

Effect of Self-Energy Corrections on the Valence-Band Photoemission Spectra of Ni

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It is shown that the experimentally observed band narrowing, the large quasiparticle damping, the small exchange splitting, and the existence of satellites can be reproduced semiquantitatively with use of the low-density approximation to describe correlations between Ni 3*d* electrons. The exchange splitting of t_{2g} states (~ 0.37 eV) is found to be considerably larger than that between e_g states (~ 0.21 eV). A new satellite is predicted about 2 eV below the main "6-eV" satellite.

The valence spectra of bulk Ni have received considerable attention since they exhibit several features which cannot be reconciled with the one-electron band model: (i) the width of the Ni 3*d* band is about 25% smaller¹ than that predicted theoretically²; (ii) the intrinsic width of spectral features in angle-resolved energy distributions is about 1.2 eV near the bottom of the *d* band,³ i.e., much larger than in the case of Cu; (iii) the measured exchange splitting³⁻⁵ (0.25–0.35 eV) is approximately half as large as that derived from band theory² (0.65 eV); and (iv) a shakeup structure is observed^{1,6} at about 6 eV below the Fermi energy.

The purpose of the present paper is (a) to predict the existence of yet another satellite at about 2 eV below the main satellite, and (b) to show

that all four observations described above can be semiquantitatively understood on the basis of correlations among *d* electrons which determine the spectral distribution of the created hole. The exchange splitting of t_{2g} states (~ 0.37 eV) is found to be nearly twice as large as that of e_g states (0.21 eV) due to the nonspherical nature of the spin density. The new satellite is predicted to have purely majority spin polarization and to exhibit very weak Fano enhancement. It is shown that this feature is the remnant of the ¹S term of the atomic d^8 multiplet. The remaining terms combine to a main satellite or merge with the *d*-band states.

The spectral function of the hole which is created in the photoemission process is given by the expression

$$A_{n\sigma}(\omega, \vec{k}) = \frac{1}{\pi} \frac{\text{Im}\Sigma_{n\sigma}(\omega, \vec{k})}{[\omega - \epsilon_{\vec{k}n\sigma} - \text{Re}\Sigma_{n\sigma}(\omega, \vec{k})]^2 + [\text{Im}\Sigma_{n\sigma}(\omega, \vec{k})]^2}, \quad (1)$$

where $\epsilon_{\vec{k}n\sigma}$ are the band energies and $\Sigma_{n\sigma}(\omega, \vec{k})$ are the diagonal elements of the self-energy matrix. It is assumed that off-diagonal elements can be ignored. The degenerate Hubbard model⁷ is used to describe the interactions between *d* electrons. Since the number of hole states in the Ni *d* band is small and the interaction between *d* electrons is short ranged, the low-density approximation is assumed to be adequate.^{8,9} In this limit, the self-energy may be written in terms of the *t* matrix, $t = (U^{-1} + G^{(2)})^{-1}$. $G^{(2)}$ denotes the two-particle Green's function and U is the intra-atomic Coulomb matrix:

$$U = \langle \varphi_{m_1}(\vec{r}_1) \varphi_{m_2}(\vec{r}_2) | H_{12} | \varphi_{m_3}(\vec{r}_1) \varphi_{m_4}(\vec{r}_2) \rangle, \quad (2)$$

where the φ_m are atomic *d* functions. Since the full \vec{k} dependence of the spectral function is not of primary interest at this point, the additional approximation is made of replacing $G^{(2)}$ by its average over \vec{k} and over band and spin indices:

$$g(\omega) = \int d\epsilon_1 \int d\epsilon_2 \frac{\rho(\epsilon_1)\rho(\epsilon_2)f(\epsilon_1)f(\epsilon_2)}{\omega - \epsilon_1 - \epsilon_2 - i\delta}, \quad (3)$$

where ρ represents the average density and f the Fermi function. The direct and exchange processes can then be shown to give the following expression for the self-energy¹⁰:

$$\Sigma_{i\sigma}(\omega) \approx - \sum_{\alpha=1}^5 \sum_{j=1}^2 A_{ij\alpha} n_{j\downarrow} \tau_{\alpha}(\omega), \quad (4)$$

with $i \equiv t_{2g}, e_g$. The $n_{i\downarrow}$ denote the number of holes per minority t_{2g} and e_g band and the τ_{α} are defined as $\tau_{\alpha}(\omega) = u_{\alpha} / [1 + u_{\alpha} g(\omega)]$, where u_{α} are the eigenvalues of the Coulomb matrix (2). These eigenvalues specify the term energies of the d^8 configuration which can be expressed in terms of the usual Coulomb integrals:

$$u_{\alpha} = F^{(0)} + a_{\alpha} F^{(2)} + b_{\alpha} F^{(4)}. \quad (5)$$

The numerical values of the coefficients in Eqs. (4) and (5) will be given elsewhere.¹⁰

Equation (4) demonstrates that each multiplet term introduces its own structure into the various components of the self-energy and, via Eq. (1), of the spectral function. The binding energy,

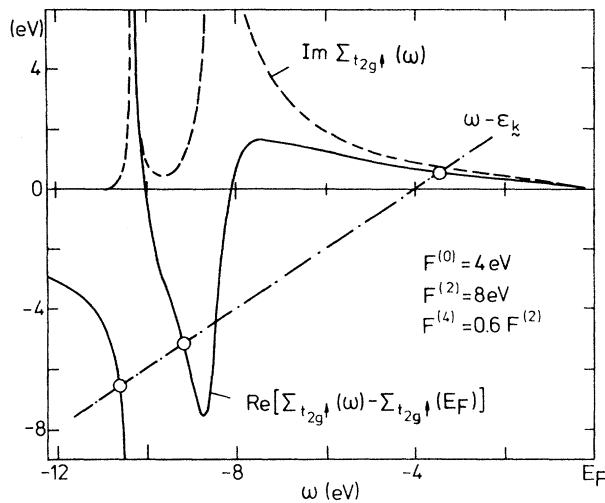


FIG. 1. Real and imaginary parts of t_{2g} up-spin self-energy. The intersections with the line $\omega - \epsilon_{\vec{k}}$ specify the shifted quasiparticle energies and the positions of the satellites.

at which such a spectral feature might appear, depends critically on the size of the term energies u_{α} . For small values of u_{α} , only a small and nearly energy-independent contribution to the self-energy is obtained. For sufficiently large values of u_{α} , on the other hand, τ_{α} exhibits singularities at energies given by the condition $1 + u_{\alpha}g(\omega_{\alpha}) = 0$. Since $g(\omega)$ behaves asymptotically as $c^2(\omega - \epsilon_2)^{-1}$, where c is the average occupancy per band and ϵ_2 the center of gravity of the two-particle density, the self-energy has poles at energies $\omega_{\alpha} = \epsilon_2 - c^2 u_{\alpha}$. Thus, in the limit of narrow bandwidth or large Coulomb energies, the excitation spectrum reflects precisely the atomic multiplet of the d^8 configuration.

For a realistic set of Coulomb integrals, the real and imaginary parts of the t_{2g} up-spin component of the self-energy are shown in Fig. 1. The density of d states, on which these results are based, is obtained from a self-consistent linear combination of muffin-tin orbitals calculation for ferromagnetic Ni, i.e., the effect of hybridization with the s - p band is included. The number of holes per t_{2g} and e_g band are 0.14 and 0.06, respectively. For the $F^{(n)}$ used in Fig. 1, the u_{α} range from 2.6 to 7.7 eV. Only the 1S term leads to a singularity in $\text{Re}\Sigma$, whereas the 1G , 3P , and 1D contributions form a single peak. The term with the smallest u_{α} , 3F , gives a weak, slowly varying contribution.

Figure 2 shows the (a) majority and (b) minority spectral densities for t_{2g} and e_g states at 4 eV be-

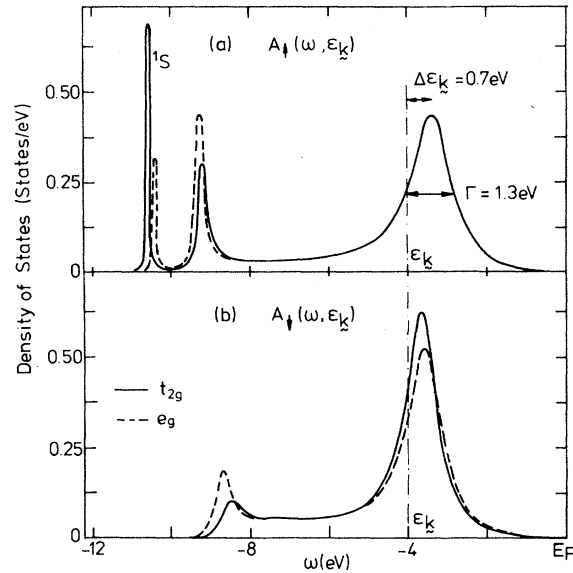


FIG. 2. Spectral distribution of (a) majority and (b) minority states at 4 eV below E_F . The peak marked 1S represents the new satellite in the majority density. The features between 8 and 9 eV in (a) and (b) represent the main shakeup structure below the d band.

low E_F . The up-spin states are shifted by about 0.7 eV toward E_F and broadened by 1.3 eV. These values compare reasonably well with measured shifts of about 1 eV and linewidths of approximately 1.2 eV for states near the bottom of the d band.³ The calculated self-energy corrections of the down-spin states, on the other hand, are noticeably smaller. Moreover, only one satellite is split off below the band. The physical origin of these differences lies in the fact that, in the case of excitation from a down-spin state, there is a partial cancellation between Coulomb and exchange processes. As a result, only $M_S = 1$ atomic final states are allowed, i.e., only the 1P and 3F states can be excited. This cancellation does not occur in the case of emission from majority states, i.e., all five configurations of the $M_S = 0$ atomic final state are allowed. Thus, the 1S satellite can appear only in the up-spin spectrum and the contributions to the main satellite are much stronger for majority states than those for minority states.

Figure 1 illustrates that the shift of band states toward E_F as well as their damping decrease roughly linearly with binding energy. The same trend is observed in angle-resolved spectra.³ The binding energy of the satellites also decreases slightly. Thus, the \vec{k} -integrated minority density has a satellite at about 8.5 eV whereas the two satellites in the majority density are located

near 9.0 and 10.5 eV. The weight of the 1S peak relative to that of the main satellite in the total density of states is about 0.2, which might make it difficult to observe this feature experimentally. Moreover, because of selection rules, the 1S term contributes only very weakly to the Auger decay of $3p$ core levels.¹¹ This implies that this satellite should show very little Fano enhancement near the $3p$ threshold.

The multiplet splitting of the Ni satellites and their partial overlap with the band states influences their net polarization. The numerically obtained ratio between the total up- and down-spin satellite intensities ranges from 2 to 4 depending on the energy range over which the intensities are integrated. Thus, there is considerable spread about the nominal statistical ratio of 2.5. It seems likely, however, that the recently predicted¹² enhancement of the satellite polarization near the $3p$ threshold will persist.

Equation (5) indicates that the magnitude of $F^{(2)}$ and $F^{(4)}$ mainly influences the splitting between satellites whereas $F^{(0)}$ determines their mean position. A decrease of $F^{(0)}$ would therefore lower the satellite binding energies in Fig. 2 by about the same amount. In this manner, better agreement with the observed peak at 6 eV could be achieved. At the same time, however, the self-energy corrections of the band states would be reduced. Possible sources of this discrepancy are the limited validity of the low-density approximation, the neglect of the \vec{k} dependence of $G^{(2)}$ in Eq. (3), and the omission of other than intra-atomic Coulomb interactions. Also, in principle, the self-energy should be calculated self-consistently. This might lead, for fixed $F^{(n)}$, to an additional band narrowing since, at each iteration step, weight is removed from states near the bottom of the band. An additional complication lies in the possible accidental overlap of the satellites with d^8p^1 excited states which are thought to be the origin of satellites seen for atomiclike Ni on carbon substrates.¹³ A careful examination of the 6 to 12 eV range of bulk Ni spectra might help to clarify this situation.

The results presented in Fig. 2 do not yet include any readjustment of the density of states due to the exchange splitting which is derived from Eq. (4). For t_{2g} and e_g states, this splitting is given by

$$\Delta_i = \sum_{\uparrow\downarrow} \epsilon_i(E_F) - \sum_{\uparrow\downarrow} \epsilon_i(E_F), \quad i = t_{2g}, e_g. \quad (6)$$

The numerical values obtained for the same $F^{(n)}$ as in Figs. 1 and 2 are $\Delta_{t_{2g}} = 0.37$ eV and $\Delta_{e_g} = 0.21$

eV. States of mixed symmetry should be split by some intermediate amount. These results are in excellent agreement with the measured exchange splittings which lie between 0.25 and 0.35 eV at different points in the Brillouin zone.³⁻⁵ It would be of interest to determine experimentally whether a systematic trend is indeed observable as the character of states changes between t_{2g} and e_g in angle-resolved spectra. The origin of the difference between $\Delta_{t_{2g}}$ and Δ_{e_g} lies in the nonspherical nature of the spin density. If an identical number of t_{2g} and e_g holes had been used, both $\Delta_{t_{2g}}$ and Δ_{e_g} would be equal to 0.31 eV. This kind of enhancement of $\Delta_{t_{2g}}$ relative to the average exchange splitting, accompanied by a reduction in Δ_{e_g} , agrees well with theoretical estimates¹⁴ based on neutron scattering data.

The calculated values of $\Delta_{t_{2g}}$ and Δ_{e_g} do not depend sensitively on the choice of the Coulomb integrals. Their magnitude is determined by the small size of the $\tau_\alpha(E_F)$ which may be interpreted as effective Coulomb energies appropriate to the energy range near E_F . The $\tau_\alpha(E_F)$ were found not to exceed a value of about 3 eV even if the u_α are as large as 6 eV. Thus, realistic estimates give for $\Delta_{t_{2g}}$ an upper limit of about 0.45 eV. A similar reduction of Δ has also been predicted to occur as a result of self-energy corrections due to electron-magnon scattering.¹⁵ However, no quantitative estimate of the importance of this effect for Ni has been given so far. As a consequence of the small exchange splittings, the t_{2g} and e_g majority bands are shifted very close to E_F . Such a shift has been shown¹⁶ to be consistent with the observed photon energy dependence of the spin polarization for Ni.¹⁷

In conclusion, it has been demonstrated that the hole spectral function contains significant self-energy correlations due to d -electron correlations. These correlations lead to atomiclike spectral features which coexist with bandlike behavior. The atomic multiplet is not fully developed, however, and the band states are considerably shifted as well as broadened. Also, the correlations ensure that the exchange splitting of the hole spectrum is only about half as large as that which characterizes the ground states. Whereas these phenomena do not occur in Cu because of its filled d shell, it clearly would be of interest to investigate analogous effects in Co and Fe. This would require an extension of the present theory because of the limited applicability of the low-density approximation in these materials.

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- ¹S. Hüfner, G. K. Wertheim, N. V. Smith, and M. M. Traum, *Solid State Commun.* **11**, 323 (1972).
²C. S. Wang and J. Callaway, *Phys. Rev. B* **15**, 298 (1977).
³W. Eberhardt and E. W. Plummer, to be published.
⁴E. Dietz, U. Gerhardt, and C. J. Maetz, *Phys. Rev. Lett.* **40**, 892 (1978).
⁵D. E. Eastman, F. J. Himpsel, and J. A. Knapp, *Phys. Rev. Lett.* **40**, 1514 (1978).
⁶C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétrouff, and L. M. Falicov, *Phys. Rev. Lett.* **39**, 1632 (1977).
⁷J. Hubbard, *Proc. Roy. Soc. London, Ser. A* **277**, 237 (1964).
⁸J. Kanamori, *Prog. Theor. Phys.* **30**, 235 (1963).
⁹D. Penn, *Phys. Rev. Lett.* **42**, 921 (1979).
¹⁰A. Liebsch, to be published.
¹¹E. Antonides, E. C. Janse, and G. A. Sawatzky, *Phys. Rev. B* **15**, 1669 (1977).
¹²L. A. Feldkamp and L. C. Davis, *Phys. Rev. Lett.* **43**, 151 (1979).
¹³G. G. Tibbetts and W. F. Egelhoff, *Phys. Rev. Lett.* **41**, 188 (1978).
¹⁴O. Gunnarsson, *J. Phys. F* **6**, 587 (1976).
¹⁵D. M. Edwards, in *Transition Metals—1977*, edited by M. J. G. Lee, J. M. Pern, and E. Fawcett, The Institute of Physics Conference Series No. 39 (The Institute of Physics, Bristol and London, 1978), p. 279; P. W. Anderson, *ibid.*, p. 729.
¹⁶J. D. Moore and J. B. Pendry, *J. Phys. C* **11**, 4615 (1978).
¹⁷W. Eib and S. F. Alvarado, *Phys. Rev. Lett.* **37**, 444 (1976).

Random Antiferromagnetic Chain

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The quantum spin- $\frac{1}{2}$ Heisenberg antiferromagnet in one dimension with randomly distributed coupling constants is solved approximately. Ground-state energies and low-temperature properties are obtained for several distributions of coupling constants (including both singular and nonsingular distributions). Power-law temperature dependence in specific heat and in susceptibility are found for all distributions studied.

The random one-dimensional Heisenberg antiferromagnet with nearest-neighbor interactions is defined by the Hamiltonian

$$H = \sum_{r=1}^L K_r \vec{S}_r \cdot \vec{S}_{r+1} \quad (1)$$

with $L \rightarrow \infty$. Here \vec{S}_r are taken to be spin- $\frac{1}{2}$ operators. The coupling constants K_r are different for different r . Their values are distributed randomly following a certain probability $P(K)$, $0 < K < J$. The random antiferromagnetic chain does not have the translational invariance of the uniform system (where all K_r 's are equal). Consequently, it does not have the spin-wave spectrum of the uniform case, which is difficult enough to have defied analytic solution. Thus, even an approximate solution becomes difficult for the random antiferromagnet, not to mention an exact analytic or numerical solution.

Earlier theoretical investigations were motivated by experimental interest. There are systems which can be modeled by (1). These include poly(metal phosphinates)¹ and $(\text{CD}_3)_4\text{NMn}_x\text{Cu}_{1-x}\text{Cl}_3$

(TMCC: Cu).² More well known are the organic charge-transfer compounds N-methyl-phenazinium tetracyanoquinodimethanide (NMP-TCNQ), quinolinium tetracyanoquinodimethanide [$\text{Qn}(\text{TCNQ})_2$], etc.^{3,4} Bulaevskii *et al.*³ transformed the problem to a Fermi-gas model. In order to explain the singular temperature dependence of the susceptibility of TCNQ, they assumed singular energy dependence of the Fermion density of states even if $P(K)$ is not singular, without theoretical justification. Their results were criticized by Theodorou and Cohen,⁴ who argued that only singular $P(K)$ can give rise to a singular susceptibility. A cluster approximation was devised by Theodorou and Cohen to study the cases of singular power-law distributions $P(K) \propto K^{c-1}$, $0 < c < 1$. Singular temperature dependence in the specific heat C and the magnetic susceptibility χ were found^{4,5}:

$$\begin{aligned} C &\propto T^c, \\ \chi &\propto T^{c-1}. \end{aligned} \quad (2)$$