Electronic structure of NiS$_{1-x}$Se$_x$ across the phase transition

D. D. Sarma, S. R. Krishnakumar, and Nirmala Chandrasekharan

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

E. Weschke, C. Schüßler-Langeheine, L. Kilian and G. Kaindl

Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin-Dahlem, Germany

(February 8, 2018)

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 possibly due to the opening of gaps along specific directions in the Brillouin zone caused by the antiferromagnetic ordering.

While metal-insulator transition has been one of the outstanding problems in condensed matter physics, the specific case of a transition in hexagonal NiS 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, while nearly equal number of groups claiming it to be a metal-metal transition. The transport and magnetic properties are a function of temperature has been possibly the most outstanding problems in condensed matter physics.

The system becomes antiferromagnetic below the transition, 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 $4 \text{ K}$, 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 $4 \text{ K}$ ($< 0.5 \text{ meV}$). 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 ($4 \text{ K} \leq T \leq 260 \text{ K}$). 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 correctly predicted the high temperature Pauli paramagnetic phase to be metallic, while the low temperature anti-ferromagnetic phase yielded a small gap. However, subsequent self-consistent band structure calculations based on local spin density approximation (LSDA) failed to yield any gap. Similarly, the LDA+U method 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, which is by far too large to be consistent with a temperature independent resistivity down to $4 \text{ K}$. Thus, neither transport measurements nor theoretical calculations have been able to resolve the controversy surrounding the ground state behavior of NiS.

Metallic and insulating behavior 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. An early optical reflectivity study showed the existence of a characteristic dip at about $140 \text{ meV}$ for the low temperature phase compared to the high temperature metallic phase; this has been cited as a 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 ($\Delta E \approx 36 \text{ meV}$) photoelectron spectrum of NiS at low temperature has been reported. While it exhibits finite spectral weight at $E_F$, the authors concluded on the basis of an analysis of the density of states (DOS) and various broadening effects such as resolution and thermal (Fermi-Dirac) broadening that there is a gap of $\approx 10 \text{ meV}$ 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, 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 \((<0.5 \text{ meV})\). 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 \( \text{NiS}_{1-x}\text{Se}_x \), 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. The samples with \( x=0.0 \) and \( x=0.11 \) showed a sharp increase of the resistivity at transition temperatures \( T_T=260 \text{ K} \) and \( 97 \text{ K} \), respectively, while for \( x=0.15 \) and \( x=0.17 \) no transition was observed \[ [7] \]. The samples were mounted on a Cu sample holder fitted to a continuous-flow He cryostat allowing measurements between 25 K and 300 K. They were cleaned in situ by repeated scraping with a diamond file; sample cleanliness was checked by valence-band PE at \( h\nu=40.8 \text{ eV} \). 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 severe requirements as well on the experimental resolution 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 \( \text{NiS}_{1-x}\text{Se}_x \) samples. The total-system resolution achieved in these experiments was \( 9\pm1 \text{ meV} \) at \( h\nu=21.2 \text{ eV} \), 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 \( \text{NiS}_{1-x}\text{Se}_x \) 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 the DOS is not slowly varying across \( E_F \). In order to avoid such ambiguities, spectra were taken also from \( \text{NiS}_{0.85}\text{Se}_{0.15} \) and \( \text{NiS}_{0.83}\text{Se}_{0.17} \) as reference systems with very similar electronic structure as NiS and \( \text{NiS}_{0.89}\text{Se}_{0.11} \), 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 \( \text{NiS}_{0.83}\text{Se}_{0.17} \) 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.

Fig. 2 displays comparative PE spectra of all four \( \text{NiS}_{1-x}\text{Se}_x \) 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 \( T=300 \text{ K} \), 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, \( \text{NiS}_{0.85}\text{Se}_{0.11} \)) and those which do not (\( \text{NiS}_{0.85}\text{Se}_{0.15} \), \( \text{NiS}_{0.83}\text{Se}_{0.17} \)). The data analysis clearly shows that the spectra of the latter group \((x=0.15 \text{ and } 0.17)\) are characterized by the same DOS both for the 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 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 \( E_F \). Due to technical reasons, the spectrum of \( \text{NiS}_{0.80}\text{Se}_{0.11} \) 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. \[ [89] \] with the Fermi level pinned very close \((<1 \text{ meV})\) 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 be, 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-squared-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 of 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$_{0.85}$Se$_{0.15}$, 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 optical properties of NiS and chromium metal, which also reveals a characteristic dip in reflectivity below the antiferromagnetic transition temperature (see Fig. 6. in [3]). This dip in the case of Cr has been convincingly demonstrated 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 $T_f$ (Figs. 2 and 3) as well as the dip in the optical reflectivity 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 work; 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 $\approx 260$ 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 ($\approx 2.1 \mu_B$) are fully developed at 260 K, with the extrapolated Neel 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.

ACKNOWLEDGMENTS

DDS thanks the Freie Universität Berlin for hospitality during part of this work. SRK thanks the CSIR, Government of India, for financial support. Financial supports from Department of science and Technology and Board of Research in Nuclear Sciences, Government of India, are acknowledged. The work in Berlin was supported by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie, project Nos. 13N-6601/0 and 05 625 KEC.

* Also at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560012, India.

[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, New York, 1990).
[2] J. T. Sparks and T. Komoto, Phys. Lett. **25A**, 398 (1967).
[3] J. T. Sparks and T. Komoto, J. Appl. Phys. **34**, 1191 (1963).
I. FIGURE CAPTIONS

Fig. 1. Photoemission (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 cut-offs. The solid line represents a fit of the Ag spectrum with an experimental resolution of 9 meV (FWHM).

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.

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 $T<T_t$. 

1. J. T. Sparks and T. Komoto, Rev. Mod. Phys. 40, 752 (1968).
2. M. G. Townsend, R. Tremblat, J. L. Horwood and L. J. Ripley, J. Phys. C: Solid St. Phys., 4, 598 (1971).
3. A. S. Barker, Jr. and J. P. Remeika, Phys. Rev. B 10, 987 (1974).
4. M. Nakamura et al., Phys. Rev. Lett. 73, 2891 (1994).
5. R. M. White and N. F. Mott, Philos. Mag. 24, 845 (1971).
6. D. B. Mcwhan, M. Marezio, J. P. Remeika, and P. D. Dernier, Phys. Rev. B 5, 2552 (1972).
7. Richard F. Koehler Jr. and Robert L. White, J. App. Phys. 44, 1682 (1973).
8. J. M. D. Coey et al., Phys. Rev. Lett. 32, 1257 (1974).
9. S. Anzai, M. Matoba, M. Hatori, and H. Sakamoto, J. Phys. Soc. Jpn. 55, 2531 (1986).
10. L. F. Mattheiss, Phys. Rev. B 10, 995 (1974).
11. A. Fujimori et al., Phys. Rev. B 37, 3109 (1988).
12. V. I. Anisimov, J. Zannen, and O. K. Anderson, Phys. Rev. B 44, 943 (1991).
13. Private communication by V. I. Anisimov.
14. Our transport measurements establish that the present samples have very similar resistivities as reported for single crystals [4].
Fig. 1  Sarma et al.
Fig. 2 Sarma et al. 

Intensity (arb. units) vs. Binding Energy (meV) for different NiS compositions: NiS, NiS$_{0.89}$Se$_{0.11}$, NiS$_{0.85}$Se$_{0.15}$, NiS$_{0.83}$Se$_{0.17}$. 

$h\nu = 21.2$ eV 

$T > T_t$ vs. $T < T_t$
Fig. 3 Sarma et al.