σ is a decreasing function of E in this energy range. It might be suspected that the opposite behavior should be observed in the lower part of the band, but this is not so, because the spectral lines in this energy range are split into bandlike states and satellite states⁹ and finally, we do have a narrowing of the main band. Note however that the satellite states have not been observed in angular resolved UPS, for low photon energies.¹ It might be that matrix elements are very different for band and satellite states. In the ferromagnetic case, we would obtain two self-energies Σ_{\uparrow} and Σ_{\downarrow} such that $\Sigma_{\uparrow}/\Sigma_{\downarrow} = \frac{5}{4}$. Therefore the upwards shift of the majority spin states will be larger than that of the minority spin states, which might explain the observed reduction of the exchange splitting¹ (~ 0.3 eV instead of 0.6 eV as obtained from band calculations).

V. AUGER SPECTRA

Closely related to the previous discussion is the behavior of Auger spectra in metals containing filled or partially filled d bands. Antonides *et al.*²⁰ and Cini²¹ have pointed out that the spectra of Ni, Cu, Zn, ..., could only be explained if quasiatomic two-hole states occur in these elements. For a completely filled shell, Sawatsky²² has calculated the two-hole spectrum, using the t -matrix approximation which is exact in that case. Neglecting again nonlocal contributions, the local two-hole Green's function $D(E)$ writes:

$$D(E) = \frac{D^0(E)}{1 - UD^0(E)}, \quad (3)$$

$$D^0(E) = \int dE_1 dE_2 \frac{n(E_1)n(E_2)}{E - E_1 - E_2},$$

which is completely equivalent to Cini's result.²¹ This is not surprising since Cini has treated correlation effects on a single atom, which is equivalent to our local approximation. In the atomic limit and within this approximation, there is a single pole related to localized two-hole bound states. It has been argued^{20,22} that the apparent absence of bandlike two-hole intensity in Auger spectra implies that this atomic limit should be used (i.e., very large values of U/W). This may be true for Cu, Zn, and beyond, but actually moderate values of this parameter can also explain the data, particularly those concerning nickel. As pointed out by Cini, and as may be seen from his Fig. 1, there is no bound state when $U/W \sim 0.4-0.6$, but the spectral intensity is clearly confined in a rather narrow energy range, much narrower anyhow than the width $2W$ corresponding to an uncorrelated state.

On the other hand and as argued above, the t -matrix approximation is probably invalid in the case of nickel. In particular, in the atomic limit two peaks are expected corresponding to initial d^{10} and d^9 configurations, and separated by $2U$. For intermediate values of U we expect a main atomiclike contribution corresponding to rather localized two-hole final states, a weak bandlike continuum at higher kinetic energies,²² and a diffuse satellite at lower energies corresponding to three-hole final states. Since there are other processes leading to such states (e.g., the Coster-Kronig $L_2L_3M_{45}$ process mentioned by Antonides *et al.*²⁰) even for an initial full d shell the latter effect may not be easily observable.

VI. CONCLUSION

So, we agree with several recent works and with the older conjecture by Mott²³ that the satellite

observed in nickel is most probably related to correlation effects within the d band, and we believe that a simple perturbation theory may be useful in the absence of better approximate solutions of the Hubbard model for the relevant range of parameters (number of holes, U/W). This satellite should also be visible in palladium, but with a weaker intensity, since U/W is probably smaller than in nickel, and since there are fewer holes in the d band. This seems to be the case, in UPS at least and at resonance.²⁴

Of course, it would be highly desirable to account for the detailed information provided by angular resolved UPS. A consistent treatment of nickel should explain not only the gross features of the satellite, but also its resonant behavior,³ its possible polarization,⁵ the narrowing of the bands,

and the small splitting between majority and minority bands.¹ Explaining all these facts using a model such as the Hubbard model with only a few parameters would be much more convincing of the importance of correlation effects than what has been done up to now. Some work is currently done in this direction. Note that there remains the problem of the bare band structure to be used, since the Hartree-Fock approximate solution of the Hubbard model is certainly not equivalent to the local-density-functional method on which are based most of the recent band calculations.

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