Li^+ ions. When the composition is changed the system passes through regions of composition where ordering fluctuations occur, leading to peaks in the "compressibility." Between the compressibility peaks the lithium form a disordered liquid. With this analogy to the thermodynamics of liquid-gas systems, it is anticipated that high-resolution and temperature-dependent electrochemical studies can be used to study the Li_xTiS_2 phase diagram in detail, including critical-exponent studies near ordered compositions.

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[1]A. H. Thompson and M. S. Whittingham, Mater. Res. Bull. 12, 741 (1977).
[2]M. S. Whittingham, Science 192, 1126 (1976), and Solid State Chem. 13, 1 (1977).
[3]B. G. Silbernagel and M. S. Whittingham, Mater. Res. Bull. 11, 29 (1976); also A. Leblanc-Soreau, M. Danot, L. Trichet, and J. Rouxel, Mater. Res. Bull. 9, 191 (1974).
[4]F. W. Boswell, A. Prodan, and J. M. Corbett, Phys. Status Solidi (a) 35, 591 (1976).
[5]A. H. Thompson, F. R. Gamble, and C. R. Symon, Mater. Res. Bull. 10, 915 (1975); J. J. Legendre, M. Huber, and M. Sauvage, Phys. Status Solidi 40, K101 (1977).
[6]E. Rost and L. Giertsen, Z. Anorg. Allg. Chem. 328, 299 (1964).
[7]B. G. Silbernagel and M. S. Whittingham, J. Chem. Phys. 64, 3670 (1976).
[8]A. J. Jacobson *et al.*, to be published.
[9]M. Kaburagi and J. Kanamori, Prog. Theor. Phys. 54, 30 (1975).
[10]M. Kaburagi and J. Kanamori, Jpn. J. Appl. Phys., Suppl. 2, 145 (1974).
[11]M. Kaburagi, Thesis, Department of Physics, Osaka University, Osaka, Japan, 1975 (unpublished).
[12]R. R. Chianelli, B. M. L. Rao, and J. Scanlon, to be published.
[13]M. S. Whittingham, J. Electrochem. Soc. 123, 315 (1976).
[14]For example, see M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill, New York, 1957), p. 292; or a text on chemical thermodynamics such as K. Denbigh, *The Principle of Chemical Equilibrium* (Cambridge Univ. Press, Cambridge, 1971).

Experimental Band Structure and Temperature-Dependent Magnetic Exchange Splitting of Nickel Using Angle-Resolved Photoemission

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Using angle-resolved photoemission and synchrotron radiation, we have determined the energy-versus-momentum valence-band dispersion relations for a Ni(111) crystal. The temperature-dependent ferromagnetic exchange splitting has been directly observed. Both the d-band width (~3.4 eV at L) and exchange splitting (0.31 eV) are much smaller than theoretical estimates (~4.5 eV wide at L with ~0.7-eV splitting, respectively, at 293 K).

Nickel has been a prototype metal for innumerable studies of various physical properties involving itinerant-electron ferromagnetism, d-band electronic structure, and transition-metal surfaces. Despite intense study, two basic aspects of Ni have remained controversial and unresolved, i.e., the overall d-band width and the exchange splitting. For example, angle-integrated photoemission estimates of the d-band resonance width[1,2] (~3.3 eV) are narrower than self-consistent one-electron band theory estimates[3-5] (~4.5 eV). One explanation given for the observed narrow d bands is that photoemission samples only a few atomic layers and band narrowing occurs at the surface.[6,7] Another recent explanation of the narrow experimental widths is that the lower d states in Ni have very short electron hole lifetimes.[8] However, several recent angle-resolved photoemission experiments report larger widths (e.g., $\simeq$ 4.2 eV)[9] or "agree" with theory.[10,11] Photoemission, optical, and theoretical studies of the magnetic exchange split-

ting[12] have been even more uncertain, with many experimental studies reporting negligible or unobservable splittings[13,1,2,6] and theoretical studies[3-5] typically reporting large (~0.6–0.9 eV) and uncertain splittings. Two recent angle-resolved photoemission studies have reported exchange splittings of ~0.3 eV[10] and 0.5 eV.[11]

Using angle-resolved photoelectron spectroscopy with linearly polarized synchrotron radiation, we have experimentally determined the energy-versus-momentum dispersion relation along the $\Gamma-L$ direction in the Brillouin zone for several bands in nickel. The magnetic exchange splitting of the upper Λ_3 d band has been directly observed ($\delta E_{ex}=0.31\pm0.03$ eV at 293 K). The minority $\Lambda_{3\downarrow}$ band is observed to cross the Fermi surface at $k_\perp/k_{BZ}^{\langle 111\rangle}\simeq 0.8$ (where $k_\perp$ and $k_{BZ}^{\langle 111\rangle}$ are the electron momentum and zone-boundary momentum), and the majority band extends from $E(\Lambda_{3\uparrow})\simeq -0.15$ eV at L to $E(\Lambda_{3\uparrow})\simeq -0.70$ eV at Γ, measured relative to the Fermi energy E_F. The temperature dependence of the exchange splitting δE_{ex} has been measured for 293 K$\lesssim T\lesssim$ 793 K). δE_{ex} is observed to decrease from 0.31 eV (293 K) to $\lesssim$0.15 eV for $T\gtrsim T_C$ (651 K). This behavior is intermediate between long-range-order models such as a simple Stoner-Wohlfarth-Slater (SWS) model[12] which predicts that $\delta E_{ex}(T)$ varies as the magnetization, and localized intra-atomic exchange models which predict no temperature dependence. Comparison of our measured E-vs-k dispersion curves for several bands with theory[4,5] shows that the individual d bands are theoretically about 1.4 times as wide as found experimentally. Likewise, the overall experimental width is ~3.4 eV (E_F to L_1), while theoretical values are[4,5] about 4.8 eV (spin-polarized von Barth–Hedin potential and Kohn-Sham potential).

Experimentally, we have used an angle-resolved cylindrical-mirror analyzer (CMA) double-pass spectrometer system and a two-dimensional (2D) display-type spectrometer that displays the angular distribution of photoelectrons within an energy pass band ΔE and a 1.8-sr solid angle (86° cone). The CMA system was used for s-polarization measurements and was operated with an angular acceptance $\delta\Theta=4°$ and overall energy resolution of ~150 meV using synchrotron radiation from the 240-MeV storage ring at the University of Wisconsin. The 2D spectrometer was used for p-polarization measurements and was operated with an angle-resolved detector set at $\delta\Theta=4°$ and an overall system resolution of ~100 meV using the same source. Count rates were typically $\sim 10^4$/sec for the Ni d bands under these conditions for $6\lesssim h\nu\lesssim 20$ eV. Both s- and p-polarization measurements were needed to determine band symmetries and to delineate bulk and surface-state emission. In both systems, a Ni(111) crystal was prepared by Ar-ion etching and annealing in the usual manner, checked for cleanliness using Auger spectroscopy, and measured in working vacuums in the 10^{-11}-Torr range. Spectra for heated samples were taken using a pulsed heating technique with the spectrometer gated off during the heating pulse to avoid spurious magnetic fields.

In Fig. 1(a) we present an angle-resolved energy distribution curve (AREDC) which shows emission from the exchange-split uppermost d band. For the experimental conditions of Fig. 1, only the uppermost d band is observed (to be discussed). A line-shape analysis using a spin-split SWS model with two Lorentzian spectral functions of equal integrated intensity yields peaks at −0.19 and −0.47 eV with a peak splitting $\Delta_{ex}=0.28\pm0.03$ eV [see Fig. 1(a)]. Because these two direct interband transitions take place at slightly different $\vec{k}$ points, the vertical d-band exchange splitting δE_{ex} differs from Δ_{ex} by a small correction factor [equal to the ratio of d-band to conduction-band slopes of 9%, neglecting the small effect ($\lesssim$3%) due to the conduction-band exchange splitting]; thus, we determine an exchange splitting $\delta E_{ex}(293\text{ K})=0.31\pm0.03$ eV. The lower peak [$\simeq$0.50 eV full width at half-maximum (FWHM)] is substantially broader than the upper peak ($\simeq$0.30 eV FWHM) because of an increased Auger

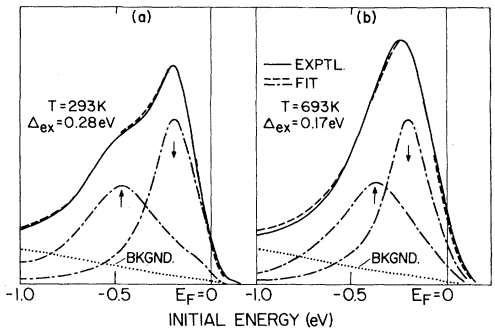

FIG. 1. AREDC's showing temperature-dependent exchange splitting $\delta E_{ex}=1.09\Delta_{ex}$ (see text). The experimental conditions {$h\nu=9$ eV, emission at $\Theta=30°$ in the $[\bar{1}\bar{1}2]$ direction in the $(1\bar{1}0)$ mirror plane with radiation polarized perpendicular to the $(1\bar{1}0)$ plane} ensure that only one band is observed within ~1 eV of E_F (see Fig. 4 inset).

lifetime broadening which increases away from E_F.

As seen in Fig. 1(b), the observed d-band line shape is narrower for $T = 693$ K (Curie point $T_C = 651$ K) than for 293 K, with the lower energy edge shifting upwards toward E_F and the peak intensity increased. This upward shift is expected since the minority band is strongly pinned with a large density of states at E_F. Using the same line-shape analysis with linewidths kept fixed yields a residual splitting of $\Delta_{ex} = 0.17$ eV, which corresponds to $\delta E_{ex}(693\ \mathrm{K}) \simeq 0.19$ eV. This result gives an upper bound for $\delta E_{ex}(693\ \mathrm{K})$, because a line-shape analysis with any additional temperature-dependent broadening for $T \gtrsim T_C$ yields a smaller estimate.[14]

A summary of our experimental $\delta E_{ex}(T/T_C)$ is given in Fig. 2 (curve 1), for which an analysis with temperature-independent linewidths was used. In Fig. 2, three curves showing possible temperature-dependent exchange splittings are also shown: (2) the measured saturation magnetization $M_s(T/T_C)/M_s(0)$, which is a measure of long-range order, (3) a temperature-independent curve, which would correspond to a localized intra-atomic exchange interaction, and (4) the short-range order-parameter curve due to Oguchi[15] (based on interacting localized $S = \frac{1}{2}$ moments).

We have measured normal emission AREDC's for Ni(111) with s- and p-polarized radiation for $5 \lesssim h\nu \lesssim 25$ eV, and have determined the E-vs-$k_\perp$ dispersions ($k_\perp$ = momentum along Λ) for the upper Λ_3 and Λ_1 d bands and the lowest Λ_1 s band. Several representative AREDC's showing direct interband transitions are given in Fig. 3, and a summary of E-vs-$k_\perp$ band dispersions is given

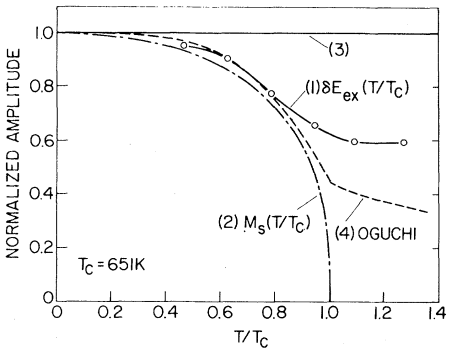

FIG. 2. Experimental temperature-dependent d-band splitting, compared with several theoretical models (see text).

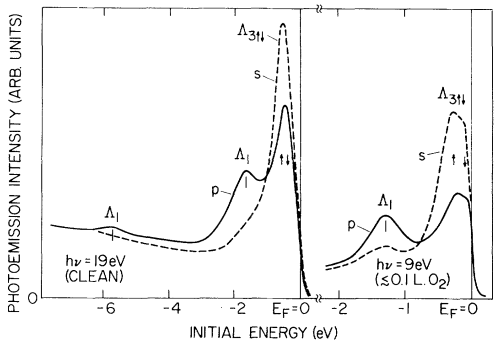

FIG. 3. AREDC's for normal emission from Ni(111) showing $h\nu$-dependent and polarization-dependent direct interband transitions.

in Fig. 4. The E and $k_\perp$ points were determined as follows: For each observed transition at a photon energy, the initial energy is directly given by the AREDC and $k_\perp$ (± 5% accuracy) is given by that of the calculated nearly-free-electron–like Λ_1 conduction band involved[16] in the transition (e.g., shown in Fig. 4 shifted down by $h\nu = 9$ eV). If we assume direct interband transitions, only one conduction band is involved for normal emission from Ni(111) with $h\nu \lesssim 20$ eV, thereby yielding unambiguous $k_\perp$ assignments. In this case, transitions from Λ_1-symmetry valence bands are allowed with p-polarized radiation (dipole approximation), while Λ_3-symmetry bands are allowed with s polarization. The selection rules permit unambiguous assignments of experimental bands (see Fig. 3; these rules are not strictly obeyed because we have mixed s and p polarization, with ~ 80% linearly polarized radiation).

In Fig. 4, we show bands (dotted lines) calculated by Wang and Callaway using a Kohn-Sham potential.[4] The Λ_1 bands have been spin-averaged since hole lifetimes preclude observation of the exchange splitting for $E_i \lesssim -0.5$ eV.[17] As seen in Fig. 4, the theoretical width of the $\Lambda_{3\downarrow}$ band (~ 0.8 eV), $E_F - \Lambda_{1\,min}{}^d$ (2.6 eV), and E_F-L (4.8 eV) are all about 1.4 times as large as experimentally observed. Likewise, the calculated exchange splitting[4] is ~ 2–3 times as large as measured.

In summary, we have determined dispersion relations for several bands in Ni and have observed exchange-split bands which show that ferromagnetic Ni can be described by a SWS spin-split band model. Our results are consistent with Fermi-surface results[4,5] and spin-polarized photoemission results,[18] and the exchange splitting is consistent with the Bohr magneton number

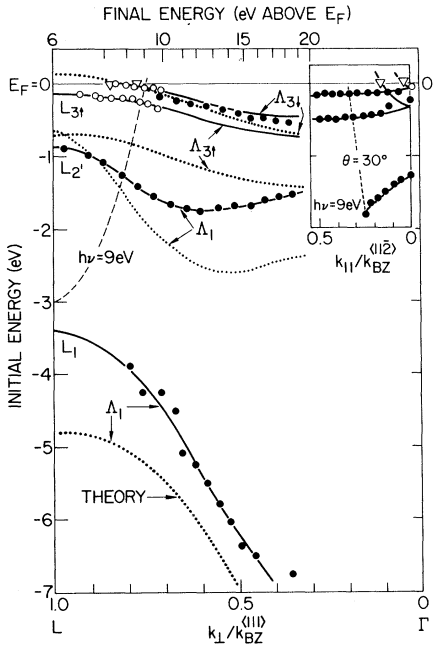

FIG. 4. Experimental E-vs-$k_{\perp}^{\langle 111\rangle}$ energy-band dispersions for Ni(111) along Λ. A single conduction band (Ref. 16) is involved for $h\nu \lesssim 20$ eV and is shown for $h\nu = 9$ eV (shifted down by $h\nu$). The hollow circles are data taken for Ni(111) + ~ 0.1 Torr-sec O_2, which removes a surface state at − 0.25 eV, but does not significantly affect bulk emission. The triangles denote bands crossing the Fermi surface as given by de Haas–van Alphen data (see Refs. 4 and 5; the spin-orbit splitting of $\Lambda_{3\downarrow}$ is shown along Λ). The light dotted curves are calculated bands (Ref. 4) (Kohn-Sham potential). The inset shows E-vs-k_{11} dispersion for k_{11} in the $[\bar{1}\bar{1}2]$ direction for $h\nu = 9$ eV; the dotted line Θ = 30° corresponds to the data in Fig. 1(a). The zone-boundary momenta are $k_{BZ}^{\langle 111\rangle} = 1.55$ Å^{-1} and $k_{BZ}^{\langle \bar{1}\bar{1}2\rangle} = 1.46$ Å^{-1}.

of Ni and Stoner gap Δ.[12,18] We find a smaller δE_{ex} and narrower d bands than given by band calculations.[3-5] The discrepancy in d-band width may be related to the fact that theoretically the d-band energy position is too far above the muffin-tin zero,[3] which is pinned near the bottom of the lowest Λ_1 band (see Fig. 4). Two recent studies have reported exchange splittings of $\delta E_{ex} = 0.3$ eV[10] and $\delta E_{ex} = 0.5$ eV.[11] In the former case, one of the two observed structures was incorrectly assigned to an indirect transition from $\Lambda_{3\uparrow}$, but is due to a Λ_1 surface-state feature (to be published). In the latter case, we have observed for the same experimental parameters that the reported 0.5-eV structure ($h\nu = 16.8$ eV) is due to two different interband transitions.

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[1]D. E. Eastman, J. Phys. (Paris) 32, C1-293 (1971).
[2]S. Hufner, G. K. Wertheim, and J. H. Wernick, Phys. Rev. B 8, 4511 (1973).
[3]J. W. D. Connolly, Phys. Rev. 159, 415 (1967).
[4]C. S. Wang and J. Callaway, Phys. Rev. B 15, 298 (1977).
[5]C. S. Wang and J. Callaway, Phys. Rev. B 9, 4897 (1974).
[6]R. Haydock, V. Heine, M. J. Kelly, and J. B. Pendry, Phys. Rev. Lett. 19, 868 (1972).
[7]M. Mehta and C. S. Fadley, Phys. Rev. Lett. 39, 1569 (1977).
[8]J. B. Pendry and J. F. L. Hopkinson, in Proceeding of the Fifth International Conference on VUV Radiation Physics, Montpellier, France, 1977 (unpublished).
[9]R. J. Smith, J. Anderson, J. Hermanson, and G. J. Lapeyre, Solid State Commun. 21, 459 (1977).
[10]P. Heimann and H. Neddermeyer, J. Phys. F 6, L257 (1976).
[11]E. Dietz, U. Gerhardt, and C. J. Maetz, Phys. Rev. Lett. 40, 892 (1978).
[12]E. P. Wohlfarth, Phys. Lett. 36A, 131 (1971).
[13]L. G. Petersson *et al.*, Phys. Rev. B 14, 4177 (1976), and references therein; L. G. Petersson and R. Erlandsson, Phys. Rev. B 17, 3006 (1978).
[14]However, it would require large extra broadening (~ 0.2 eV) to reduce δE_{ex} to zero for $T > T_C$. Broadening from sources of nonmagnetic origin can be ruled out because we have measured temperature-dependent line shapes for comparable transitions and temperatures in Cu and find negligible broadening. For $T/T_C \gtrsim 1$, the experimental line shape indicates that there is some additional broadening ($\gtrsim$ 100 meV, possibly due to spin disorder broadening; S. Liu, private communication).
[15]T. Oguchi, Prog. Theor. Phys. (Kyoto) 13, 148 (1955).
[16]V. Moruzzi, SCF $X\alpha$ calculation; the conduction band was shifted down by 0.5 eV to agree with experiment at L (private communication).
[17]We have omitted one flat d band of Λ_3 symmetry in Fig. 4 which we know from measurements on Cu(111) to have such a small emission intensity that we can not resolve it for Ni; this flat band is estimated to extend across the Brillouin zone at ~ − 1.2 eV.
[18]E. P. Wohlfarth, Phys. Rev. Lett. 38, 524 (1977).