Bound hole pairs in Ni: Evidence from photoemission

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I show that the Ni d-band density of states contains a peak due to excitations of bound hole pairs. The density of states is observed directly in photoemission experiments which show a satellite peak below the bottom of the d bands.

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In this paper I present a theory for the physical origin of the satellite that is observed at approximately 7 eV below the Fermi energy in photoemission experiment on Ni. The satellite has been observed[1,2] in both x-ray and ultraviolet photoemission spectroscopy (XPS and UPS) at a binding energy of roughly 7 eV. The d band peak observed in both XPS and UPS is narrowed relative to the calculated d band peak[3] and a narrowing is predicted by the present theory. However, Eastman et al.[4] have also observed a band narrowing at photon energies below 20 eV where the satellite is not seen.

The simplest explanation for the satellite would be the excitation of a 5 eV Ni plasmon (the satellite is located at 6 eV below the main d-band peak). However, an examination of electron scattering and optical data shows that this is not the answer. I show that the satellite is caused by a shake-up process which involves the excitation of two-hole virtual bound states following photoexcitation of d band electrons. The states consist of two itinerant d-holes that are correlated in such a way that there is a relatively high probability that they are located on the same atom. These holes have a higher energy than two uncorrelated holes due to the intra-atomic coulomb interaction and consequently the satellite peak is at lower kinetic energy than the main d-band peak. The hole-pair states are derived mainly from the bottom of the d band and thus reduce its width.

This work supports earlier suggestions by Mott[5] and Hüfner and Wertheim[6] that the satellite is caused by photoexcitation of a d electron followed by the creation of a second hold of the same atom. However, the atomic model does not yield a quantitative explanation for the satellite. Other work along similar lines to the present work has been done by Penn,[7] Edwards[8] and Davis and Feldkamp.[9]

The photoemission spectrum, $I(\omega)$, is directly related to the d band spectral density, $\mathrm{Im}\{g\}$, by

$$I(\omega) = C \sum_{kn\sigma} \mathrm{Im}\{g_{kn\sigma}(\omega)\} \tag{1}$$

where $g_{kn\sigma}$ is the d-hole Green function, $\{kn\sigma\}$ label the electron momentum, band index, and spin and C is a constant. Equation (1) is valid if the interaction between the photoexcited electron and the remaining electrons can be neglected as can variations of the matrix element of $(e/mc)\vec{A}\cdot\vec{P}$ with respect to the initial and final state of the photoexcited electron. These conditions obtain for x-ray photoemission spectroscopy.

The d band electrons are assumed to obey the degenerate Hubbard Hamiltonian

$$H = \sum_{kn} \varepsilon_k a^{\dagger}_{kn\sigma} a_{kn\sigma} + \frac{1}{2} \sum_{\ell n\sigma n'\sigma'} U_{n\sigma,n'\sigma'} n_{\ell n\sigma} n_{\ell n'\sigma'} \tag{2}$$

where ε_k is the band energy of a Bloch electron composed of a linear combination of atomic ϕ states with z component of angular momentum n, i.e., the five d band are assumed degenerate. Each band is composed of atomic wavefunctions of a single angular momentum component. The second term is the intra-atomic Coulomb interaction between two electrons located on the lattice site ℓ and

$$U_{n\sigma,n'\sigma'} = U(1 - \delta_{n\sigma,n'\sigma'}). \tag{3}$$

The intra-atomic Coulomb interaction has strength U and the delta function represents the effect of the Pauli principle. The Hubbard Hamiltonian defined by Eq. (2) treats the band structure in an oversimplified manner but allows an analytic solution for the self energy.

The one electron Green function is given by

$$g_{kn\sigma}(\omega) = 1/[\omega - \varepsilon_k - \Sigma_{kn\sigma}(\omega)] \tag{4}$$

where ε_k is the d band energy and $\Sigma_{kn\sigma}(\omega)$ is the self energy due to the electron-electron interaction. The self energy is approximated by[10,11]

$$\Sigma_{kn\sigma}(\omega) \simeq -i \sum_{n'\sigma'} \int \frac{d^3\kappa}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \frac{t(\omega',n\sigma,n'\sigma',\kappa)}{\omega-\omega'-\varepsilon_{\kappa-k,n'\sigma'}+i\delta_{\kappa-k}} \tag{5a}$$

where $\delta_{\kappa-k} \to -0$ if $\kappa-k$ is less than the Fermi momentum and $\varepsilon_{kn\sigma}$ is the Hartree-Fock hole energy;

$$\varepsilon_{kn\sigma'} = \varepsilon_k - \sum_{k'n'\sigma'} (1 - f_{k'n'\sigma'}) U_{n\sigma,n'\sigma'} \tag{5b}$$

t satisfies the integral equation.[10,11] The Hartree-Fock energies correspond to the usual band structure.[3]

$$t = v + v\,G\,t \tag{5c}$$

where v is the Coulomb interaction defined in Eq. (2) and G is the two particle Green function. For two holes with total momentum κ, G is approximated by

$$G_o(\xi,n\sigma,n'\sigma',\kappa) = \sum_q \frac{f_{\frac{\kappa}{2}+q,n,\sigma} f_{\frac{\kappa}{2}-q,n'\sigma'}}{\xi - \varepsilon_{\frac{\kappa}{2}+q,n\sigma} - \varepsilon_{\frac{\kappa}{2}-q,n'\sigma'} - i\delta} \tag{5d}$$

Use of Eq. (2) and Eq. (5d) in Eq. (5c) gives

$$t(\xi,n\sigma,n'\sigma',\kappa) = U_{n\sigma,n'\sigma'}/[1+U\,G_o(\xi,n\sigma,n'\sigma',\kappa)] \tag{6}$$

In the limit that $(U/W) \ll 1$ where W is the d band width, $t \simeq U_{n\sigma,n'\sigma'}$, and Eq. (5) is simply the Hartree-Fock approximation for the hole energy, $\varepsilon_{kn\sigma}$.

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G_o is next replaced by its average over κ, $\bar{G}_o$, and the relatively small exchange splitting is ignored with the result

$$\bar{G}_o(\xi)=\iint d\varepsilon d\varepsilon' \; \rho_o(\varepsilon)\rho_o(\varepsilon')f(\varepsilon)f(\varepsilon')/(\xi-\varepsilon-\varepsilon'-i\delta) \qquad (7)$$

where $\rho_o(\xi)$ is the Hartree-Fock d-band density of states and f is the Fermi function. Use of Eq. (7) in Eq. (6) yields

$$t(\xi,n\sigma,n'\sigma') \equiv t(\xi)(1-\delta_{n\sigma,n'\sigma'})$$
$$= \{U/[1+U\bar{G}_o(\xi)]\}(1-\delta_{n\sigma,n'\sigma'}) \qquad (8)$$

and the self energy is given by the use of Eq. (8) in Eq. (5a)

$$\Sigma_{kn\sigma}(\omega)=-\sum_{k'n'\sigma'}(1-f_{k'n'\sigma'})(1-\delta_{n\sigma,n'\sigma'})t(\omega+\varepsilon_{k'n'\sigma'}) \qquad (9)$$

from which,

$$\Sigma_{kn\uparrow}(\omega) \simeq -.6t(\omega+\varepsilon_f) \qquad (10a)$$

$$\Sigma_{kn\downarrow}(\omega) \simeq -.48t(\omega+\varepsilon_f) \qquad (10b)$$

where we have used the fact that the empty states in Ni are at the Fermi energy, ε_f, and there is .6 hole per atom in the Ni d spin down band. Given U and $\rho_o(\omega)$ the photoemission spectrum can be calculated from Eqs. (1)-(10).

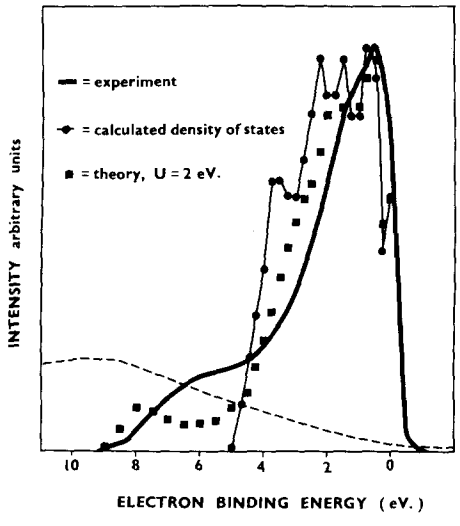

Fig. 1 The solid curve is the experimental Ni d band XPS spectrum[1] minus an estimate of the secondary electron contribution indicated by the dashed line. The XPS spectrum predicted from band structure calculations[3] alone is given by the circles. The present theory, for the case U = 2.0 eV, is represented by squares.

The physics described by Eqs. (1)-(10) is as follows. The single hole spectrum is coupled to the two hole spectrum as indicated by Eq. (5a) which describes a process where a hole at $\{kn\sigma\}$ is filled in an Auger event when a d electron is scattered into the hole and a second d electron is scattered to an empty d state. The two remaining holes multiply scatter. Their spectrum is determined by the t matrix and the two-hole interaction is $t=U/(1+UG_o)$ rather than the Hartree-Fock approximation of U. The denominator of t represents multiple scattering and results in a strong energy dependence of t and consequently of $\Sigma_{k,n,\sigma}(\varepsilon)$ an effect which is neglected in Hartree-Fock and gives rise to the satellite.

The Ni band is almost filled so it is reasonable to expect that its two hole excitation spectrum is similar to that of Cu. The two hole spectrum for materials with filled d bands has been discussed by Sawatsky[12] and by Cini[13] in reference to valence band Auger spectra. In the limit of large U they show the two d holes excited in the Auger process are left in a correlated atomic-like state and consequently the Cu Auger spectrum is atomic-like as is observed experimentally. However, in the case of materials with filled d bands the two hole state is not coupled to the single hole excitation spectrum because there are no empty d states to scatter into and thus the Cu photoemission spectrum does not exhibit a satellite.

The Ni XPS spectrum is calculated from Eqs. (1)-(10).[3] ρ_o is taken from the work of Wang and Callaway.[4] Figure (1) shows the experimental spectrum,[1] solid curve, after a background subtraction shown by the dashed curve. The XPS spectrum predicted by band calculation[3] in the absence of correlation effects, U = 0, is shown by the circles; it is determined by ρ_o which is normalized so that there is good agreement between theory and experiment near the Ni Fermi energy. The results of the present calculation for U = 2.0 eV are given by the squares.

For larger values of U, the satellite moves to lower energies and removes more weight from the main d band spectrum. However, not until U ≃ 5 eV is the weight removed from the d bands sufficient to reproduce all of the narrowing shown in the experimental spectrum and for U ≃ 5 eV the satellite peak is predicted to be roughly 13 eV below ε_f.

It is generally agreed that Auger spectroscopy establishes a value for U of about 4.5 eV. The failure of the present theory to predict the correct position of the satellite for U=4.5 eV is due to (a) the oversimplified band structure and (b) the approximations used in calculating the Greens function.[14] An improved Greens function combined with the present model for the band structure places the satellite at roughly 9.5 eV below the Fermi energy for U=4.5 eV.

With respect to other metals; the satellite cannot be excited in metals with filled d bands and has not been observed in such materials nor has a satellite been observed in Pd despite a value of U similar to Ni. However Pd has fewer 3d holes and a calculation predicts a lifetime tailing of the main d band peak but no satellite.

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