Correlation effects on the energy band of Ni

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The experimental band structure of Ni obtained by Eastman *et al.*, using angle-resolved photoemission, differs markedly in several respects from the self-consistently calculated bands of Wang and Callaway. We demonstrate that two major discrepancies may be accounted for by correlation effects: (i) band narrowing for which several models, none of them entirely satisfactory, have been proposed and (ii) a reduction in the exchange splitting well in excess of that obtained using the von Barth–Hedin potential for which we present a simple calculation.

Eastman *et al.*[1] have interpreted their angle-resolved photoemission data for (111) Ni to obtain a d-band width of 3.4 eV and an exchange splitting of the upper Λ_3 d band of 0.31 ± 0.03 eV. Wang and Callaway[2] (WC) in an extremely carefully performed self-consistent calculation found a d-band width of 4.8 eV and an exchange splitting for the upper L_3 level of 0.84 eV [Kohn-Sham (KS) exchange potential[3]] or 0.60 eV [von Barth–Hedin (vBH) exchange and correlation potential[4]]. At the top of the d bands (X_5 and $W_{1'}$) the WC exchange splitting is 0.88 eV (KS) and 0.63 eV (vBH). Another important discrepancy is that the experimental majority-spin L_3 level lies about 0.15 eV below E_F and 0.70 eV above $L_{2'}$ whereas the WC (vBH) L_3 lies 0.47 eV below E_F and 0.09 eV *below* $L_{2'}$ with even larger discrepancies when the KS potential is used. The experimental ordering is confirmed by the discovery of a surface state[5] in the $L_{2'}$-L_1 gap that lies below L_3 and therefore has its dispersion downward in energy rather than upward as does the corresponding nearly-free-electron surface state in copper.[6]

We[7] have recently explained the photoelectron-spin-polarization reversal[8] which occurs 0.1 eV above threshold for (100) and (111) Ni as being due to a surface state band lying just above the majority-spin bulk d bands and just below the Fermi energy. In order that it lie close enough to the Fermi energy, it was necessary to reduce the WC X_5 exchange splitting to 0.44 eV. Moore and Pendry[9] explain the polarization reversal without a surface state by having the majority spin d bands lie sufficiently close to the Fermi energy. This requires an X_5 exchange splitting of 0.33 eV. Because the (100) surface-state band has been seen in angle-resolved photoemission throughout much of the two-dimensional Brillouin zone by Plummer *et al.*[10,11] and an exchange splitting of 0.33 eV would put it above E_F, we believe the exchange splitting cannot be much less than 0.44 eV. Furthermore, if as we believe, the WC bandwidth is correct and the experimentally observed narrowing is due to final state effects, the calculated magneton number will not agree with experiment if the exchange splitting is further reduced.

von Barth and Hedin[4] have extended the Kohn-Sham[3] theory to the spin polarized case and derived an exchange and correlation potential in the local density approximation. Because the exchange hole arguments of Slater[12] are equally valid for partially or completely filled core shells or for nearly free electrons, one expects and experience has proven that local approximations for the exchange potential work fairly well. On the other hand, the correlation between a pair of electronic states occurs through the admixture of unoccupied states. For electrons in a partially filled shell there are unoccupied states, degenerate in energy and with large Coulomb matrix elements, available for admixing. For electrons in a filled shell, however, the only states available for admixing lie far away in energy and have smaller Coulomb matrix elements. Manifestly, potentials for these two vastly different cases cannot both be derived in a local free-electron-gas approximation. In the Appendix we derive a formula

$$E_\sigma = -[0.064 n_\sigma (5 - n_\sigma)^2 + 0.040 n_{\bar\sigma}(5 - n_\sigma)(5 - n_{\bar\sigma})] U^2/\epsilon \quad (1)$$

for the energy of a d-band Bloch electron of spin σ due to correlation with all the other d electrons and with the restriction that only other d-band states may be admixed. Here n_σ is the number of electrons in the d bands with spin σ and $n_{\bar\sigma}$ the number with spin $-\sigma$. U is an effective Coulomb matrix element

$$U = \langle \phi_\alpha(\vec{r}_1)\phi_\beta(\vec{r}_2) | H_{12} | \phi_\alpha(\vec{r}_1)\phi_\beta(\vec{r}_2) \rangle , \quad (2)$$

where the ϕ's are atomic orbitals. Because we are interested in the correlation energy of an X_5 electron at the top of the d bands, the energy denominator ϵ in Eq. (1) is slightly less than the excitation energy of the electrons with which it is interacting; this on the average is half the bandwidth. Equation (1) is similar to an equation of Friedel and Sayers[13] for the total d-d correlation energy. Note that if σ represents a majority spin, $n_\sigma=5$ and $E_\sigma=0$; if σ represents a minority spin, $n_{\bar{\sigma}}=5$ and $n_\sigma=4.4$ so that

$$E_{\min}=-0.1014U^2/\epsilon\,. \tag{3}$$

This represents most of the decrease in the X_5 exchange splitting due to correlation. Although there are other contributions to the X_5 correlation energy involving sp electrons, these should be almost as large for the majority spins as the minority. If we wish to reduce the WC X_5 exchange splitting from 0.88 eV to 0.42 eV taking ϵ = 2.4 eV (half the WC bandwidth), it requires U = 3.33 eV. This is in the middle of the range of values usually assumed for U so that we are confident that the discrepancy between the WC and the observed exchange splitting is due to the inadequacy of the vBH potential. This lowering of the minority-spin d bands will lower the Fermi level so that the WC majority spin L_3 will lie about 0.30 eV below E_F, only 0.15 eV above its experimental position. The relative position of the majority spin L_3 and $L_{2'}$ levels will not be improved; however, the minority spin $L_{2'}$, L_3 separation will be reduced so that the discrepancy in the $L_{2'}$ position becomes more consistent for the two spins.

It has been shown[14] that the d-band width is linearly proportional to the separation between the bottoms of the s and d bands at $\vec{k}=0$. Comparing the WC Ni calculation with Burdick's[15] Cu calculation and using either Burdick's 3.29-eV bandwidth or the experimental[16] Cu d-band width of 3.1 eV one finds that the WC bands are actually slightly narrower than one would expect. Thus it is extremely unlikely that the discrepancy between WC and the experimental d-band width is due to an error in the WC calculation. Pendry[17] has proposed that the lifetime of a hole in the lower third of the d-bands is so short that it spreads the energy of those holes over such a large range that they are not observed, hence narrowing the observed region of the d-bands. This theory, although attractive, is not consistent with the interpretation Eastman *et al.* made of their experimental data. They believe they see the top and bottom states of the d band separated by 3.4 eV and not that they fail to observe the bottom third of the band.

Penn[18] has proposed that a satellite observed 6 eV below the Fermi level is caused by the excitation of two-hole virtual bound states following photoexcitation of d-band electrons. These modes remove spectral weight from the Ni d bands and thus narrow them. Unfortunately U=2 eV places the satellite 8 eV below the Fermi level but only narrows the d-bands by 0.35 eV. An unphysically large value of U=5 eV places the satellite another 5 eV lower in energy and still only reduces the d-band width by 1.1 eV. The fact that the satellite has been observed[19] in atomic Ni where it corresponds to an excited final-state Ni ion in the d^8p^1 configuration makes it less likely that the Penn mechanism accounts for either the satellite or the band narrowing.

Van Vleck[20] suggested 25 years ago that rather than containing all configurations d^n $(0\leq n\leq 10)$ as band theory requires, Ni has 40% of its atoms in the d^{10} configuration and the other 60% in the d^9. He estimated that this would reduce the bandwidth by $\frac{1}{3}$. This is exactly the amount needed to make the WC bands agree with experiment. We find this theory unsatisfactory on two counts. The reduction in bandwidth is attributed to the inability of an electron to jump away from a d^9 site because this would create a d^8 site which is assumed to be forbidden. However, when one measures a bandwidth one measures the bandwidth of the excited hole. If an electron is excited off a d^9 site creating a d^8 site the hole is free to hop to other d^9 sites because that does not create an *additional* d^8 site. A more serious defficiency of the theory is that it is based upon the assumption that the average configuration in metallic Ni is $d^{9.4}s^{0.6}$ when in fact it is $d^{8.8}(sp)^{1.2}$. (There are 0.6 holes in the d-band but there are an additional 0.6 d electrons hybridized out of the d bands into the sp bands above the Fermi energy.[7]) Thus not only is the d^8s^2 configuration not forbidden in the metal, it is actually more prevalent than the d^{10}. This should not surprise anyone since d^8s^2 is the ground-state configuration for the atom.

In conclusion, we have shown that correlation will easily reduce the WC X_5 exchange splitting of 0.88 eV down to what we consider the most likely value, 0.42 eV, or even down to the experimental value of 0.31 eV. On the other hand, while we believe that correlation can also account for the band narrowing, none of the three theories we have examined is satisfactory. This, together with the fact that several other experimentalists[11,21,22] obtain bandwidths closer to WC's calculated value, leaves the question of the d-band width in Ni still open.

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APPENDIX

Second-order perturbation theory gives for the correlation energy of ψ_k due to scattering from all $\psi_{q'}$

$$E=-\sum_{qk'q'}\frac{|\langle A\psi_k(\vec{r}_1)\psi_q(\vec{r}_2)|H_{12}|A\psi_{k'}(\vec{r}_1)\psi_{q'}(\vec{r}_2)\rangle|^2}{\epsilon_{kq;k'q'}}f_q(1-f_{k'})(1-f_{q'})\,, \tag{A1}$$

where A is the antisymmetrizing operator, f_q is 1 (0) for ψ_q below (above E_F, $\epsilon_{kq;k'q'}$ is the energy to excite the pair of electrons k,q to states k',q', and band indices which must also be summed over have been surpressed. Here

$$\psi_k(\vec{r}_1)=N^{-1/2}\sum_{i\alpha}a_\alpha^{(k)}\phi_\alpha(\vec{r}_1-\vec{R}_i)e^{i\vec{k}\cdot\vec{R}_i}\,, \tag{A2}$$

where N is the number of sites in the crystal, $\phi_\alpha(\vec{r}-\vec{R}_i)$ is an atomic orbital of symmetry α located on site i, and $a_\alpha^{(k)}$ is a coefficient determined from a band calculation. We assume integrals involving ϕ's on different sites may be neglected; then the sum over the remaining $\vec{R}_i$ yields $N\delta(\vec{k}+\vec{q}-\vec{k}'-\vec{q}')$, giving

$$E=-\sum_{qp}\frac{|\sum_{\alpha\beta\gamma\delta}a_\alpha^{(k)}a_\gamma^{(k+p)}a_\beta^{(q)}a_\delta^{(q-p)}\langle A\phi_\alpha(\vec{r}_1)\phi_\beta(\vec{r}_2)|H_{12}|A\phi_\gamma(\vec{r}_1)\phi_\delta(\vec{r}_2)\rangle|^2}{N^2\epsilon_{kq;k+p,q-p}}f_q(1-f_{k+p})(1-f_{q-p})\,. \tag{A3}$$

If we replace $\epsilon_{kq;k+p,q-p}$ by its average value ϵ, the sum over q and p yields $N^2[n_\sigma(5-n_\sigma)^2+n_{\bar\sigma}(5-n_\sigma)(5-n_{\bar\sigma})]$, where σ is the spin of ψ_k and both spins have been included in the sum over ψ_q's. The integrals in (A3) are large only when $\gamma=\alpha$ and $\delta=\beta$ (direct term) or $\delta=\alpha$ and $\gamma=\beta$ (exchange term). If $\alpha=\beta=\gamma=\delta$ the exchange and direct terms cancel. Thus we obtain

$$E=-\left(2\sum_{\alpha\neq\beta}\langle a_\alpha^2\rangle^2\langle a_\beta^2\rangle^2 n_\sigma(5-n_\sigma)^2+\sum_{\alpha,\beta}\langle a_\alpha^2\rangle^2\langle a_\beta^2\rangle^2 n_{\bar\sigma}(5-n_\sigma)(5-n_{\bar\sigma})\right)U/\epsilon\,, \tag{A4}$$

where U is given in Eq. (2). If we neglect sp hybridization, $\langle a_\alpha^2\rangle=\frac{1}{5}$ but there are 20 and 25 terms in the double sums so Eq. (1) is immediately obtained. Hybridization will tend to reduce the correlation energy whereas the inclusion of interatomic terms will increase it so that Eq. (1) is probably a very good estimate for the d-band correlation energy.

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