Opening of a Correlation-Induced Band Gap in NiS

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We have measured high-resolution photoemission spectra of NiS, which undergoes a nonmetal-metal transition at $T_t \sim 260$ K. Below T_t, a small band gap opens; the band edge is essentially a step function broadened only by ~ 15 meV. This observation is difficult to reconcile with one-electron band theory, which predicts a much broader band edge, implying a dramatic influence of electron correlation on quasiparticle excitations and on the opening of a band gap in 3D antiferromagnetic insulators.

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Metal-insulator transitions induced by electron correlation (Mott transitions) have been the subject of much debate [1]: In particular, it has been controversial to what extent one-electron band theory can describe antiferromagnetic (AF) insulators (so-called Mott insulators) and their transitions to metallic states and to what extent electron correlation is important. Band-structure calculations using the local-(spin)-density approximation [L(S)DA] failed to predict band gaps or predicted gaps that were an order of magnitude too small for AF insulators such as NiO and CoO [2]. Recently, however, the band gaps as well as the magnetic moments of these compounds have been almost correctly predicted within one-electron theory using the self-interaction corrected (SIC) LDA [3], LDA + U [4], and unrestricted Hartree-Fock (UHF) methods [5], where unphysical self-interaction in LDA has been eliminated. Nevertheless, their photoemission spectra show satellites (d^{n-1} final states) at considerably higher binding energies than the occupied d bands predicted by these calculations. Also the spectra exhibit substantial spectral-weight transfer from the satellite to the main band (corresponding to $d^n\underline{L}$ final sates, where $\underline{L}$ denotes a hole in the p band), compared to the calculated density of states (DOS) [6], indicating that the description of single-particle excitations is beyond one-electron band theory [7].

Recent theoretical studies using the Hubbard model in two [8,9] and infinite dimensions [10] have provided considerable insight into the properties of correlated electrons systems. From quantum Monte Carlo studies of the doping-induced chemical potential shift, Furukawa and Imada [8] have proposed that the DOS of a 2D AF insulator diverges at the band edges as $E^{-1/2}$ even in the absence of Fermi surface nesting, indicating that a gap opens on the entire Fermi surface(s), in striking contrast with one-electron band theory or spin-density wave (SDW) theory. Quasiparticle dispersions calculated by Bulut *et al.* [9] are consistent with this picture. In infinite dimension, the band edges of insulators at half-filling appear to show the same DOS singularity as in the noninteracting case [10]. On the other hand, the situation is still unclear for 3D AF insulators.

In this Letter, we report a high-resolution photoemission study of the hexagonal form of NiS, which exhibits a first-order nonmetal-metal transition at $T_t \sim 260$ K [11]; the metallic phase above T_t shows Pauli paramagnetism and the nonmetallic phase below T_t shows antiferromagnetism. The latter phase is in fact a p-type degenerate semiconductor, where a small amount ($\sim 0.2\%$) of Ni vacancies act as acceptors [12]. The magnitude of the band gap has been estimated to be $>\sim 100$ meV from an optical study [13]. Although a previous non-self-consistent band-structure calculation indicated a small band gap in the AF state [14], recent self-consistent LSDA [15,16] and LAD + U calculations [4] failed to yield a finite gap. Indeed, photoemission studies have shown that the band gap of NiS is of a S-3p-to-Ni-3d charge-transfer type rather than of a classical d-d Mott-Hubbard type [15] and that the charge-transfer nature is essential to interpret high-energy excitations such as the photoemission satellite and its persistence above T_t. According to these studies [15], however, the highest occupied states are not pure p states but are "effective d states," which have local d symmetry with respect to the Ni atom and are pushed out of the original p band as a result of strong hybridization with the d^7 states. This would justify the following discussions implicitly based on an "effective" Hubbard model instead of more realistic but complicated p-d models as far as low-energy excitations are concerned.

Melt-quenched polycrystals of NiS and sintered polycrystals of $Ni_{0.75}Fe_{0.25}S$ were prepared as described elsewhere [12,17]. The latter sample had the hexagonal lattice parameters of $a = 3.448$ Å and $c = 5.532$ Å at room temperature and had a higher T_t of 352 K,

consistent with those of Ref. [18]. The bulk nature of the transitions was confirmed by capacity measurements. Photoemission measurements were performed using a spectrometer having a base pressure of $\sim 1 \times 10^{-10}$ Torr equipped with a He discharge lamp ($h\nu = 21.2$ eV). The samples were cooled down to ~30 K using a closed-cycle He refrigerator. Temperature was monitored with an accuracy of −0 K to +5 K. The calibration of binding energies was made to within ±1 meV in the whole temperature range and the instrumental resolution was evaluated to be ~22 meV [19] using the Fermi edge of Au evaporated onto the samples. Clean surfaces were obtained by scraping with a diamond file or cleaving *in situ*.

Figure 1 shows spectra of NiS taken at various temperatures. The peak located at 1.2–1.3 eV below the Fermi level E_F (referred to as the $d^8\underline{L}$ peak) is gradually shifted towards higher binding energies with decreasing temperature (by ~30 meV in going from 30 to 300 K or by ~0.1 meV/K), consistent with the previous result [15]. Figure 2(a) shows the spectra of NiS and $Ni_{0.75}Fe_{0.25}S$ near E_F. In the 300 K spectrum of NiS, the E_F is located at the center of the leading edge, indicating a metallic Fermi edge. Indeed, Fig. 3 shows that the spectrum could successfully be fitted using a nearly flat DOS multiplied by the Fermi distribution function at 300 K. At low temperatures, the edge becomes steeper and is shifted towards higher binding energies by ~10 meV as shown in Figs. 2(a) and 3, signaling the opening of a gap below T_t. A close inspection reveals, however, that the 190 K spectrum is a little sharper than the Fermi distribution function at the same temperature (which has been shifted towards higher binding energy by ~10 meV to match the measured spectrum), indicating that a very sharp band edge (essentially of a step function) undergoes a "thermal broadening" to a lesser extent than the Fermi distribution function. The band edge of $Ni_{0.75}Fe_{0.25}S$ is broader and its center is located ~15 meV below E_F already at 300 K, consistent with its nonmetallic behavior below $T_t \sim 350$ K.

In order to characterize the thermal broadening in the nonmetallic phase, we have broadened and shifted the 30 K spectra to reproduce the spectra taken at higher temperatures, as shown in Fig. 4(a). Here we have assumed that the thermal broadening is simulated by a convolution with a Gaussian function [20] whose FWHM ($\equiv \Delta E_T$) is proportional to k_BT: $\Delta E_T \equiv \alpha k_BT$. Since there is also an instrumental broadening represented by a Gaussian FWHM ΔE_i, each spectrum undergoes a broadening with FWHM $\Delta E_{\text{tot}} = (\Delta E_i^2 + \Delta E_T^2)^{1/2}$. Thus in the nonmetallic phase, a spectrum taken at $T = T_1$ is created by convoluting a spectrum taken at a lower temperature T_2 with $(\Delta E_{T_1}^2 - \Delta E_{T_2}^2)^{1/2}$. The coefficient α was thus found to be 2.7 ± 0.1 for NiS and 2.9 ± 0.1 for $Ni_{0.75}Fe_{0.25}S$, values that are significantly smaller than what would be expected for the Fermi distribution function, $\alpha \sim 3.8$ [21]. One origin of the thermal broadening is phonon emission and absorption which occur simultaneously with the emission of a photoelectron [20]. Thermal distribution of electrons at the band edge and unresolved acceptor levels may also contribute to the apparent broadening.

Having modeled the thermal broadening, one may deduce the "hypothetical" spectra for $\Delta E_i = \Delta E_T = 0$ meV as follows. We assume the hypothetical spectra to be Gaussian-broadened (FWHM = ΔE_0) step functions, as shown by bold solid curves in Fig. 4(b), where the original step functions are shown by dashed lines. ΔE_0 has been determined by least-squares fitting the Gaussian-convoluted step function to the measured spectra. Thus we find $\Delta E_0 = 15$ meV for NiS and $\Delta E_0 = 34$ meV for $Ni_{0.75}Fe_{0.25}S$. (For NiS, addition of an additional sharp peak just at the band edge somewhat reduced the standard deviation, whereas cutting off the corner of the step function degraded the fit. Therefore, although we do not argue that the sharp peak indeed exists, we can safely argue that

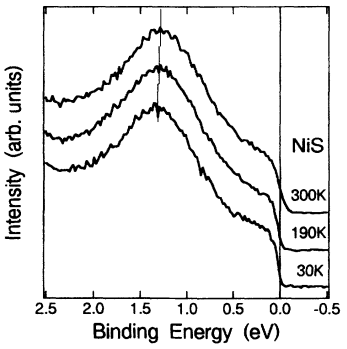

FIG. 1. Photoemission spectra of NiS.

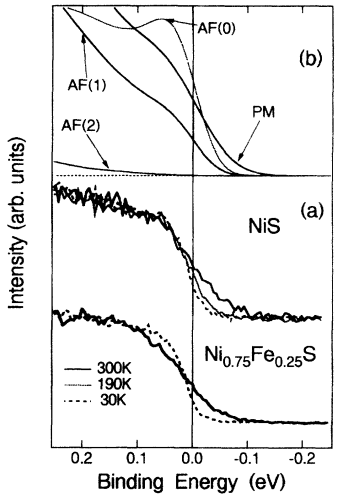

FIG. 2. (a) Photoemission spectra of NiS and $Ni_{0.75}Fe_{0.25}S$ near E_F. (b) DOS of NiS given by band-structure calculations. PM: paramagnetic metal in LDA; AF(1): AF metal in LSDA; AF(2): AF insulator in LSDA; AF(0): AF metal in LDA + U [4]. The calculated DOS have been broadened to simulate the instrumental and thermal broadening.

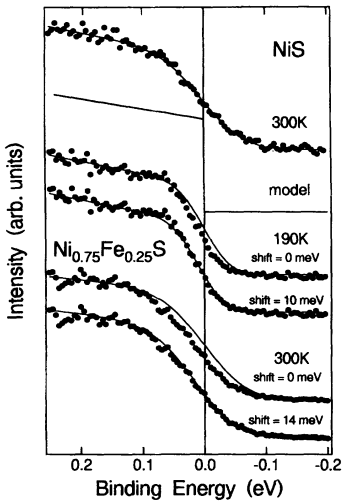

FIG. 3. Comparison of the spectra (dots) with a nearly flat DOS multiplied by a Fermi distribution function (solid curves). For $T < T_t$, the Fermi function has been shifted towards higher binding energies.

the band edge is at least as steep as the broadened step function.)

Two alternative interpretations of the present analysis may be possible. In one case, the hypothetical spectra represent the intrinsic spectral functions of the bulk compounds at $T = 0$ K, apart from the possible existence of features whose widths are narrower than ΔE_{tot}. In the other case, the original step functions are intrinsic at 0 K, and the broadening of $\Delta E_0 = 15-35$ meV is caused by some extrinsic effects such as the small amount (~0.2%) of Ni vacancies, work function inhomogeneity, etc. In the latter case, there should also be contributions from the Ni-Fe atomic disorder to the extra broadening for $Ni_{0.75}Fe_{0.75}S$. In either case, the upper limit for the intrinsic width of the band edge is ~15 meV for NiS and ~34 meV for $Ni_{0.75}Fe_{0.25}S$.

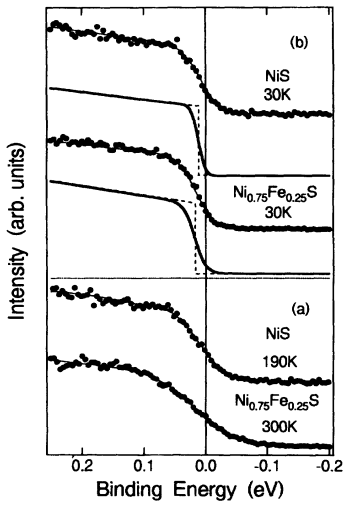

FIG. 4. (a) Spectra taken at 30 K are thermally broadened (solid curves, see text) and are fitted to the spectra taken at higher temperatures (dots). (b) Bold solid curves show hypothetical spectra at $T = 0$ K taken with infinite resolution, which have been obtained by Gaussian broadening the original step functions (dashed lines). The hypothetical spectra are further broadened by the instrumental and thermal broadening (thin solid curves), being fitted to the spectra taken at 30 K (dots).

The step functions used in the above analysis start ~10 meV below E_F for NiS and ~16 meV below E_F for $Ni_{0.75}Fe_{0.25}S$. These small values are not necessarily inconsistent with the larger optical gap (>~ 100 meV) [13], since the E_F would lie near the acceptor levels and hence near the top of the valence band in the p-type semiconductors. It should be noted that the temperature-induced shift of the band edge within the nonmetallic phase, less than 0.01 meV/K, is much smaller than that of the $d^8\underline{L}$ peak, ~0.1 meV/K, indicating a rather high stability of the small band gap.

In Fig. 2, we compare the measured spectra with DOS given by L(S)DA band-structure calculations [15,16]. As the self-consistent AF solution [curve AF(1) in Fig. 2(b)] did not yield an insulating gap, an external staggered magnetic field was applied to enhance the exchange splitting, leading to the insulating state [AF(2)]. The calculations, however, show that the AF ordering strongly reduces the DOS around E_F over a wide energy range of several hundred meV, compared to that of the paramagnetic metallic state (PM). This is particularly true in the insulating AF states [AF(2)], in striking disagreement with experiment. The LDA + U calculation by Anisimov *et al.* [4] [AF(0)] shows a high DOS at E_F in spite of the AF ordering, but it also fails to give a band gap.

The suppression of the calculated DOS at E_F in going from the paramagnetic to the AF insulating states can be understood as follows: Our LDA calculations using the linearized-augmented-plane-wave method have revealed complicated multiple Fermi surfaces of 3D character without nesting features. Under this circumstance, in order for a band gap to open, the exchange splitting of energy bands that cross E_F should exceed their band widths which are at least several hundred meV [14]; this inevitably leads to the suppression of the DOS around E_F over that energy range. If a band gap were to open in SIC-LDA, LDA + U, or UHF calculations, the highest occupied states would be expected to consist of relatively pure, broad S $3p$ bands [3,4,5] and therefore the band edge would not have a sharp step-function-like DOS as is observed experimentally. In the measured spectra, the opening of the band gap only affects the spectra in the vicinity of E_F, as if a small SDW gap were opened on the entire Fermi surfaces as a result of (nearly) perfect Fermi-surface nesting. Although no serious theoretical studies have been made for 3D systems, it is tempting to consider that in the nonmetallic phase of NiS, electron

correlation leads to the opening of the small, rather uniform band gap on the entire Fermi surface in the absence of nesting as in 2D electron systems [8].

In conclusion, we have found that the photoemission spectrum at the band edge of NiS in the nonmetallic phase is an unusually sharp step function. Because it is hard to reconcile this unusual result with one-electron band theory, electron correlation must play a fundamental role in the quasiparticle excitations at the band edge and in the opening of the band gap of the 3D AF insulator. For more detailed information, it is desired to study quasiparticle dispersions by angle-resolved photoemission. It is also interesting to study how the single-particle excitations near the band edge change in going from an AF insulator to a paramagnetic insulator.

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[19] Because of an experimental problem, only the 30 K spectrum of NiS could be taken with a resolution of ~36 meV rather than ~22 meV. This has been taken into account throughout the present analyses.

[20] The tails of optical band gaps behave as e^{-E/k_BT^*} (so called an Urbach tail), where T^* is an "effective temperature" $>\sim T$. In order to reproduce this behavior, we also convoluted the 30 K spectra using the derivative of the Fermi distribution function, but the results were indistinguishable from hose using the Gaussians.

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