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Mapping of unoccupied minority spin bands of Co and Ni using inverse photoemission

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Angle-resolved inverse photoemission (or bremsstrahlung spectroscopy) with a tunable light detector is used to determine the energy-band dispersion of unoccupied minority-spin $3d$ states in Co and Ni. For Co, a ferromagnetic exchange splitting of 0.93 ± 0.1 eV between the unoccupied spin-down and occupied spin-up states (measured with photoemission) is derived. The full width at half maxiumum of empty $3d$ states in Ni is 0.25 ± 0.1 eV.

Band dispersions of electron energy bands in crystalline solids can be measured by using angle-resolved photoemission techniques (for a review see Ref. 1). However, states between the Fermi level and the vacuum level are inaccessible by photoemission. Inverse photoemission[2–5] (or bremsstrahlung spectroscopy) is capable of sampling such unoccupied electronic states. Recently, it has been shown that the momentum is conserved in angle-resolved inverse photoemission,[4,5] analogous to angle-resolved regular photoemission. This makes standard band-mapping techniques[1] applicable and the current model of photoemission can be used with minor modifications.[3] Particularly appealing[3] for such measurements are the unoccupied minority-spin states of ferromagnets (e.g., Fe, Co, Ni). In a *strong* ferromagnet such as Ni, the empty $3d$ states are completely spin polarized opposite to the sample magnetization. The ferromagnetic exchange splitting between energy bands of opposite spin has been a challenge for first-principles band theory.[6–9] To date, there exists no band-dispersion measurement for unoccupied minority-spin states.

The major obstacle for using inverse photoemission has been the very low cross section for this process (about 10^{-8} photons in the $3d$ band per incident electron[3,10]). Previously, only spectrometers with a fixed photon energy of 9.7 eV and an energy-band pass of ~ 0.7 eV (Refs. 2, 4, 5) have been used. We are analyzing the emitted photons with a monochromator (for details see Ref. 10) which gives us a total energy resolution of 0.3 eV (electrons + photons). This is close to the intrinsic width of the $3d$ states. The photon energy can be varied (from ~ 10–30 eV) which is required for the most common band-mapping techniques.[1]

Figure 1 shows a measurement technique for determining $E(\vec{k})$ band dispersions from angle-resolved inverse-photoemission data, which is analogous to the angle-resolved photoemission measurement of the occupied Co$3d$ bands.[11] Electrons impinge normal to the basal Co(0001) surface and occupy a free-electron-like energy band (Δ_1, Δ_2) inside the solid. From there they drop down into the unoccupied section of the $3d$ band (Δ_6, Δ_5) and emit the energy difference as a uv photon. Subtracting the photon energy $h\nu$ from the initial energy of the electron we obtain the energy of the $3d$ band state, the high-energy cutoff of the photon spectrum corresponds to the Fermi level E_F which we obtained with an accuracy of 0.05 eV from a polycrystalline Au sample which has flat density of states near E_F. The momentum $(\vec{k}^{\parallel}, k^{\perp})$ of the $3d$ state is given as follows: Since the momentum parallel to the surface is conserved (up to a reciprocal lattice vector), one has $\vec{k}^{\parallel} = 0$ in our geometry which corresponds to the line $\Gamma\Delta A$ in $\vec{k}$ space shown in Fig. 1. The momentum perpendicular to the surface is obtained from the band dispersion of the free-electron-like Δ_1, Δ_2 band which is known semiempirically[11] from angle-resolved photoemission data for the critical points combined with a band calculation to interpolate between critical points. Since the emitted uv photon carries negligible momentum, the final state in the Δ_6, Δ_5 band has the same $k^{\perp}$ as the initial state in the Δ_1, Δ_2 band. By tuning the electron energy (and, consequently, the photon energy) we are able to map part of the $E(k^{\perp})$ band dispersion of the minority-spin Δ_6, Δ_5 band.

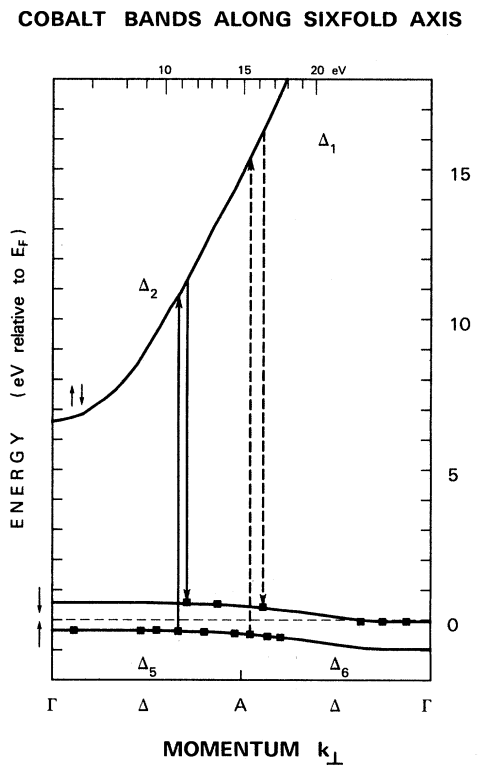

FIG. 1. Determining $E(\vec{k})$ band dispersions for Co with angle-resolved inverse photoemission (transitions downwards) and photoemission (transitions upwards). The energy bands of Co are unfolded according to Ref. 11.

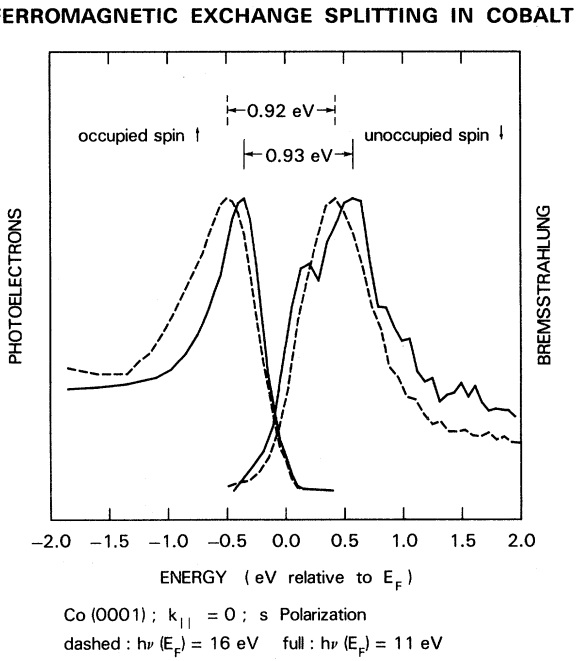

FIG. 2. Photoemission (left) and inverse-photoemission (right) spectra from Co(0001) showing the ferromagnetic exchange splitting of 0.93 eV between occupied spin-up and unoccupied spin-down states. A band dispersion (peak shift) of 0.15 eV is observed between the two transition energies of 16 and 11 eV (see Fig. 1).

The data points for occupied states in Fig. 1 have been obtained with angle-resolved photoemission (from Ref. 11) in an analogous way (transitions upwards from $\Delta_6\Delta_5$ to $\Delta_1\Delta_2$ for photoemission versus transitions downwards for inverse photoemission).

In Fig. 2, angle-resolved photoemission and inverse-photoemission data are compared for two different transition energies, i.e., different momenta $k^\perp$ (shown in Fig. 1). The band dispersion (peak shift) observed between these two momenta is 0.15 eV for unoccupied as well as for occupied states. The peaks in the inverse-photoemission spectra are located at 0.43 and 0.58 eV above E_F. Together with the photoemission data from Ref. 11 for the occuppied states, we obtain a ferromagnetic exchange splitting of 0.93 ± 0.1 eV for the $\Delta_6\Delta_5$ band. This is measured between occupied and unoccupied states. Previously, an exchange splitting of 0.85 ± 0.25 eV (Ref. 11) was determined for the section of the $\Delta_6\Delta_5$ band where both spin states are occupied. Thus, within the experimental errors, the exchange splitting between occupied and unoccupied states is the same as between occupied states only. As noted before[7–9,11] this experimental exchange splitting of ~ 0.9 eV is substantially smaller than the splitting of ~ 1.6 eV obtained

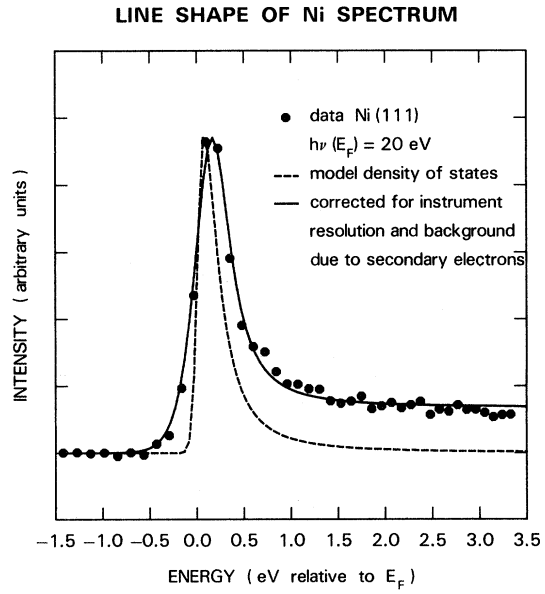

FIG. 3. Angle-resolved inverse-photoemission spectrum (dots) from Ni(111) for a transition near the top of the *d* band (Ref. 13). The full line is a fit to the data using a Lorentzian model density of states (dashed, after multiplication with the Fermi function). The background of secondaries was approximated using a steplike electron-energy-loss function and the resulting spectrum was convoluted with the instrument resolution function.

in first-principles ground-state calculations.[6] However, such ground-state calculations describe energy bands which cannot be probed experimentally because one always needs to create a hole when probing an occupied state or has to add an electron to the system in order to probe an unoccupied state. Recent theoretical work[8] has attributed this discrepancy to an excited-state effect which is tied to other anomalies such as a d-band narrowing and the existence of two electron satellite excitations observed in photoemission.[9] Since the unoccupied d bands measured with inverse photoemission are narrower than the calculated ground-state bands, one should expect two electron satellites to show up in inverse photoemission as well. We have not seen such satellites. X-ray isochromat spectra[12] do not give any evidence for satellite structure either. However, the satellites seen in photoemission become very weak for photon energies below ~ 30 eV and one would have to look near the $3p$ threshold where a resonance is found for the photoemission satellite.

In Ni, excited-state effects in photoemission[7,9] are stronger than in Co but harder to resolve since the exchange splitting is only 0.3 eV.[7] Therefore we have only attempted to determine the width of the unoccupied $3d$ minority-spin states. Figure 3 shows an angle-resolved inverse-photoemission spectrum for a geometry where the transition happens into states near the top of the Ni $3d$ band.[13] The peak of the spectrum lies 0.15 eV above E_F and the full width half maximum of our model density of states in Fig. 3 is 0.28 eV. This number could be larger than the real empty d-band width because of d-like surface states[14] split off by up to 0.05 eV from the bulk or it could be smaller than the real width by up to 0.1 eV because the transition does not happen exactly at the right point in $\vec{k}$ space.[13] These errors are comparable to our experimental uncertainties. Although our data provide a first experimental estimate[15] of the unoccupied d-band width in Ni, a further improvement in resolution is needed for an accurate measurement which is only limited by the intrinsic width ($\lesssim 0.1$ eV) of these states.

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[1]F. J. Himpsel, Appl. Opt. 19, 3964 (1980).
[2]G. Denninger, V. Dose, and H. Scheidt, Appl. Phys. 18, 375 (1979).
[3]J. B. Pendry, Phys. Rev. Lett. 45, 1356 (1980); J. Phys. C 14, 1381 (1981).
[4]G. Denninger, V. Dose, and H. P. Bonzel, Phys. Rev. Lett. 48, 279 (1982).
[5]D. P. Woodruff and N. V. Smith, Phys. Rev. Lett. 48, 283 (1982).
[6]J. W. D. Connolly, Phys. Rev. 159, 415 (1967); Int. J. Quantum Chem. 2, 257 (1968); C. S. Wang and J. Callaway, Phys. Rev. B 15, 298 (1977); V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978); J. R. Anderson, D. A. Papaconstantopoulos, L. L. Boyer, and J. E. Schirber, Phys. Rev. B 20, 3172 (1979).
[7]D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. 40, 1514 (1978); F. J. Himpsel, J. A. Knapp, and D. E. Eastman, Phys. Rev. B 19, 2919 (1979); D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. 44, 95 (1980).
[8]D. R. Penn, Phys. Rev. Lett. 42, 921 (1979); A. Liebsch, *ibid.* 43, 1431 (1979); Phys. Rev. B 23, 5203 (1981); L. C. Davis and L. A. Feldkamp, Solid State Commun. 34, 141 (1980); G. Treglia, F. Ducastelle, and D. Spanjaard, Phys. Rev. B 21, 3729 (1980); V. Korenman and R. E. Prange, Phys. Rev. Lett. 44, 1291 (1980); L. Kleinman and K. Mednick, Phys. Rev. B 24, 6880 (1981).
[9]F. J. Himpsel, P. Heimann, and D. E. Eastman, J. Appl. Phys. 52, 1658 (1981).
[10]Th. Fauster, F. J. Himpsel, J. J. Donelon, and A. Marx (unpublished).
[11]F. J. Himpsel and D. E. Eastman, Phys. Rev. B 21, 3207 (1980); 22, 5014 (1980).
[12]R. R. Turtle and R. J. Liefeld, Phys. Rev. B 7, 3411 (1973).
[13]The data in Fig. 3 were taken with electrons coming in 35° from the sample normal in the $(0\bar{1}1)$ plane. Photons with $h\nu(E_F)=20$ eV and $\vec{E}\perp(0\bar{1}1)$ were detected. For this geometry, we have $\vec{k}_{\parallel}=0.78\,\bar{\Gamma}\bar{M}$ where $\bar{M}$ is the middle of the side of the surface Brillouin zone. $\bar{M}$ corresponds to the line $LXLX$ in three-dimensional $\vec{k}$ space along which the topmost d band is almost flat. The deviation from the top of the d band at X_5 is estimated to be about 0.1 eV for our geometry (see Ref. 14).
[14]P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. B 20, 3059 (1979).
[15]Previous isochromat data on Ni had a resolution of 1 eV (Ref. 12) and 0.7 eV (Refs. 2,5) which is much larger than the empty d-band width.