

Electron correlation and magnetism in NiS: Implications of photoemission spectra

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The photoemission spectra of NiS in both antiferromagnetic and Pauli paramagnetic phases show similar characteristic features of localized d electrons. This finding is in contrast with the results of band-structure calculations which predict drastic spectral changes between the two phases. It is suggested that fluctuations of the Ni $3d$ local moments due to hybridization with S $3p$ states near the Fermi level are responsible for the Pauli paramagnetic behavior.

Many transition-metal compounds are known to exhibit a metal-nonmetal transition as a function of temperature, pressure, or chemical composition,¹ but in most cases its mechanism has not yet been well understood. The hexagonal form of NiS exhibits a first-order phase transition at $T_i \sim 260$ K, as the temperature is lowered, from a metallic phase with Pauli paramagnetism to a less conductive antiferromagnetic phase (semiconductor or semimetal).² Mott-Hubbard mechanisms have been proposed by several authors, according to which the intra-atomic Coulomb energy of the Ni $3d$ electrons, U , and the d -band width W , have comparable magnitudes and a small change in U causes the transition between the localized and itinerant states.³⁻⁵ On the other hand, it has been suggested that the transition is entirely due to magnetic ordering within the one-electron band model, as a band-structure calculation has given a gap at the Fermi energy (E_F) in the antiferromagnetic state.⁶

Recent photoemission studies on a typical Mott-Hubbard insulator NiO (Refs. 7 and 8) have cast doubt upon the above models for NiS. Namely, the top of the NiO valence band was found to be oxygen p -like (corresponding to $d^8\bar{L}$ final states, where \bar{L} denotes a ligand hole) rather than d -like (d^7 final states). It was consequently suggested that U remains large as compared to W in NiS and that the breakdown of the Mott insulation is due to a closing of the charge-transfer (p - d or $d^8\bar{L}$ - d^9) gap owing to the lower electronegativity of the S atom rather than the closing of the Mott-Hubbard (d - d or d^7 - d^9) gap.⁹

In this paper, we present the results of photoemission studies on NiS above and below the transition temperature and compare them with local-density-functional band-structure calculations and configuration-interaction (CI) local-cluster calculations. Based on the new infor-

mation outlined above and the present results, we will discuss the nature of the electronic and magnetic properties of both phases and the mechanism of the phase transition.

Samples were cut from polycrystalline ingots which had been obtained by annealing stoichiometric melt at 700°C for two days and at 500°C for 10 days and then quenching it in ice water. They were checked before and after photoemission measurements to show a transition at $T_i \approx 250$ K. Photoemission experiments were performed at the Synchrotron Radiation Laboratory using a modified Rowland-mount monochromator, and also at National Institute for Inorganic Materials using a Mg x-ray source and a He discharge lamp. The samples were introduced into the spectrometer having a base pressure of $\sim 1 \times 10^{-10}$ Torr via an entry airlock, and the surface was scraped *in situ* with a diamond file. In order to obtain the low-temperature phase, the samples were cooled using a liquid-nitrogen cryostat down to ~ 80 K, well below T_i .

Photoemission spectra taken at room temperature and at liquid-nitrogen temperature were virtually identical (Fig. 1) for various photon energies ranging from $h\nu = 21$ eV (HeI) to $h\nu = 1254$ eV (MgK α) as previously mentioned in Ref. 10. Following the new assignment for NiO,^{7,8} the prominent peak at binding energies $E_B = 0-3$ eV (main band) is attributed to $d^8\bar{L}$ final states resulting from screening of the d holes via ligand-to- d charge transfer, the emission at $E_B = 2-6$ eV to S $3p$ states, and the broad emission feature at $E_B = 6-9$ eV (satellite) to unscreened d^7 final states.⁹ This assignment can be tested by measuring resonant photoemission spectra using photon energies in the Ni $3p \rightarrow 3d$ core-excitation region: As the ground state is predominantly d^8 -like, the intensities of the d^7 final states are enhanced via interference between the direct emission ($3d^8 + h\nu \rightarrow 3d^7 + e$) and the Auger decay of the $3p$ -core excitation ($3p^6 3d^8 + h\nu$

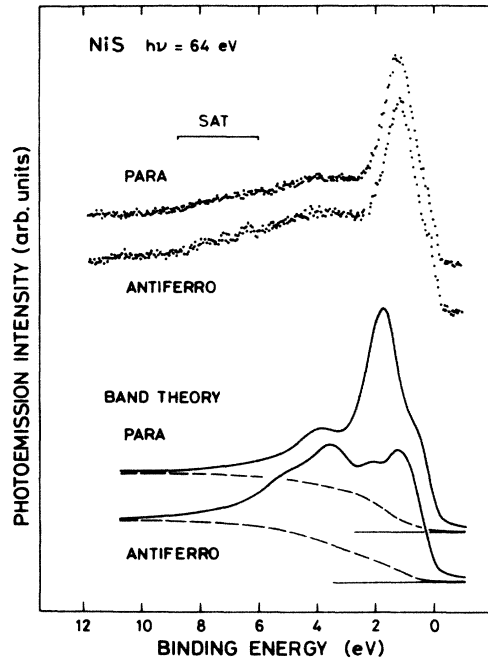


FIG. 1. Valence-band photoemission spectra of NiS in the paramagnetic and antiferromagnetic phases compared with the theoretical spectra calculated from the energy-band densities of states. The dashed curves represent backgrounds due to secondary electrons.

→ $3p^5 3d^9 \rightarrow 3p^6 3d^7 + e$), while the $d^8 \underline{L}$ final states show an antiresonance dip rather than a peak as a function of photon energy.^{7,11} We have indeed found experimentally such a characteristic behavior.

As in the case of NiO,⁷ we have performed a CI calculation on an octahedral NiS_6^{10-} cluster. In this model, intra-atomic correlation at the Ni site and hybridization between neighboring Ni $3d$ and S $3sp$ orbitals are exactly treated, while interaction between different Ni sites is neglected.⁷ The ground state has a form of

$$\Psi_g = a |d^8\rangle + b |d^9 \underline{L}\rangle, \quad (1)$$

and the final state

$$\Psi_f = c_f |d^7\rangle + d_f |d^8 \underline{L}\rangle + e_f |d^9 \underline{L}^2\rangle. \quad (2)$$

This representation of the ground and final states would be relevant at least for the antiferromagnetic phase realized in a semiconductor or a semimetal. The best fit to experiment as shown in Fig. 2 has been obtained by using parameters

$$\langle d^9 \underline{L} | H | d^9 \underline{L} \rangle - \langle d^8 | H | d^8 \rangle \equiv \Delta = 2 \pm 0.3 \text{ eV},$$

$$\langle d^8 \underline{L} | H | d^8 \underline{L} \rangle - \langle d^7 | H | d^7 \rangle \approx \Delta - U = -2 \pm 0.3 \text{ eV},$$

$$\langle d^9 \underline{L}^2 | H | d^9 \underline{L}^2 \rangle - \langle d^8 \underline{L} | H | d^8 \underline{L} \rangle = 0.5 \pm 0.5 \text{ eV},$$

$$(pd\sigma) \approx -2(pd\pi) \approx -0.8(sd\sigma) = -1.5 \pm 0.1 \text{ eV}$$

[cf. $\Delta = 4$ eV, $\Delta - U \approx -3.5$ eV, and $(pd\sigma) \approx -1.1$ eV for NiO (Ref. 7)]. Decomposition of the final states into d^7 , $d^8 \underline{L}$, and $d^9 \underline{L}^2$ components shown in Fig. 2 confirms the above assignment. The degree of Ni $3d$ -S $3sp$ hybridization thus estimated gives a d occupancy of 8.3 and a

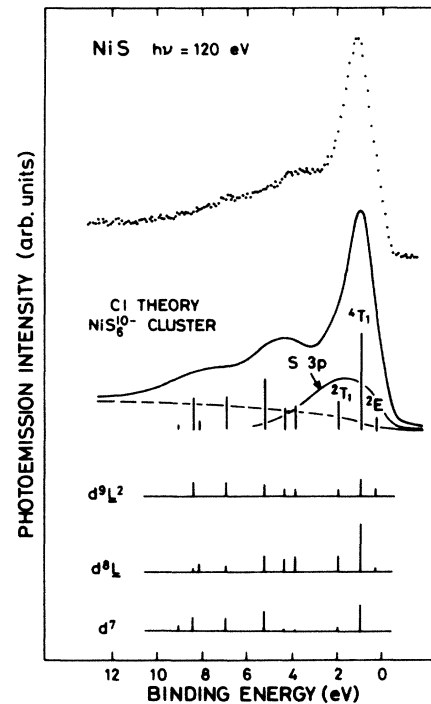


FIG. 2. Valence-band photoemission spectrum of NiS compared with the configuration-interaction (CI) calculation on the NiS_6^{10-} cluster. This spectrum was taken at room temperature but is virtually identical to that taken at liquid-nitrogen temperature.

magnetic moment of $1.7\mu_B$ at the Ni site [cf. $2\mu_B$ for the free Ni^{2+} ion and $1.8\mu_B$ for NiO (Ref. 7)], in good agreement with the result of neutron diffraction experiment, $(1.7 \pm 0.2)\mu_B$.^{5,12}

The U value, 4 ± 0.5 eV, thus deduced, is significantly larger than the one-electron d -band width $W \lesssim 3$ eV of the paramagnetic state calculated below. This is incompatible with the basic assumption in the Mott-Hubbard model, $U \sim W$ (~ 1 eV).³⁻⁵ In order to properly take into account the large U value and the p -band position within the original Mott-Hubbard ($d^7 - d^9$) gap, it seems more appropriate to use the periodic Anderson model¹³ which is an extension of the cluster model to a periodic lattice and explicitly treats the d - p hybridization.

The virtually identical spectra between the two phases seem to imply that the large U ($> W$) suppresses charge fluctuations between Ni sites significantly even in the metallic phase and that the local electronic configuration of the NiS_6 cluster which determines the spectroscopic behavior is not much different between the two phases. However, the cluster model inevitably leads to the $S=1$ local moment, which is apparently inconsistent with the Pauli-paramagnetic behavior in the high-temperature phase.

As Pauli paramagnetism is naturally explained by band theory and that good agreement between photoemission spectra and band theory has been reported for NiAs, a Pauli-paramagnetic metal,¹⁴ we have carried out local-density-functional calculations by using the self-consistent linearized-augmented-plane-wave (LAPW) method. The

results are compared with experiment in Fig. 1, where the calculated partial densities of states (DOS) have been multiplied by photoionization cross sections¹⁵ and broadened for the instrumental resolution (~ 0.5 eV) and lifetime widths. For the antiferromagnetic phase, however, spin-polarized calculations did not converge to give a finite magnetic moment,¹⁶ so that we fixed the exchange potential at the value of the free Ni^{2+} ion within the Ni muffin-tin sphere throughout the iteration cycles. Thus we could obtain a magnetic moment of $\sim 1\mu_B$, but it is still too small as compared to the experimental value of $\sim 1.7\mu_B$. As can be seen in Fig. 1, the d band at $E_B = 0-3$ eV in the paramagnetic state becomes considerably broadened on going to the antiferromagnetic state due to an exchange splitting of ~ 2 eV. Thus, while agreement between theory and experiment is reasonable for the paramagnetic phase, the theory fails to reproduce the spectrum in the antiferromagnetic phase. These difficulties in the antiferromagnetic phase would be due to the limitation of the local-density approximation or the one-electron approximation itself. Therefore, the apparent success in the Pauli paramagnetic phase may not readily be taken as an applicability of the one-electron band model to NiS.

In order to reconcile the localized spectroscopic behavior with the Pauli paramagnetism, we consider quantum fluctuations of the Ni $3d$ local moments in a time scale slower than that detected by photoemission spectroscopy ($\sim 10^{-15}$ sec). Such fluctuations would have resulted from interactions of the local moments with conduction electrons or holes and therefore would become increasingly important with increasing carrier concentration. This mechanism naturally explains the disappearance of the local moments and the appearance of the metallic conductivity that occur simultaneously on going to the high-temperature phase. Then the continuous reduction of the ordered magnetic moment with increasing x in Ni_{1-x}S (Ref. 5) and the extreme sensitivity of T_i on x , where T_i drops to ~ 0 K for $x = 0.033$,¹⁷ may be explained as follows: Since the top of the valence band is $d^8\bar{L}$ -like or $S3p$ -like and since Ni defects act as acceptors, the antiferromagnetic phase is doped with S $3p$ holes for $x > 0$; this will enhance the spin fluctuations, thereby reducing the ordered moment and lowering T_i . Substitution of Se for S also lowers T_i : T_i becomes ~ 0 K for $y = 0.133$ in $\text{NiS}_{1-y}\text{Se}_y$.¹⁸ The Se substitution will reduce (and collapse) the band gap, as the Se $4p$ levels are higher than S $3p$. This increases the number of conduction electrons and/or holes and thus enhances the spin fluctuations. The Pauli-paramagnetic susceptibility χ_P (Refs. 18 and 19) which is relatively enhanced over the specific-heat

coefficient γ (Ref. 20) by a factor of ~ 3 may be an indication of magnetic fluctuations.²¹ Also, the electrical resistivity of $\text{Ni}_{0.98}\text{S}_{1-y}\text{Se}_y$ has shown a T^2 dependence²² as predicted by the spin-fluctuation theory of nearly antiferromagnetic metals.²³

Disappearance of local moments has also been observed in the α phase of Ce metal, and explained as due to fluctuations of the $4f^1$ ($J = \frac{5}{2}$) local moment through hybridization with conduction electrons within the impurity model, namely, as due to a $4f^1 - 4f^0$ valence-fluctuation effect.²⁴ Valence fluctuations in the case of NiS, however, occur between two magnetic configurations d^8 ($S = 1$) and d^9 ($S = \frac{1}{2}$) unlike Ce, and therefore would not lead to a nonmagnetic (Pauli-paramagnetic) ground state within the impurity model.²⁵ Consequently, fluctuations involving different Ni sites should be considered. In the antiferromagnetic phase, as the DOS at E_F is low, ordinary superexchange coupling between the local moments dominates as in magnetic insulators. Presumably, this antiferromagnetic correlation between the fluctuating local moments persists in the Pauli-paramagnetic phase. Such type of magnetic correlation has been proposed to be responsible for the Pauli-paramagnetic behavior of heavy-fermion systems,²⁶ and may be experimentally detected by neutron scattering.²⁷

In conclusion, d electrons in NiS have so strong intratomic Coulomb interaction that they are nearly localized in both the antiferromagnetic and Pauli-paramagnetic phases. The paramagnetic behavior is suggested to be due to fluctuations of the local moments resulting from hybridization with S $3p$ -band states in the vicinity of E_F . This situation is qualitatively analogous to heavy Fermion systems, in which also nearly localized f electrons give rise to Pauli paramagnetism at low temperatures.²⁸ Therefore, for fundamental understanding of the electronic and magnetic properties of NiS as well as of other $3d$ transition-metal compounds, theoretical efforts to explain both the high-energy spectroscopic and low-energy (magnetic, transport, and thermal) properties using the periodic Anderson model with the new parameter set are necessary. A crucial experimental test of the spin fluctuations would be neutron scattering experiments. Finally, we would like to point out the similarity between Ni_{1-x}S and the recently discovered superconducting Cu oxides that a transition from local-moment antiferromagnetism to Pauli paramagnetism is observed when the system is doped with p -hole carriers.²⁹

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¹N. F. Mott, *Metal Insulator Transitions* (Taylor and Francis, London, 1974).

²J. T. Sparks and T. Komoto, *Phys. Lett.* **25A**, 398 (1967); S. Anzai and K. Ozawa, *J. Phys. Soc. Jpn.* **24**, 271 (1968).

³R. M. White and N. F. Mott, *Philos. Mag.* **24**, 845 (1971).

⁴D. K. Ray and F. Kajzar, *Proc. R. Soc. London Ser. A* **373**, 253 (1980).

⁵J. M. D. Coey, R. Brusetti, A. Kallel, J. Schweizer, and H. Fuess, *Phys. Rev. Lett.* **32**, 1257 (1974).

⁶L. F. Mattheiss, *Phys. Rev. B* **10**, 995 (1974).

⁷A. Fujimori, F. Minami, and S. Sugano, *Phys. Rev. B* **29**, 5225 (1984); **30**, 957 (1984).

⁸G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.* **53**, 2239 (1984); S. Hüfner, J. Osterwalder, T. Riesterer, and F. Hul-

- liger, *Solid State Commun.* **52**, 793 (1984).
- ⁹S. Hüfner, *Z. Phys. B* **58**, 1 (1984); **61**, 135 (1985); S. Hüfner, T. Riesterer, and F. Hulliger, *Solid State Commun.* **54**, 689 (1985); J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985); *J. Magn. Magn. Mater.* **54–57**, 607 (1986); T. Riesterer, L. Schlapbach, and S. Hüfner, *Solid State Commun.* **57**, 109 (1986).
- ¹⁰S. Hüfner and G. K. Wertheim, *Phys. Lett.* **44A**, 133 (1973).
- ¹¹L. C. Davis, *Phys. Rev. B* **25**, 2912 (1982); G. van der Laan, *Solid State Commun.* **42**, 165 (1982).
- ¹²J. T. Sparks and T. Komoto, *Rev. Mod. Phys.* **40**, 752 (1968).
- ¹³J. W. Allen, *J. Magn. Magn. Mater.* **47,48**, 168 (1985).
- ¹⁴W. P. Ellis, R. C. Albers, J. W. Allen, Y. Laissailly, J.-S. Kang, B. B. Pate, and I. Lindau, *Solid State Commun.* **62**, 591 (1987).
- ¹⁵J. J. Yeh and I. Lindau, *At. Data Nucl. Data Tables* **32**, 1 (1985).
- ¹⁶A calculation using the full-potential version of the LAPW method has given the same result.
- ¹⁷R. Brusetti, J. M. D. Coey, G. Czjzek, J. Fink, F. Gompf, and H. Schmidt, *J. Phys. F* **10**, 33 (1980).
- ¹⁸S. Anzai, M. Matoba, M. Hatori, and H. Sakamoto, *J. Phys. Soc. Jpn.* **55**, 2531 (1986).
- ¹⁹R. F. Koehler and R. L. White, *J. Appl. Phys.* **44**, 1682 (1973).
- ²⁰J. M. D. Coey and R. B. Brusetti, *Phys. Rev. B* **11**, 671 (1975).
- ²¹The experimental values $\gamma = 6.2 \pm 0.4$ mJ/molK² (Ref. 17) and $\chi_F = (2.0-2.5) \times 10^{-6}$ emu/g (Refs. 19 and 20) for the metallic phase are ~ 1.8 and ~ 5 times larger than those obtained by the present band-structure calculations, respectively.
- ²²M. Matoba and S. Anzai, *J. Magn. Magn. Mater.* **70**, 213 (1987).
- ²³K. Ueda, *J. Phys. Soc. Jpn.* **43**, 1497 (1977).
- ²⁴J. W. Allen and R. M. Martin, *Phys. Rev. Lett.* **49**, 1106 (1985).
- ²⁵Y. Kuramoto, *Z. Phys. B* **65**, 29 (1986).
- ²⁶G. Aeppli, H. Yoshizawa, Y. Endo, B. Bucher, J. Hufnagel, Y. Onuki, and T. Komatsubara, *Phys. Rev. Lett.* **57**, 122 (1986).
- ²⁷P. Blankenbecler, J. R. Fulco, W. Gill, and D. J. Scalapino, *Phys. Rev. Lett.* **58**, 411 (1987).
- ²⁸P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, *Comments Condens. Mater Phys.* **12**, 99 (1986), and references therein.
- ²⁹A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **36**, 1075 (1987); *Solid State Commun.* **63**, 857 (1987).