Metal-insulator crossover behavior at the surface of NiS$_2$

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We have performed a detailed high-resolution electron spectroscopic investigation of NiS$_2$ and related Se-substituted compounds, NiS$_{2-x}$Se$_x$, which are known to be gapped insulators in the bulk at all temperatures. A large spectral weight at the Fermi energy of the room temperature spectrum, in conjunction with the extreme surface sensitivity of the experimental probe, however, suggests that the surface layer is metallic at about 300 K. Interestingly, the evolution of the spectral function with decreasing temperature is characterized by a continuous depletion of the single-particle spectral weight at the Fermi energy and the development of a gap-like structure below a characteristic temperature, providing evidence for a metal-insulator crossover behavior at the surfaces of NiS$_2$ and of related compounds. These results provide a consistent description of the unusual transport properties observed in these systems.

I. INTRODUCTION

The properties of two-dimensional (2D) electron systems, particularly in the presence of strong interaction and disorder, are a matter of considerable interest. While the ground state of a noninteracting disordered 2D electron system is predicted to be an insulator,¹ a recent experiment involving semiconductor inversion-layer devices has suggested a metal-insulator transition (MIT) in such a system.² This initiated a number of studies³ that aim at understanding whether such a quantum phase transition can occur in two dimensions. The question arises if electron interaction can lead to a metallic ground state even in a disordered 2D system. This has actually been suggested assuming that electron interaction opposes the effects of disorder.⁴ A recent theoretical study, however, predicts the absence of a true MIT in a 2D system in the simultaneous presence of disorder and interaction and proposes instead a crossover behavior.⁵ The very nature of the mentioned systems based on Si metal-oxide semiconductor field effect transistors and various semiconducting heterostructures with very low electron densities,² however, does not allow one to study their electronic structure by photoemission (PE), a method that has been applied successfully to MITs in 3D systems.⁶

The surface of NiS$_{2-x}$Se$_x$ (x≈0.4) represents a well-suited system for addressing several central questions concerning the ground-state electronic structure of 2D systems as well as for studying the evolution of the electronic structure by PE across a metal-insulator-like transition in a strongly correlated 2D system. While for bulk NiS$_{2-x}$Se$_x$, with x>0.4, an x- and T-driven MIT is well known and has been the subject of several studies,⁷⁻¹¹ we focus here on x≈0.4, where remarkable transport properties have been observed. While optical studies show that the bulk material is a gapped insulator at all T,¹² this is not reflected in the dc resistivity data.¹³,¹⁴ Near room temperature, the resistivity exhibits an activated behavior, with a gap of ≈0.2 eV, in agreement with optical conductivity/reflectivity measurements.¹² Below 120 K, however, no activated behavior is observed, and the resistivity even decreases with decreasing T. On the basis of detailed transport and Hall-effect measurements on samples with different surface-to-volume ratios, it was concluded that this resistivity behavior is due to a metallic surface layer with a thickness of a few unit cells.¹³ This is remarkable in view of the inevitable presence of disorder in real systems that should ensure a 2D insulating ground state.¹ And in fact, this is suggested by the recent observation of a steep increase in resistivity at low temperatures,¹⁴ rendering the formation of a metallic surface layer at higher temperatures¹⁵ even more intriguing.

Many questions arise from these experimental observations, e.g., how the low-T insulating phase connects to the high-T metallic phase, whether there is a real phase transition or rather an unusual crossover behavior, and whether the surface is metallic at higher temperatures or the transport properties have to be interpreted in a different way. It is known that the bulk (3D) insulating behavior of NiS$_2$ at all temperatures is due to the formation of a Mott-Hubbard gap in the single-particle excitation spectrum driven by electron-electron interaction, while so far there is no information on the nature of the low-T insulating phase of the 2D surface of this system. One may ask if its insulating state is induced by
electron-electron interaction or by Anderson localization in view of the increased effect of disorder in the lower dimension.

Here we present the results of a high-resolution PE study of the surface electronic structure of NiS$_2$, giving evidence for a metallic state at high temperatures as suggested by the resistivity data. In addition, we find that the unusual transport properties of this compound and of the related NiS$_{2-x}$Se$_x$ system, with $x \leq 0.4$, are reflected in $T$-dependent changes of the surface electronic structure. With electron interaction and disorder driving the system towards localization instead of opposing each other, the ground state of this 2D system is proposed to be an Anderson-localized insulator despite the presence of strong electron interaction.

II. EXPERIMENT

The experiments were performed on both single crystals and sintered polycrystalline samples; the details of sample preparation were described earlier in Ref. 9. All samples were single phase as checked by x-ray diffraction, and the stoichiometries were confirmed by an energy-dispersive x-ray analysis in a scanning electron microscope. Photoelectron spectroscopic experiments were carried out in spectrometers that are equipped with Scienta analyzers, Gammadata vacuum ultraviolet (VUV) lamps and monochromators to suppress the satellite radiations. We have used the high-intensity He I VUV radiation ($h\nu = 21.2$ eV) for these experiments. The total-system energy resolutions were set at 8 meV full width at half maximum (FWHM) for most of the measurements. The samples were cooled by continuous-flow He cryostats and the temperature was controlled within $\pm 0.5$ K at any given temperature. The Fermi energy ($E_F$) was determined at each temperature from spectra of polycrystalline Ag in electrical contact with the sample. Single-crystalline samples were primarily cleaved and used for angle-resolved band mapping at a few selected temperatures, while scraped polycrystalline samples were used to study in more detail the variation of the spectral weight at $E_F$ as well as to check reproducibility in case of thermal cycling.

III. RESULTS AND DISCUSSION

In order to address subtle temperature-dependent changes in the electronic structure of any material with respect to the transport properties, it is most relevant to monitor the spectral changes at and near the Fermi energy, $E_F$. However, this requires a reliable normalization procedure before different spectra can be compared. In general, two distinct approaches have been adopted in the literature for this purpose. In one approach, different spectra are scaled to match at a given binding energy (BE); the specific BE (typically 0.5–0.6 eV) is normally chosen to be sufficiently removed from $E_F$, such that subtle changes in the electronic structure of the system that can be induced by temperature, are not expected to have any effect in the vicinity of the chosen BE. In the other method, the total integrated area under the spectrum over a certain energy window is normalized, referring to the conservation of the number of electrons in the system. In the present system, we find that both of these approaches converge and lead to the same result, as illustrated in the inset to Fig. 1(a) for the spectra of NiS$_2$ recorded at two extreme temperatures of 20 and 300 K. The spectra are normalized at a 0.6-eV BE; interestingly, this normalization leads to the matching of the two spectra down to 1.6 eV starting from the 0.5-eV BE. This extensive matching over the entire high-BE window ensures that the two spectra shown in the inset of Fig. 1(a) have almost the same total integrated areas. In fact, a normalization based on total integrated areas leads to spectra essentially indistinguishable from those given in the inset. It is also evident that there are no gross changes in the spectra as a function of $T$, which could influence the normalization procedure.

In fact, temperature-dependent changes occur only close to $E_F$ over a narrow energy range, as illustrated in the main panels of Figs. 1(a) and 1(b) for single-crystalline and polycrystalline samples, respectively. Interestingly, the data from single- and polycrystalline samples are almost identical. In order to understand this observation, we have carried out a detailed angle-resolved PE study of single-crystalline samples (not shown here). While we found extensive dispersions of the main intense valence band spectral region appearing at higher binding energies, our angle-resolved measurements established a relative insensitivity of the spectral features close to $E_F$ with respect to the angle of detection. This is consistent with the striking similarity of the spectral features from the single-crystalline and polycrystalline samples.

In order to discuss the changes close to $E_F$ in more detail, in Fig. 2 we show (main panel) a set of representative spectra covering a narrow energy scale at various temperatures. Far
below \(E_F\) (BE > 0.5 eV), the spectra are essentially identical, as already illustrated in Fig. 1 for the two extreme temperatures. In the BE region between 100 and 500 meV, however, there is a systematic and continuous, though small, depletion of spectral weight with decreasing temperature, suggesting some changes in the spectral weight over this energy window as a function of \(T\). However, these high energy states are not directly related to the transport properties. Therefore, we focus here on the electronic states close to \(E_F\), responsible for the transport properties, which exhibit remarkable changes with temperature. It is well known that in the case of a metal the spectral weight at and near \(E_F\) changes significantly with temperature, which is easily understood in terms of the Fermi-Dirac statistics. The changes observed here, however, are distinctly different from the Fermi-Dirac type, as we shall show below by a more detailed analysis.

Already without recourse to a detailed analysis, several important features can be recognized, which are particularly interesting in connection with the transport data reported for NiS\(_2\). On the basis of the shown PE spectra, there is compelling evidence for the surface of NiS\(_2\) to be metallic at room temperature. These proofs are as follows. (i) There is a large spectral weight at \(E_F\) in the room-temperature spectrum. (ii) There is a continuous and substantial spectral weight up to about 100 meV above \(E_F\) in the same spectrum. (iii) The spectral weight above \(E_F\) shows a characteristic Fermi-Dirac type depletion of spectral intensity with decreasing temperature, spread over the expected energy scale related to the thermal energy. In view of the total experimental energy resolution of the present PE experiments of 8 meV (FWHM), none of these observations can be explained by broadening due to finite resolution. The observations are clearly incompatible with the optical data that show NiS\(_2\) to be a wide-gap insulator. On the other hand, the results are consistent with the Hall-effect data\(^{13}\) and suggest that the surface of NiS\(_2\) is metallic, particularly when considering the high surface sensitivity of PE with a mean sampling depth of \(\approx 7\) Å. Thus, the surface layer of NiS\(_2\), only a few unit cells thick, has metallic character near room temperature, while the bulk of the sample, inaccessible to PE, remains an insulator.

It is interesting to note that the variation of the spectral function with temperature, shown on the main panel of Fig. 2, is very different from that of a normal metal. This can be inferred from the inset that displays corresponding spectra of polycrystalline Ag metal taken with the same setup. Here, the observed \(T\) changes in the spectral function of Ag are readily understandable in terms of Fermi-Dirac (FD) statistics alone. With an essentially constant density of states in the vicinity of \(E_F\) \((D(E_F))\), this causes the spectrum to recover the weight lost above \(E_F\) with decreasing temperature almost in a symmetrical manner and immediately below \(E_F\), thus preserving the total spectral weight. Another consequence of \(D\) being unchanged with \(T\) is that all spectra of Ag go through a common point at \(E_F\) in spite of changing \(T\), since the Fermi-Dirac statistics does not affect the spectral weight at the Fermi energy. An almost identical behavior of the spectral function is also observed for NiS (see second inset in Fig. 2). In contrast, the behavior of the PE spectra of NiS\(_2\) is qualitatively different. In particular, the redistribution of the spectral function below \(E_F\) takes place over a much wider energy range than one would expect explicitly on a thermal scale, while above \(E_F\) it appears to be controlled by \(T\). Hence, the changes in the spectral function of NiS\(_2\) cannot be understood in terms of a fixed \(D\) around \(E_F\) and FD statistics, in contrast to normal metals. Instead, we are forced to conclude from the raw data that the single-particle excitation spectrum of the surface of NiS\(_2\) is characterized by a temperature dependence of \(D\) itself.

Due to the presence of thermal broadening and resolution broadening, a quantitative estimate of \(D(E_F)\) at various temperatures cannot be obtained without recourse to simulations of the spectra in terms of a model \(D(E)\). With the high energy resolution achieved in the present PE experiments, thermal broadening is by far the dominant effect. This contribution, however, can be readily removed from the spectra by assuming a symmetric \(D(E)\)\(^{16}\) or by dividing the raw spectra by the FD distribution function\(^{17}\). We illustrate the results of the latter analysis by the inset in Fig. 3, demonstrating a remarkable depletion of spectral weight with decreasing temperature over a wide energy range, with the strongest effects at \(E_F\). As pointed out further above, the corresponding amount of spectral weight is recovered almost uniformly distributed over the BE range from 0.15 to 0.45 eV, with the effects of FD distribution being virtually absent at such a high BE.

Besides these two methods, the \(T\) dependence of \(D(E_F)\) was also obtained by direct fitting of the spectra of Fig. 2 with a \(D(E)\) described by a polynomial function, multiplied by the FD distribution at a given \(T\) and convoluted by a Gaussian for the known resolution. All these different analyses result in similar values of \(D(E_F)\), demonstrating an insensitivity on details of the model. The resulting \(D(E_F)\) are plotted in the main part of the upper panel of Fig. 3 as a function of \(T\), with error bars that contain the variations of \(D(E_F)\) from the different analyses. \(D(E_F)\) increases slightly with decreasing temperature from 297 to 260 K, and then

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**FIG. 2.** PE spectra of polycrystalline NiS\(_2\), recorded at various temperatures. Insets: corresponding spectra for polycrystalline Ag and polycrystalline NiS.
NiS$_2$ alone. As mentioned before, the related compounds 

Data for NiS$_{1.6}$Se$_{0.4}$ are included in Fig. 3, and they clearly 

fully developed and $x$-temperatures with increasing 

particle excitation spectrum form at progressively lower tem-

\begin{align*} 
&\text{NiS}_2 \quad \text{NiS}_2 \\
&\text{Se} \quad \text{Se} \\
&1.6 \quad 0.4 \\
&\text{NiS}_2 \\
\end{align*} 

again similar, with the formation of a gaplike structure at 

of NiS$_2$ as a function of temperature, adopted from Ref. 14. 

resistivity is known to increase.$^{14}$ In order to illustrate this, 

we show in the lower panel of Fig. 3 the resistivity behavior 

of NiS$_2$ as a function of temperature, adopted from Ref. 14. 

The high temperature resistivity clearly shows the activated 

behavior of the bulk in the temperature range 150–300 K; 

the metallic conductivity of the surface region causes a per-

ceptible deviation from the activated behavior below 150 K, 

and the most pronounced metallic behavior below about 110 

K. However, with a further lowering of the temperature, the 

resistivity of this surface layer begins to increase where the 

gaplike structure forms in $D(E_F)$, as indicated by the arrow 

in Fig. 3.

The interesting change in $D(E_F)$ with $T$ is not specific to 

NiS$_2$ alone. As mentioned before, the related compounds 

NiS$_{2-x}$Se$_x$ are also bulk insulators, with the resistivity data 

suggesting a 2D metallic overlayer for $x \approx 0.4$.\textsuperscript{14} PE spectra 

of NiS$_{2-x}$Se$_x$, with $x = 0.3$ and 0.4, were recorded at various 

temperatures and reveal a behavior similar to that of NiS$_2$. 

Data for NiS$_{1.6}$Se$_{0.4}$ are included in Fig. 3, and they clearly 

resemble the behavior of NiS$_2$, with a tiny initial increase in 

$D(E_F)$ between 297 and 260 K, followed by a moderate 

decrease down to 75 K, and then the signature of a gap at 

$\approx 35$ K. The PE results for NiS$_{1.7}$Se$_{0.3}$ (not shown here) are 

again similar, with the formation of a gaplike structure at 

$\approx 55$ K. Interestingly, the gaplike structures in the single-

particle excitation spectrum form at progressively lower tem-

peratures with increasing $x$, i.e., at about 75, 55, and 35 K for 

$x = 0, 0.3,$ and 0.4, respectively. This follows the trend of 

decreasing $T$, at which the upturn in resistivity has been ob-

erved for NiS$_{2-x}$Se$_x$,\textsuperscript{14} and establishes a close relationship 

between the transport properties and the observed decrease of $D(E_F)$.

The details of the temperature-dependent surface electronic structure, as derived from the PE spectra of NiS$_2$ and related compounds, further suggest several important implications. We first note that $D(E_F)$ for any of the three compounds studied, in spite of the pronounced gaplike structure, does not vanish completely, even at the lowest $T$. While the gaplike structure in $D(E)$ at the low-$T$ limit is presumably driven by strong correlation effects, the persistence of a finite $D(E_F)$ suggests that the ground state is not a Mott insulator with a fully developed energy gap; it rather indicates that Anderson localization driven by disorder is the origin of the insulating behavior.

The overall dependence of $D$ on $T$ displayed in the upper 

panel of Fig. 3 shows that the gaplike structure disappears 

over a relatively narrow temperature range of $\approx 40$ K rather 

than by a gradual filling of the gap over a larger $T$ interval. 

This cannot be explained by thermal excitations of charge 

carriers alone implying that the underlying electronic structure 

itself changes rapidly, accompanying the metal-insulator 

crossover over a narrow $T$ range. This behavior might be 

related to a temperature-dependent screening of correlation 

effects by itinerant electrons. At high temperatures the 

screening is highly effective, leading to a less correlated state 

and consequently to the disappearance of the gaplike structure 

in the single-particle excitation spectra. At lower temperatures, however, an Anderson localization of the electrons leads to less effective screening, with a gap forming in the excitation spectrum. While this may possibly be a continuous changeover with temperature, as suggested by the slow change of $D(E_F)$ at higher $T$, it is most remarkable in a 

narrow temperature interval, where a change in the transport 

properties was observed. If indeed such a screening mechanism is relevant, it has to have a nontrivial dependence on $T$ beyond the thermal excitation of mobile charge carriers.

At this point, it is tempting to rationalize the presence of metal-like surface layers in these systems. One obvious possibility is a deviation of the surface stoichiometry from the bulk, leading to a doping of the surface layer with charge 

carriers. However, the large $D(E_F)$ observed near room temperature would correspond to a very high doping level and hence to a significant deviation from stoichiometry. This is incompatible with the intensity ratios of core-level PE spectra from Ni, S, and Se, which were found to follow the nominal bulk compositions in all samples. Moreover, if the doped charge carriers arising from nonstoichiometry were indeed mobile, without altering the underlying electronic structure, there would be no reason for the charge carriers to reside only in the surface layer.

A possible explanation is obtained from the unusual properties of NiS$_2$ compared to CoS$_2$ and CuS$_2$. While NiS$_2$ is a bulk insulator, the latter two are bulk metals.\textsuperscript{18} The exceptional behavior of NiS$_2$ shows up also in the lattice parameters being larger than expected from their systematic variation in the pyrite family, $MS_2$, with $M = \text{Mn-Zn}$.\textsuperscript{18} The unusually expanded lattice of NiS$_2$ is expected to lead to a
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11 A. Husmann et al., Science 274, 1874 (1996).
12 R. L. Kautz, M. S. Dresselhaus, D. Adler, and A. Linz, Phys. Rev. B 6, 2078 (1972).
13 T. Thio and J. W. Bennett, Phys. Rev. B 50, 10574 (1994); T. Thio, J. W. Bennett, and T. R. Thurston, ibid. 52, 3555 (1995).
14 X. Yao, J. M. Honig, T. Hogan, C. Kannewurf, and J. Spalek, Phys. Rev. B 54, 17469 (1996).
15 One change that could have been expected is a reduction in the phonon broadening of the spectral features. This contribution, however, is obviously so small as compared to the overall width of the observed feature, that it is not noticeable at all.
16 M. R. Norman et al., Nature (London) 392, 157 (1998); H. Ding et al., ibid. 382, 51 (1996).
17 T. Susaki, Y. Takeda, M. Arita, K. Mamiya, A. Fujimori, K. Shimada, H. Namatame, M. Tanighchi, N. Shimizu, F. Iga, and T. Takabatake, Phys. Rev. Lett. 82, 992 (1999).
18 I. A. Wilson, in The Metallic and Nonmetallic States of Matter, edited by P. P. Edwards and C. N. R. Rao (Taylor and Francis, London, 1985), pp. 215–260.
19 N. Mori, T. Mitsui, and S. Yomo, Solid State Commun. 13, 1083 (1973).
20 Priya Mahadevan (private communication).