Electronic Structure of $NiS_{1-x}Se_x$ across the Phase Transition

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We report very highly resolved photoemission spectra of $NiS_{1-x}Se_x$ across the so-called metal-insulator transition as a function of temperature as well as composition. The present results convincingly demonstrate that the low temperature, antiferromagnetic phase is metallic, with a reduced density of states at E_F. This decrease is due possibly to the opening of gaps along specific directions in the Brillouin zone caused by the antiferromagnetic ordering. [S0031-9007(97)05260-5]

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While metal-insulator transition has been one of the outstanding problems in condensed matter physics [1], the specific case of a transition in hexagonal NiS [2] as a function of temperature has been possibly the most controversial, spanning a period of three decades. The controversy relates to the very basic issue of the nature of the transition, with various groups describing it as a metal-insulator transition [2–7], while a nearly equal number of groups claim it to be a metal-metal transition [8–12]. The transport and magnetic properties are that NiS is a highly conducting ($\approx 10^{-5}$ ohm cm) Pauli paramagnetic metal at room temperature with a characteristic metallic dependence of resistivity on temperature [10,11]. Near 260 K, the system undergoes a first order phase transition, with a nearly two orders of magnitude increase in resistivity ($\approx 10^{-3}$ ohm cm) [10,11]. The system becomes antiferromagnetic below the transition [3], showing a volume expansion of about $\approx 1.9\%$ without any change in crystal symmetry. While it is generally agreed that the high temperature phase represents an example of a highly conducting metallic compound, the controversy continues to exist concerning the nature of the low temperature phase. Normally one would expect that transport measurements would readily resolve the question concerning the metallic or insulating phase of the ground state. A very unusual nearly temperature-independent resistivity down to about 4 K [10,11], however, does not provide any unambiguous clue. While in a metallic system the resistivity is expected to decrease with temperature, in contrast to the observed behavior, an insulating ground state should have very manifest exponentially increasing resistivity, when the temperature scale is lower than the band gap. Thus, if the low temperature phase is insulating, the band gap should be much smaller than 4 K (<0.5 meV). On the other hand, if it is metallic, it has to be an unusual state where the resistivity is nearly independent of temperature over a wide range of temperature ($4 \leq T \leq 260$ K). Unfortunately, theoretical studies have not been of much help in settling these discussions in favor of either of the views. The earliest non-self-consistent band structure calculations [13] correctly predicted the high temperature Pauli paramagnetic phase to be metallic, while the low temperature antiferromagnetic phase yielded a small gap. However, subsequent self-consistent band structure calculations [14] based on local spin density approximation (LSDA) failed to yield any gap. Similarly, the LDA + U method [15] obtained a metallic state for the low temperature phase. In contrast, a recent improved version of the LDA + U method has obtained a band gap for the low temperature phase [16], which is by far too large to be consistent with a temperature-independent resistivity down to 4 K. Thus, neither transport measurements nor theoretical calculations have been able to resolve the controversy surrounding the ground state behavior of NiS.

Metallic and insulating behaviors are distinguished by the presence or the absence of finite density of states (DOS) at the Fermi energy, which can be probed by various spectroscopic techniques. These have so far favored an insulating ground state for NiS [7]. An early optical reflectivity study showed the existence of a characteristic dip at about 140 meV for the low temperature phase compared to the high temperature metallic phase [6]; this has been cited [7] as proof for the existence of a band gap of the same order. Photoelectron spectroscopy, which is the only technique that can directly probe the density of states at E_F, also provided evidence for an insulating state of NiS at low temperature. Specifically, a moderately high resolution ($\Delta E \approx 36$ meV) photoelectron spectrum of NiS at low temperature has been reported [7]. While it exhibits finite spectral weight at E_F, the authors concluded on the basis of an analysis of the density of states and various broadening effects such as resolution and thermal (Fermi-Dirac) broadening that there is a gap of ≈ 10 meV in the occupied part of the DOS. The analysis also suggested a finite DOS at the band edge, which is very unusual for a system with a three-dimensional crystal structure. Since discontinuous band edges are only expected in one and two dimensions, this finding is of special significance,

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implying a novel consequence of electron correlations [7]. Thus, the combination of various spectroscopic results suggests that (1) there is a total band gap of about 140 meV in NiS, and (2) the leading edge of the occupied DOS is about 10 meV below E_F, with the remaining part (130 meV) of the band gap presumably occurring in the unoccupied part. Such a scenario, however, is in complete disagreement with the temperature-independent transport data, which suggest an upper limit of the band gap, if any, to be less that 4 K (<0.5 meV). In order to address this unresolved puzzle concerning the nature of the transition and the ground state of NiS, we have reinvestigated the electronic structures in NiS and several related compounds using temperature-dependent photoelectron spectroscopy performed with very high energy resolution. Our study conclusively shows that the ground state is metallic and, thus, the phase transition represents a metal-to-*anomalous-metal* transition with decreasing temperature.

Temperature-dependent photoemission (PE) experiments were carried out on polycrystalline samples of $NiS_{1-x}Se_x$, with $x = 0.0$, 0.11, 0.15, and 0.17, which were prepared by solid state reaction in sealed quartz tubes [12]. The samples were characterized before and after the PE experiments by x-ray diffraction. Proper bulk and surface stoichiometries were verified by x-ray fluorescence spectroscopy and core-level PE, respectively, and scanning electron microscopy revealed that disturbing grain boundary regions are small. The samples with $x = 0.0$ and $x = 0.11$ showed a sharp increase of the resistivity at transition temperatures $T_t = 260$ and 97 K, respectively, while for $x = 0.15$ and $x = 0.17$ no transition was observed [17]. The samples were mounted on a Cu sample holder fitted to a continuous-flow He cryostat allowing measurements between 25 and 300 K. They were cleaned *in situ* by repeated scraping with a diamond file; sample cleanness was checked by valence-band PE at $h\nu = 40.8$ eV. PE spectra were recorded with a Scienta SES-200 electron energy analyzer using a Gammadata VUV-5000 photon source for excitation.

Addressing the question of the DOS close to E_F in a PE experiment imposes several requirements on the experimental resolution as well as on the stability of the experimental Fermi-level position. In our experiment, both were monitored by repeatedly recording the Fermi edge region of polycrystalline Ag mounted close to the $NiS_{1-x}Se_x$ samples. The total-system resolution achieved in these experiments was 9 ± 1 meV at $h\nu = 21.2$ eV, as determined from the Ag Fermi edge at 25 K (see Fig. 1). Furthermore, from the numerous Ag spectra, which were always recorded as reference before and after taking data from the $NiS_{1-x}Se_x$ samples, we found the position of E_F to be reproducible within 1 meV. As indicated in Fig. 1, even a shift as small as 2 meV would be clearly visible. Another issue which has to be considered is the difficulty in determining the Fermi-level position from a PE spectrum in a system where

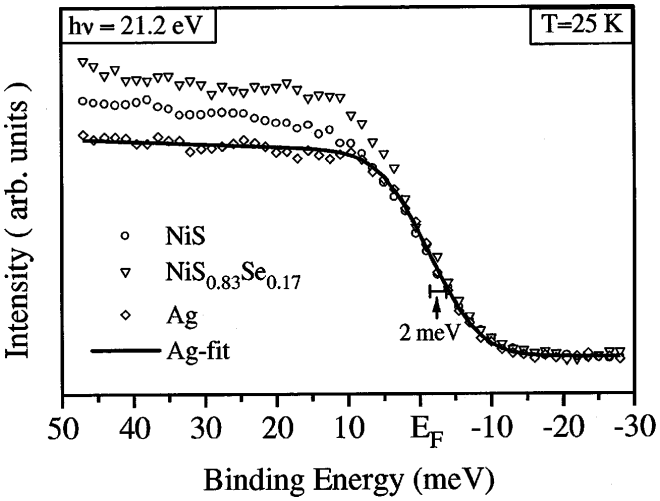

FIG. 1. PE spectra of polycrystalline NiS, $NiS_{0.83}Se_{0.17}$, and Ag in a narrow region around E_F recorded at 25 K. Within experimental accuracy (<1 meV), all spectra show completely overlapping Fermi cutoffs. The solid line represents a fit of the Ag spectrum with an experimental resolution of 9 meV (FWHM).

the DOS is not slowly varying across E_F. In order to avoid such ambiguities, spectra were also taken from $NiS_{0.85}Se_{0.15}$ and $NiS_{0.83}Se_{0.17}$ as reference systems with very similar electronic structure as NiS and $NiS_{0.89}Se_{0.11}$, which, however, do not undergo the phase transition and stay metallic in the whole temperature range relevant in this study. Together with NiS, Fig. 1 displays PE spectra of $NiS_{0.83}Se_{0.17}$ taken at 25 K, and an arbitrarily scaled Ag spectrum. Evidently, the inflection points of all curves are at the same energy. We have analyzed the three spectra in Fig. 1 in terms of polynomial expressions for the DOS in order to determine the Fermi energy in each case. It is found that the three independently determined Fermi energies for these three systems coincide within less than 1 meV. This result strongly suggests that the DOS of NiS is metallic also in the low temperature phase, which will be demonstrated further in the following.

Figure 2 displays comparative PE spectra of all four $NiS_{1-x}Se_x$ compounds taken above T_t at 300 K (left panel), and below T_t (right panel). As shown in the insets, all spectra are normalized to equal intensities at 680 meV binding energy (BE), which leads to proper normalization over the whole spectral range at higher BE's including the Ni d bands. At $T = 300$ K, the spectra of all systems are identical in the narrow range around E_F, reflecting identical metallic DOS. Below T_t, distinct differences are observed between those systems, which undergo the phase transition (NiS, $NiS_{0.89}Se_{0.11}$) and those which do not ($NiS_{0.85}Se_{0.15}$, $NiS_{0.83}Se_{0.17}$). The data analysis clearly shows that the spectra of the latter group ($x = 0.15$ and 0.17) are characterized by the same DOS for both 300 and 25 K spectra; the same DOS is also consistent with the 300 K spectra of $x = 0.0$ and 0.11, as is evident

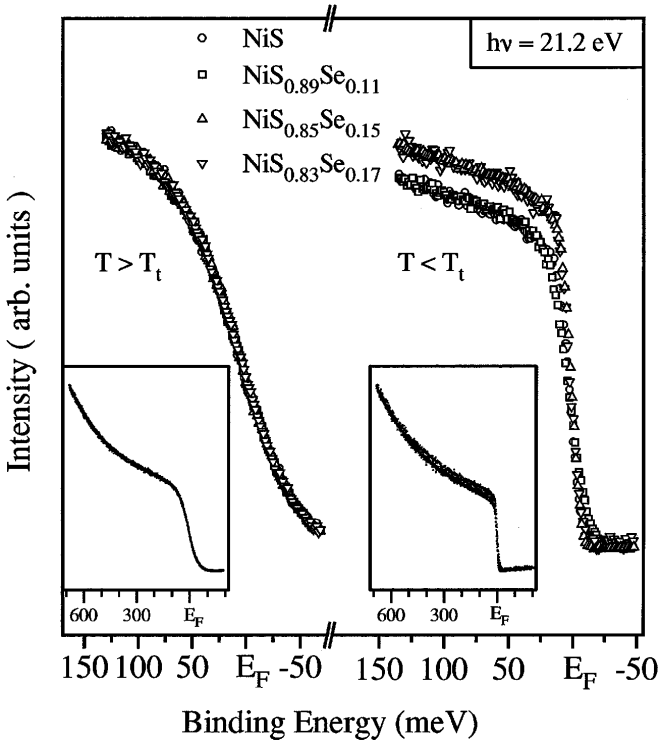

FIG. 2. PE spectra of $NiS_{1-x}Se_x$ with $x = 0.0$, 0.11, 0.15, and 0.17, recorded above (left) and below (right) the transition temperature T_t. For $T > T_t$ all samples show the same spectral weight at E_F, while for $T < T_t$ a substantial decrease is observed for NiS and $NiS_{0.89}Se_{0.11}$. The insets display a wider energy range, demonstrating the proper normalization of the spectra.

in the left panel of Fig. 2. In sharp contrast, the low temperature ($T < T_t$) spectra of $x = 0.0$ and 0.11 clearly show a decrease of the DOS at E_F. Because of technical reasons, the spectrum of $NiS_{0.89}Se_{0.11}$ was not recorded at 25 K but at 80 K, which, nevertheless, is also well below T_t. However, apart from the reduced DOS below T_t, all systems are characterized by a finite DOS at E_F. It should be noted that significant changes are observed here in the PE spectra, which are obviously related to the phase transition. This means that the surface sensitivity of the method does not appear to be a crucial drawback in the particular case of these correlated systems.

The above results clearly show that within the experimental accuracy there is no gap between E_F and the leading edge of the spectrum of NiS at low temperature. However, this does not rule out the possibility of an abrupt band edge as proposed in Ref. [7] with the Fermi level pinned very close ($\ll$1 meV) to this edge. Therefore, these results are not sufficient to prove the ground state of NiS to be metallic with an absence of a gap in the DOS. To establish that there is no gap directly above E_F, the unoccupied DOS was probed using highly resolved PE spectroscopy at various temperatures, progressively populating states above E_F with increasing temperature. Since an insulator with a band gap directly above E_F cannot be populated, while a metal with continuous and finite DOS above E_F can, the temperature dependence of the spectra of a metal and an insulator are fundamentally different. We show the near-E_F spectra of NiS collected at four different temperatures within the low temperature phase in Fig. 3 (open symbols). At all temperatures, the spectra cross a common energy point which, within experimental uncertainty, is the Fermi energy. Furthermore, there is clear evidence of a progressive and systematic development of spectral weight above E_F and a corresponding depletion below E_F with increasing temperature. This is a convincing demonstration of finite DOS above E_F which is thermally populated. In order to put this on a quantitative basis, we have carried out a least-squares-error analysis of these spectra. It turns out that all four spectra can be described in terms of a *single* DOS by only including the Fermi-Dirac distribution for the respective temperatures (solid lines). For comparison, Fig. 3 also displays the spectrum of NiS at 300 K, i.e., well above the transition. The inset in Fig. 3 summarizes the results of the present study, showing the extracted DOS of NiS of both the high temperature and the low temperature phases. It is evident that both phases are metallic, with a smaller DOS at E_F in the low-temperature phase. This decrease of the DOS at E_F is clearly correlated to the phase transition, since it is only observed for NiS and $NiS_{0.89}Se_{0.11}$, while for $NiS_{0.85}Se_{0.15}$ and $NiS_{0.87}Se_{0.17}$, which do not undergo the phase transition, the DOS does not change (see Fig. 2).

The results discussed so far establish that the ground state of NiS and related compounds is definitely metallic with a large and continuous DOS across E_F, and the increase in resistivity across the phase transition is contributed by a decrease in the DOS at and near E_F. For a possible explanation of this decrease, it is interesting to note the similarity between the temperature-dependent

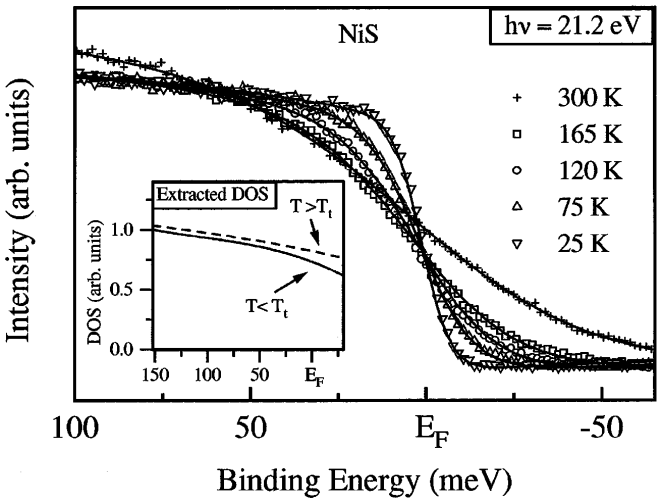

FIG. 3. PE spectra of NiS recorded at various temperatures below the phase transition temperature T_t (open symbols), together with a 300 K spectrum. The inset displays the derived DOS for $T > T_t$ and $T < T_t$.

optical properties of NiS and chromium metal, which also reveals a characteristic dip in reflectivity below the antiferromagnetic transition temperature (see Fig. 6 in Ref. [6]). This dip in the case of Cr has been convincingly demonstrated [18] to arise from the antiferromagnetic ordering, opening up gaps in the electronic band structure only along specific directions in the Brillouin zone, with the total DOS being continuous across E_F. From these results, it appears reasonable to interpret the observed decrease of the DOS at E_F in NiS below T_t (Figs. 2 and 3), as well as the dip in the optical reflectivity [6] as a reflection of the opening of gaps along specific directions only, caused by the antiferromagnetic ordering. The present results do not offer any clear explanation for the observed temperature independence of the resistivity below the transition down to the lowest temperatures. This question is, of course, outside the scope of the present paper; however, it is tempting to speculate on the mechanism of such a metal-to-anomalous-metal transition. If a metallic state exhibits a temperature-independent resistivity below a certain temperature, it is evident that a temperature-independent scattering dominates the transport properties, since there is no evidence for further modification of the DOS with temperature within the low temperature phase (see Fig. 3). The well-known mechanism of impurity scattering, which gives rise to the constant resistivity of metals at low temperatures (<10 K), is unlikely to dominate the transport properties up to temperatures as high as ≈ 260 K. A rather plausible mechanism, on the other hand, could be spin scattering, if the antiferromagnetic order is incommensurate with the lattice. Since the antiferromagnetic moments ($\approx 2.1 \mu_B$ [3]) are fully developed at 260 K, with the extrapolated Néel temperature being 1000 K, the spin scattering mechanism may possibly be insensitive to temperature changes. It is necessary, however, to specifically address such issues both theoretically and experimentally in order to establish whether such scattering mechanisms could be independent of temperature over such a wide temperature range and be dominant over other mechanisms to explain the detailed temperature dependence of the transport properties across the phase transition. In conclusion, the present results establish that the first order phase transition observed in NiS and related compounds is a metal-to-anomalous-metal transition, instead of being a metal-to-insulator transition, settling the age-old debate on this issue.

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