Exact Solution of a Four-Site *d*-Electron Problem: The Nickel-Metal Photoemission Spectrum

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(Received 24 June 1985)

Exact calculated results for the nickel density of electron states, as would be measured in valence-band photoemission, are presented. A realistic local-density-approximation one-electron structure, sampled at four wave vectors, and an intrasite electron-electron interaction of full generality are used. This new approach to the Ni photoemission problem yields accurately the experimental bandwidth, exchange splitting, satellite position, and relative intensities. Physical conclusions about the true Ni many-body states are drawn.

PACS numbers: 75.10.Lp, 71.45.Gm, 79.60.Cn

Nickel metal has a very narrow one-electron *d*-band width: It is approximately 4.5 eV according to calculations[1,2] based on the local-density approximation (LDA). It exhibits also a considerable electron-electron interaction: The ratio of the intra-atomic Coulomb integral to *d*-band width has been estimated[3] to be in the range of 0.5 to 1. Thus the electronic structure of Ni metal presents the theoretical challenge of an almost intractable, full many-body problem.

Photoemission experiments provide a useful probe of this many-body system:

(1) Core-level photoemission[4,5] exhibits satellites approximately 6 eV below the main lines. This spectrum is attributed[5,6] to the presence of either zero (main lines) or one (satellites) *d* hole on the atom from which the core electron has been emitted.

(2) Resonant photoemission is observed[7] for photon energies of approximately 67 eV. The resonant satellite, both its origin and polarization,[7,9] was correctly explained by consideration of the virtual excitation of a $3p$ electron into the $3d$ conduction band and the subsequent Auger-type decay into the $3p$ hole and a free electron.

(3) Valence-band photoemission shows an apparent *d*-band width and exchange splittings reduced[10-12] by 25% and 50%, respectively, relative to the calculated LDA one-electron band structure. A satellite[5,12] also appears at approximately 6 eV below the Fermi level.

A large body of theoretical work[13-19] has been focused on these problems with, to date, only partial success. Liebsch[13] has shown that the assumption of a wave-vector–independent self-energy and the inclusion of only certain kinds of scattering processes provide a qualitative understanding of photoemission within the degenerate Hubbard model. Davis and Feldkamp,[14] with the assumption of a core-hole self-energy for the valence hole, solved the problem exactly and obtained a bandwidth only slightly larger—less than 10%—than that measured by photoemission. They obtain, however, an exchange splitting considerably too large. Both these calculations assume a wave-vector–independent self-energy, which has been shown to be incorrect.[17] A more complete review of the strengths and deficiencies of previous calculations is provided elsewhere.[3,17]

We report here a calculation of the Ni-metal density of emitted states. The calculation is *exact* within the context of a full many-body scheme. Sampling is restricted to four wave vectors in the face-centered-cubic Brillouin zone. We use a one-electron spectrum calculated in LDA and an on-site electron-electron interaction which is the most general allowed by atomic symmetry. We do not use perturbation theory, and do not assume either a low-density approximation or wave-vector–independent self-energies. We explicitly acknowledge the equal importance of both band-structure effects and electron-electron interactions. Results are in excellent agreement with photoemission data and many of them, including the calculated photoemission bandwidth, are independent of reasonable choices of the electron-electron interaction parameters.

We sample four vectors in the Brillouin zone: the central Γ point and the three X points, centers of the square faces. This restricted sampling scheme[20,21] is identical to consideration of a four-atom fcc crystal: the four atoms within the basic cubic cell and complete periodic boundary conditions. We use the one-electron band structure[1] of Wang and Callaway, used in previous studies, and we average up- and down-spin energies to produce the required spin-independent one-electron energies (see Table I, column 4).

We use an intra-atomic electron-electron interaction, which is the dominant contribution.[22] It should be noted that the nearest-neighbor Coulomb term, the next largest one, makes a constant contribution within the four-atom crystal and may be neglected. The intra-atomic terms we considered are the most general allowed by atomic symmetry.[23,24] They include a direct Coulomb integral U, an average exchange integral J, and an exchange anisotropy

$$\Delta J = (\tfrac{1}{2}[J(e_g,e_g) - J(t_{2g},t_{2g})].$$

The ratio U:J has been amply discussed in the literature.[22,25,26] A fit to atomic-term values[27] yields $U = 16$ eV; $J = 1$ eV; $\Delta J = \frac{1}{8}$ eV. Atomic and solid-

TABLE I. Binding energies for spin-averaged levels.[a]

Symmetry	Experiment		Theory		
	HKE[b]	EP[c]	This work	WC[d]	DF[e]
$\Gamma'_{25}(\Gamma_4)$	1.2	1.1	1.6	2.04	1.62
$\Gamma_{12}(\Gamma_3)$	0.5	0.4	1.0	0.92	0.74
X_1	· · ·	3.3	3.6	4.31	3.55
X_3	· · ·	2.8	3.2	3.81	3.03
X_2	· · ·	0.85	0.4	0.18	0.14[f]
X_5	0.1	· · ·	0.2	−0.01	0.01[f]

[a]Energies in electronvolts below the Fermi level.
[b]References 10 and 11.
[c]Reference 12.
[d]Reference 1.
[e]Reference 14.
[f]Estimation based on a 0.5-eV exchange splitting.

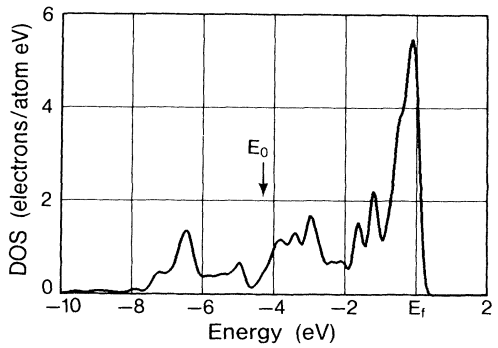

FIG. 1. Total density of calculated emitted one-electron states. The location of the lowest single-electron state at X in the d band according to Ref. 1 is denoted by E_0.

state values are not expected to be similar. However, these numbers provide two useful limits: (i) U is screened in the solid more than J; the ratio of U:J should be therefore less than 16:1. (ii) J is smaller in the solid than in the atom; thus $J < 1$ eV.

Within these constraints *the exact ratio of U:J chosen is found to make essentially no difference*[28] *either in the main-line spectra or in the position of the satellite.* We have assumed an intermediate ratio U:J:ΔJ equal to 56:8:1 and we have scaled U to provide a proper satellite position.

We make full use of space, spin, and particle-exchange symmetries of the Hamiltonian in order to diagonalize the complete many-electron matrices. The space group[23] consists of a total of 192 operations and contains the inversion. Leaving aside the trivial inversion properties there are in all ten irreducible representations, five at Γ (dimensions 1, 1, 2, 3, and 3) and five at X (dimensions 3, 3, 3, 3, and 6). All many-electron eigenvalues and eigenstates were obtained numerically by means of a symmetry-adapted computer algorithm.

We consider a Ni ground state consisting of 0.5 hole per atom, i.e., two holes in the four-site crystal. We include only the d states. The s-like conduction band has "absorbed" two electrons; this may be viewed as the s-like one-electron states spreading into a wide s band. The two states at Γ lie 9 eV below the Fermi level and are fully occupied; the six states at X are well above the Fermi level and are empty. Our d-band occupancy is in good agreement with theoretical[2] and experimental[29] estimates of 0.56 d hole per Ni atom.

For two holes in the cluster our Hamiltonian yields an accidentally degenerate ground state of symmetries $^3X_2$, $^1\Gamma_2$, and $^1\Gamma_3$. When nearest-neighbor exchange is considered $^3X_2$ has the lowest energy; we consider $^3X_2$ as our ground state. This state is found to contain only holes from the X_5 one-electron states and has zero probability of having two holes in one site. As a consequence there is no contribution from the on-site electron-electron interaction.

The photoemission process introduces a third hole into the system. The 9880 three-hole states factorize into twenty distinct symmetries; the matrices to diagonalize are, at most, of order 238. The resulting eigenstates are obtained and the projection of an extra hole in the ground state $^3X_2$ onto these states produces the desired photoemission density of states. Figure 1 shows the angle-, symmetry-, and spin-integrated results. We have used a value $U = 4.3$ eV which positions the satellite properly. Interestingly, the photoemission bandwidth is (within 0.2 eV) *independent of any reasonable choice of interaction parameter* (values 3.5 eV $\leqslant U \leqslant$ 8.6 eV were tested). Figure 1 is to be compared with x-ray photoemission spectra[5]: Good agreement is found not only in the existence and in the (fitted) position of the satellite, but also in its relative intensity and in the width of the main line.[30]

Projected densities of emitted states with symmetries X_5 and X_3 of the created hole are shown in Fig. 2. States of X_5 symmetry, at or near the Fermi level, are characterized by a single narrow peak. States of X_3 symmetry (within the satellite structure and near the bottom of the conduction band) show three distinct peaks which correspond to the known multiplets and band-structure broadening. The X_3 symmetry of Fig. 2 may be compared with Fig. 4 of Ref. 12.

A detailed analysis of our results yields the following conclusions:

(a) Three-hole eigenstates corresponding to the "main-line" spectrum exhibit greatly reduced probability of finding two holes in one atom: 20% at the Fermi level, 5% at the bottom of the band, as opposed to 50% in a random state created from the $^3X_2$ ground state.

(b) As a consequence of (a), exchange splitting within the main line must be small for any reasonable values of U and J. We find exchange splittings of 0.25

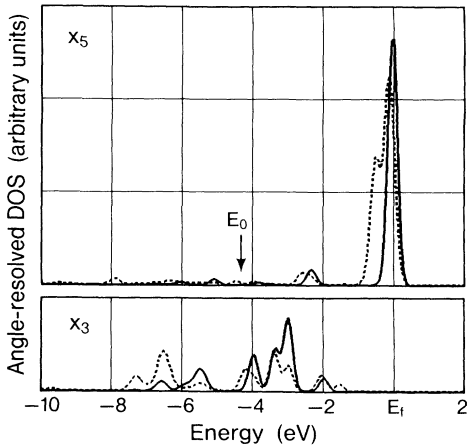

FIG. 2. Density of emitted states projected on the wave vector and symmetry of the emitted electron. Solid lines correspond to the minority-spin states; dashed lines are for majority-spin states.

and 0.15 eV for $X_5(t_{2g})$ and $X_2(e_g)$, respectively, both near the Fermi level. These numbers appear to be in good agreement with experiment,[10,12] where values of approximately 0.3 eV were found (for other symmetry points) near E_F.

(c) The exchange splitting for e_g states decreases near the bottom of the band; the t_{2g} splitting remains at a value of approximately 0.2 eV throughout.

(d) Three-hole eigenstates in the satellite part of the spectrum have a very high probability of finding two holes in one atom, which leads to a sizable exchange splitting.

(e) Our calculation leads naturally to a reduced bandwidth. Main-line quasiparticle energies are shown in Table I along with comparative data. Our calculated bandwidth,

$$E(X_5) - E(X_1) = 3.4 \text{ eV},$$

is in excellent agreement with the experimental value[10–12] of 3.3 eV and considerably reduced from LDA bands[1] (~ 43 eV).

(f) We have reassigned the X_5 "majority"-spin line of Ref. 11 to a combination of majority- and minority-spin bands. It is obvious that minority X_5 one-electron states must be occupied in a true many-body ground state, albeit with smaller probability amplitude than that of majority-spin states. Experimental failure to detect separate lines means that the exchange splitting was probably irresolvably small.

(g) Our Fermi level is 0.2 eV higher than the experimental value, which reflects the true bandwidth of our X_5 spectrum (see Fig. 2). Experimental data do not yield an accurate value of the Fermi level because of instrumental resolution; a higher value may in fact be compatible with the observations.

(h) With a correction of 0.2 eV for the Fermi level most of our quasiparticle energies are in good agreement with experiment (see Table I). However, and similarly to previous theoretical work,[14] we find significant disagreement for $E(X_2)$. No obvious explanation is apparent.

Our realistic Hamiltonian and method of calculation—exact solution within a restricted sampling—has yielded an excellent spectrum: a narrow main line, with mostly one hole per atom, and a deeper lying satellite, with high probability of two holes in one site. The exchange splitting is correspondingly reduced in the main-line spectrum. The strong electron-electron interaction forces states nominally "above the Fermi level" to be occupied with non-negligible probability, a point often ignored in the past. The considerable success of our calculation suggests once more that single-particle energies calculated within LDA are accurate for all transition metals, even the strongly magnetic ones like nickel.

The authors would like to acknowledge the kind hospitality of Laboratoire pour l'Utilisation du Rayonnement Electromagnétique and the University of Paris-South (Orsay), where the initial steps of this research were carried out. One of us (R.H.V.) has been the holder of an AT&T Bell Laboratories Fellowship, under whose sponsorship this work was done. The support of the National Science Foundation through Grant No. DMR 81-06494 is gratefully acknowledged.

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[1]C. S. Wang and J. Callaway, Phys. Rev. B **15**, 298 (1977).

[2]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[3]G. Treglia, F. Ducastelle, and D. Spanjaard, Phys. Rev. B **21**, 3729 (1980).

[4]Y. Baer, P. F. Heden, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, Phys. Scr. **1**, 55 (1970).

[5]S. Hufner and G. K. Wertheim, Phys. Lett. **51A**, 299 (1975).

[6]L. A. Feldkamp and L. C. Davis, Phys. Rev. B **22**, 3644 (1980).

[7]C. Guillot, Y. Ballu, J. Paigne, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Petroff, and L. M. Falicov, Phys. Rev. Lett. **39**, 1632 (1977).

[8]R. Clauberg, W. Gudat, E. Kisker, E. Kuhlmann, and G. N. Rothberg, Phys. Rev. Lett. **47**, 1314 (1981).

[9]L. A. Feldkamp and L. C. Davis, Phys. Rev. Lett. **43**, 151 (1979).

[10]D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. **40**, 1514 (1978).

[11]F. J. Himpsel, J. A. Knapp, and D. E. Eastman, Phys. Rev. B **19**, 2919 (1979).

[12]W. Eberhardt and E. W. Plummer, Phys. Rev. B **21**, 3245 (1980).

[13]A. Liebsch, Phys. Rev. Lett. **43**, 1431 (1979), and Phys. Rev. B **23**, 5203 (1981).

[14]L. C. Davis and L. A. Feldkamp, Solid State Commun. **34**, 141 (1980).

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

[16]N. Martensson and B. Johansson, Phys. Rev. Lett. **45**, 482 (1980).

[17]L. Kleinman and K. Mednick, Phys. Rev. B **24**, 6880 (1981).

[18]R. Clauberg, Phys. Rev. B **28**, 2561 (1983).

[19]T. Aisaka, T. Kato, E. Haga, Phys. Rev. B **28**, 1113 (1983).

[20]L. M. Falicov and R. H. Victora, Phys. Rev. B **30**, 1695 (1984).

[21]The accuracy of the small-cluster approach can only be assessed *a posteriori,* and in our case it results in good agreement with experiment. Such agreement is expected because (a) the physical effects we study here are instrinsically of short range, and (b) sampling only a few points in the Brillouin zone is a technique that has been successfully used in one-electron calculations.

[22]C. Herring, in *Magnetism: A Treatise on Modern Theory and Materials,* edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. 4.

[23]M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).

[24]Ref. 22, p. 174. This statement may be proved within our restricted basis set of five d electrons. The approximately 5% s-like character of X_1 is ignored, which yields errors in calculated position of approximately 0.05 eV.

[25]R. E. Watson, *Electrons in Crystalline Solids* (IAEA, Vienna, 1973), pp. 355–416.

[26]J. Friedel, in *Physics of Metals, Electrons,* edited by J. M. Ziman (Cambridge Univ. Press, Cambridge, England, 1969), Vol. 1, p. 376.

[27]C. E. Moore, *Atomic Energy Levels* (U.S. National Bureau of Standards, Washington, D.C., 1971), Vol. 2, p. 98.

[28]The difference is less than 0.1 eV.

[29]H. Dannan, R. Heer, and A. J. P. Meyer, J. Appl. Phys. **39**, 669 (1968). The measured Ni moment, $0.616\mu_B$, is believed to reflect a net spin imbalance of 0.56, with a g factor of 2.2.

[30]The multipeaked structure of our spectra is a direct consequence of our limited wave-vector sampling; our curves are plotted with a narrow Gaussian broadening of 0.15 eV half-width.