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Photoemission study of the metal-nonmetal transition in NiS

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We have observed small changes in the ultraviolet photoemission spectra of NiS across the temperature-induced phase transition between the Pauli-paramagnetic metal and the antiferromagnetic nonmetal. In going from the nonmetallic to the metallic phases, the main band ($d^8\underline{L}$) within ~ 3 eV below the Fermi level E_F is shifted toward E_F by 0.05 eV. This observation is consistent with the closing of a S $3p$–Ni $3d$ charge-transfer gap and cannot be reconciled with that of a band gap of antiferromagnetic origin. The spectrum loses a small fraction of intensity in the vicinity of E_F as the gap is collapsed. The virtually identical line shape of the main band between the two phases is consistent with the persistence of short-range antiferromagnetic correlation in the paramagnetic phase.

I. INTRODUCTION

The hexagonal form of NiS undergoes a first-order metal-nonmetal transition at $T_t \sim 260$ K: The high-temperature phase is a Pauli-paramagnetic metal and the low-temperature phase is an antiferromagnetic semiconductor or semimetal.[1,2] This transition has previously been explained in terms of electron correlation within the Ni $3d$ band. Namely, the transition has been attributed to the opening of a Mott-Hubbard gap (d^7-d^9 gap) in the nonmetallic phase.[3] However, recent photoemission studies combined with Anderson-model or cluster-model analyses have revealed that the lowest ionization state of this compound is not d^7 as is assumed in the Mott-Hubbard type model but is $d^8\underline{L}$, in which the Ni $3d$ hole d^7 is screened by charge transfer from the S atoms, where $\underline{L}$ denotes a ligand (S $3p$) hole.[4–6] Unscreened d^7 states are located well (5–10 eV) below the Fermi level E_F, as confirmed by a resonant photoemission study in the Ni $3p \rightarrow 3d$ core absorption region.[5] Thus NiS is classified into the charge-transfer regime rather than the Mott-Hubbard regime of the Zaanen-Sawatzky-Allen diagram for the transition-metal compounds.[7]

According to the cluster-model analysis,[6] the overall features of the photoemission spectra are characterized by large energy-scale parameters such as the Ni d intra-atomic Coulomb energy U (~ 4 eV), the S p to Ni d charge-transfer energy Δ (~ 2 eV), and the p-d transfer integrals $[(pd\sigma) \simeq -2(pd\pi) \sim -1.5 \text{ eV}]$. No pronounced spectral changes have been observed below and above T_t[5,6,8] in contrast with the results of band-structure calculations which predict considerable changes (on the energy scale of a few eV) between the paramagnetic and antiferromagnetic phases.[5,6]

While the large band gap of NiO (~ 4 eV) is naturally explained as a $d^8\underline{L}$-d^9 charge-transfer gap using the large energy-scale parameters of this compound,[9,10] it is not obvious whether the small band gap (or pseudogap) in the nonmetallic phase of NiS (~ 0.1 eV)[11] is of the same origin or not. Although standard one-electron band theory breaks down in predicting the overall features of the photoemission spectra due to the strong correlation among the Ni $3d$ electrons, band theory might remain valid for states in the vicinity of E_F in the metallic state and possibly in the nonmetallic state in the sense of renormalized band theory. Then the antiferromagnetic ordering might open a gap at E_F as described in an earlier band-structure calculation.[12] In this paper we report on the results of ultraviolet photoemission measurements on NiS performed with higher energy resolution than in our previous work[5,6] in an attempt to detect changes in the electronic structure across the metal-nonmetal transition associated with the formation of the small band gap.

II. EXPERIMENT

We have studied polycrystalline samples with relatively large (2–3 mm) grains cut from an ingot which had been annealed at 700 °C for 2 days and at 500 °C for 10 days and then quenched in ice water. The ingot showed a transition at $T_t \sim 250$ K and a heat of transition 1000 J/mole (corresponding to $1-x \sim 0.995$ in Ni_{1-x}S)[13] with a width of ~ 5 K. The photoemission spectra of these samples were free from emission centered at ~ 7 eV below E_F which can be attributed to oxygen $2p$ states from contamination. Indeed, oxygen and carbon signals were below the detectability limit of core-level x-ray photoemission spectroscopy (XPS) both at liquid-nitrogen and room temperatures.

The spectra were taken with a spectrometer having a base pressure of $\sim 1 \times 10^{-10}$ Torr equipped with a He discharge lamp for ultraviolet photoemission spectroscopy (UPS) and a Mg x-ray source for XPS. The samples were introduced into the spectrometer via an airlock and were mounted on a liquid-nitrogen-cooled cryostat. The samples were cooled to ~ 80 K, well below T_t, in order to obtain a nonmetallic phase. The instrumental resolution was $\gtrsim 0.1$ eV for UPS and the thermal broadening ($\sim 4kT$) was $\lesssim 0.1$ eV at room temperature. Binding energies were calibrated using the Fermi edge of Cu metal and were reproducible to within ~ 0.01 eV for different series of experiments.

III. RESULTS

Figure 1 shows valence-band photoemission spectra taken with He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) radiation at room temperature. The broad emission centered at a binding energy $E_B \sim 5$ eV is due to the S $3p$ band. This emission is suppressed in going from $h\nu = 21.2$ eV to 40.8 eV because of the Cooper minimum of the S $3p$ atomic-orbital cross section around ~ 50 eV.[14] Therefore the 40.8-eV spectrum can be viewed approximately as a Ni $3d$-derived photoemission spectrum. In the bottom of Fig. 1, the 40.8-eV spectrum is compared with the result of the NiS_6 cluster-model calculation,[6] according to which the main band at 0–3 eV is predominantly due to $d^8\underline{L}$ final states and the broad satellite at 5–10 eV is due to d^7 final states. As reported previously,[5,6,8] no appreciable changes are observed on this energy scale across T_t.

Figure 2 shows $h\nu = 21.2$ eV spectra for both phases within ~ 3 eV below E_F. The metallic phase shows a Fermi edge with a relatively high density of states (of the order of a few states/eV Ni atom). Although the previous lower resolution spectra have revealed no appreciable changes between the two phases,[6] the present results clearly show that the spectrum is slightly shifted to lower binding energy in going from the nonmetallic to the metallic phases. (In the higher binding energy region, the spectra are so broad that no clear difference between the two phases could be established.)

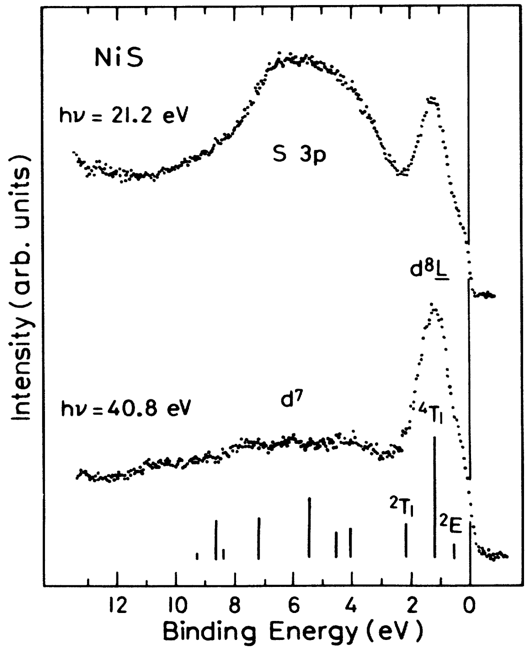

FIG. 1. Photoemission spectra of NiS at room temperature. The vertical bars at the bottom show the result of the NiS_6 cluster calculation (Ref. 6).

In order to highlight the changes between the two spectra we plot their difference curves in the same figure. Here, the two spectra have been normalized to the peak height of the main ($d^8\underline{L}$) band. Prior to subtraction, the low-temperature spectrum had been broadened by $\sim 4kT$ in order to correct for the thermal broadening effect (but this did not affect the resulting difference spectra appreciably.) The difference spectrum without energy shift ("shift = 0.0 eV" in Fig. 2) resembles the derivative spectrum shown at the bottom of Fig. 2, except for the structure in the vicinity of E_F. Indeed, the difference spectrum vanishes by shifting the room-temperature spectrum toward higher binding energy by 0.05 eV prior to subtraction (shift = 0.05 eV in Fig. 2), except for the re-

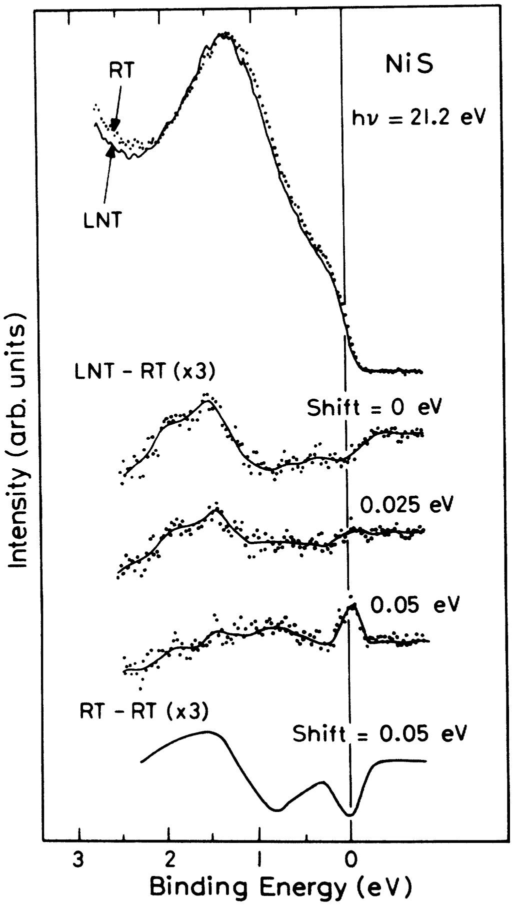

FIG. 2. Photoemission spectra of NiS at room temperature (RT) (dots) and liquid-nitrogen temperature (LNT) (solid line). Differences between the two spectra are shown below them. The room-temperature spectrum has been shifted to higher binding energy prior to subtraction by the amount shown in the figure. At the bottom is shown the derivative curve of the room temperature spectrum (which has been obtained by subtracting the spectrum form itself by shifting it by 0.05 eV).

sidual intensity at E_F and the background slowly decreasing toward higher binding energy. This indicates that the amount of the shift is 0.05 eV between the two phases for the most part of the spectrum. (The background results from the different secondary-electron backgrounds for the different surface conditions: When cooling the sample below T_t, the jump in the lattice constants resulted in microcracks.) The presence of the residual intensity at E_F in the "shift=0.05 eV" spectrum confirms that the energy shift between the two phases is real and not an artifact of experiment due to, e.g., insufficient reproducibility of binding energies. Indeed, this result was reproducible between different samples.

The residual signal at E_F in the "shift=0.05 eV" spectrum suggests that new occupied states appear in this energy region when the gap or pseudogap is opened, or that some occupied states disappear from the top of the valence band when the gap is collapsed. Since the total number of occupied states should not change across the temperature-induced transition, the disappeared states may be converted to states with lower photoionization cross sections (for this photon energy, the photoionization cross section of Ni 3d is lower than that of S 3p by a factor of ~ 2)[14] or may be redistributed into a wider energy range in the metallic phase.

IV. DISCUSSION

The observed shift between the two phases is consistent with the closing of the band gap in the high-temperature phase. The magnitude of the shift (0.05 eV) is also consistent with the magnitude of the gap (0.1 eV) estimated from the optical study,[11] since E_F in a nonmetallic sample can be located anywhere within the band gap depending on the position of pinning levels.

We have previously shown[5,6] that the metal-nonmetal transition in NiS cannot be explained within the conventional one-electron band theory because the theory predicts a large (~ 2 eV) exchange splitting of the Ni 3d band in the antiferromagnetic state. Even in the sense of renormalized band theory, in which band widths are renormalized due to electron correlation, the present results show no evidence for exchange splitting within the present energy resolution. For a small exchange splitting, a gap could in principle be opened at the Brillouin-zone boundary, but the formation of such a gap cannot be reconciled with the complex redistribution of the photoemission intensity since redistribution of states due to this formation is limited in the vicinity of E_F and would not lead to changes in the emission intensity at E_F.

Starting from the nonmetallic side of the transition, the experimental results are consistent with the simple closing of the $d^8\underline{L}$-d^9 charge-transfer gap. The lattice parameters decrease in going to the metallic phase (by $\sim 1\%$),[1,2,13,15] which increases $d^8\underline{L}$-d^7 hybridization hence $d^8\underline{L}$-d^7 repulsion consistent with the shift of the $d^8\underline{L}$ band toward E_F. Thus NiS seems to lie actually very close to the metal-insulator boundary within the charge-transfer regime. This view appears reasonable considering the existence of another change-transfer insulator, NiS_2, in which the magnitude of the charge-transfer gap is a little larger (0.3 eV).[16] Further, considering the facts that the structure magnetic ordering affects the band structure considerably,[17] it would be difficult to explain the opening of the gaps of the same order of magnitudes for such different crystal structures as NiS (hexagonal NiAs-type) and NiS_2 (cubic FeS_2-type) in terms of magnetic ordering.

Thus we may reasonably attribute the band gap to a charge-transfer gap and the metal-nonmetal transition to the collapse of this charge-transfer gap, whereas the description of the resulting metallic state and its photoemission spectra is far from trivial. While the d^8 state is the stable configuration for the nonmetallic ground state, the closing of the gap results in a charge fluctuation of the type $d^8\underline{L} \leftrightarrow d^8 \leftrightarrow d^9$ in the metallic ground state. Thus, as illustrated in Fig. 3, part of the $d^8 \rightarrow d^8\underline{L}$ electron-removal spectral weight (in the photoemission spectra) is transferred to above E_F to become $d^8\underline{L} \rightarrow d^8$ electron-addition spectral weight, while part of the $d^8 \rightarrow d^9$ electron-addition spectral weight above E_F is transferred below E_F to become $d^9 \rightarrow d^8$ electron-removal spectral weight. The decrease in the photoemission intensity in the vicinity of E_F may thus be associated with the loss of the $d^8 \rightarrow d^8\underline{L}$ electron-removal spectral weight. The newly added $d^9 \rightarrow d^8$ electron-removal weight is not clearly identified in the present spectra because it may be spread over a wider energy region due to many-body

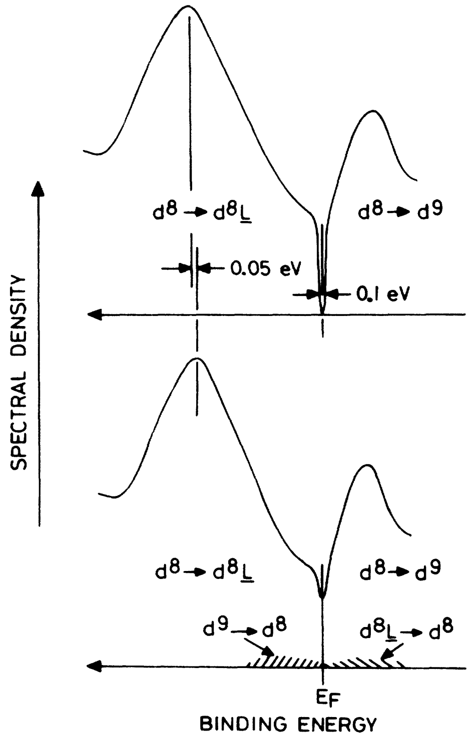

FIG. 3. Schematic representation of the spectral densities near E_F for the metallic (bottom) and nonmetallic (top) states. The actual distribution of the $d^9 \rightarrow d^8$ and $d^8\underline{L} \rightarrow d^8$ spectral weight (shaded) is not known at the moment. Higher energy resolution is needed to determine the detailed spectral line shapes in the vicinity of E_F.

effects, or may have a smaller photoionization cross section than for the $d^8 \rightarrow d^8\underline{L}$ component.[13]

The metallic state of NiS is complicated also from the view point of its transport properties. The gap closing introduces the same numbers of electrons (d^9) and holes ($d^8\underline{L}$) into the charge-transfer insulator. One may thus expect that the mobility of the holes is larger than that of the electrons because the holes are created in the wide S $3p$ band and the electrons are created in the narrow Ni $3d$ band, but actually the thermoelectric power is negative in the metallic region.[18,19] (In the nonmetallic phase, both thermoelectric power and Hall coefficients are indeed positive.[18,20]) This means that the picture of electrons and holes introduced into the charge-transfer insulator may not necessarily be valid to understand the nature of the metallic state of NiS, as in the case of highly doped $La_{2-x}Sr_xCu_4$ or $Nd_{2-x}Ce_xCuO_4$ (>0.2–0.3 carriers/Cu atom), where a Fermi liquid picture becomes more appropriate than the picture of doped charge-transfer insulators.[21] In the case of NiS in the metallic phase, the number of electrons or holes may be estimated from the density of states at E_F (a few states/eV Ni atom) and the energy shift across the phase transition (0.05 eV) to be of the order of 0.1/Ni atom, which may be large enough considering the high background polarizability of sulfer atoms compared to that of oxygen.

Finally, we discuss implications of the experimental fact that, except for the small changes mentioned above, the spectra remain virtually unchanged between the two phases. While the electronic structure of the local NiS_6 cluster determines the gross energy distribution of the spectral intensities in terms of the discrete energy levels as shown in Fig. 1, the intercluster hopping of holes broadens these levels into bands and determines the widths and line shapes of the photoemission spectra, particularly for states near E_F where the lifetime broadening effect is relatively small. Since such a hopping process is crucially dependent on the arrangement of Ni spins, the virtually identical line shapes of the $d^8\underline{L}$ band between the two phases suggest that the spin correlations are not much different. We expect that the nearest-neighbor spin correlation along the c axis is certainly most important for the intersite hopping because of the short Ni-Ni atomic distance (~ 2.7 Å compared with ~ 3.4 Å within the c plane for the NiAs structure)[22] and that the photoemission results may be explained by the persistence of short-range antiferromagnetic correlation along the c axis even in the paramagnetic state. Indeed, the Ni-Ni exchange coupling along the c axis is unusually strong, ~ 1000 K,[3,23] which is much higher than T_t. This situation may be analogous to the two-dimensional short-range antiferromagnetic correlation observed for $La_{2-x}Sr_xCuO_4$.[24] In order to study the possible dynamical spin correlation in NiS, magnetic diffuse neutron scattering experiments would be of great interest.

In conclusion, we have observed small changes in the photoemission spectra of NiS across the metal-nonmetal transition. The results are consistent with the closing of the $d^8\underline{L}$-d^9 charge-transfer gap in going from the nonmetallic to metallic phases, and cannot be explained by a band gap resulting from the antiferromagnetic ordering in the sense of conventional nor renormalized band theory. The complex intensity redistribution involving the states in the vicinity of E_F possibly reflects the many-body nature of the correlated metallic state. Otherwise, the $d^8\underline{L}$-band line shape is virtually identical between the two phases, which suggests that short-range antiferromagnetic correlation may persist in the paramagnetic phase.

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