

Metal-insulator Crossover Behavior at the Surface of NiS₂

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Abstract

We have performed a detailed high-resolution electron spectroscopic investigation of NiS_2 and related Se-substituted compounds $\text{NiS}_{2-x}\text{Se}_x$, 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 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.

PACS numbers: 71.30.+h, 71.23.-k, 71.28.+d, 79.60.-i

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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 non-interacting 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 studies [3] 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 MOSFET's and various semiconducting heterostructures with very low electron densities [2], however, does not allow to study their electronic structure by photoemission (PE), a method that has been applied successfully to MIT's in 3D systems [6].

The surface of $\text{NiS}_{2-x}\text{Se}_x$ ($x \leq 0.4$) 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 $\text{NiS}_{2-x}\text{Se}_x$, with $x > 0.4$, an x - and T -driven MIT is well known and has been the subject of several studies [7, 8, 9, 10, 11], we focus here on $x \leq 0.4$, 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 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 temperatures even more intriguing [13].

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 $\text{NiS}_{2-x}\text{Se}_x$ 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. EXPERIMENTAL

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 energy-dispersive x-ray analysis in a scanning electron microscope. Photoelectron spectroscopic experiments were carried out in spectrometers that are equipped with Scienta analyzers, Gamdata vacuum ultra-violet (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 ± 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. 1a for the spectra of NiS₂ recorded at two extreme temperatures of 20 K and 300 K. The spectra are normalized at 0.6-eV BE; interestingly, this normalization leads to the matching of the two spectra down to 1.6 eV starting from 0.5-eV BE. This extensive matching over the entire high-BE window ensures that the two spectra shown in the inset of Fig. 1a 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 [15], 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. 1a and 1b for single- 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- and polycrystalline samples.

In order to discuss the changes close to E_F in more detail, we show in Fig. 2 (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, though small, depletion of spectral weight with increasing temperature that compensates for the increase in spectral weight above E_F with T . Here, we focus 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 non-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 NiS₂. On the basis of the shown PE spectra, there is compelling evidence for the surface of NiS₂ to be metallic at room temperature. These evidences are: (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 NiS₂ 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 NiS₂ is metallic, particularly when considering the high surface sensitivity of PE with a mean sampling depth of ≈ 7 Å. Thus, the surface layer of NiS₂, 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 ($\mathcal{D}(E_F)$), 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 \mathcal{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 NiS₂ 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 NiS₂ cannot be understood in terms of a *fixed* \mathcal{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 NiS₂ is characterized by a temperature dependence of \mathcal{D} itself.

Due to the presence of thermal broadening and resolution broadening, a quantitative estimate of $\mathcal{D}(E_F)$ at various temperatures cannot be obtained without recourse to simulations of the spectra in terms of a model $\mathcal{D}(E)$. 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 $\mathcal{D}(E)$ [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 eV to 0.45 eV, with the effects of FD distribution being virtually absent at such high BE.

Besides these two methods, the T dependence of $\mathcal{D}(E_F)$ was also obtained by direct fitting of the spectra of Fig. 2 with a $\mathcal{D}(E)$ 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 $\mathcal{D}(E_F)$, demonstrating an insensitivity on details of the model. The resulting $\mathcal{D}(E_F)$ are plotted on the main panel of Fig. 3 as a function of T , with error bars that contain the variations of $\mathcal{D}(E_F)$ from the different analyses. $\mathcal{D}(E_F)$ increases slightly with decreasing temperature from 297 K to 260 K, and then decreases progressively down to 115 K. Between 115 K and 75 K, there is a more pronounced decrease in $\mathcal{D}(E_F)$, suggesting the opening of a gap-like structure in the single-particle excitation spectrum; below 75 K, the gap-like structure is fully developed and $\mathcal{D}(E_F)$ remains essentially unchanged. The formation of an energy gap in the electronic structure of NiS₂ thus occurs in the very temperature range, where the resistivity is known to increase [14].

This behavior is not specific to NiS₂ alone. As mentioned before, also the related compounds NiS_{2-x}Se_x are bulk insulators, with the resistivity data suggesting a 2D metallic overlayer for $x \leq 0.4$ [14]. PE spectra of NiS_{2-x}Se_x, with $x = 0.3$ and $x = 0.4$, were recorded at various temperatures and reveal a behavior similar to that of NiS₂. Data for NiS_{1.6}Se_{0.4} are included in Fig. 3, and they clearly resemble the behavior of NiS₂, with a tiny initial increase in $\mathcal{D}(E_F)$ between 297 and 260 K, followed by a moderate decrease down to 75 K, and then the signature of a gap at ≈ 35 K. The PE results for NiS_{1.7}Se_{0.3} (not shown here) are again similar, with the formation of a gap-like structure at ≈ 55 K. Interestingly, the gap-like structures in the single-particle excitation spectrum form at progressively lower temperatures with increasing x , i.e., at about 75 K, 55 K, 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 observed for NiS_{2-x}Se_x [14], and establishes a close relationship between the transport properties and the observed decrease of $\mathcal{D}(E_F)$.

The details of the temperature-dependent surface electronic structure, as derived from the PE spectra of NiS₂ and related compounds, further suggest several important implications. We first note that $\mathcal{D}(E_F)$ for any of the three compounds studied, in spite of the pronounced gap-like structure, does not vanish completely, even at the lowest T . While the gap-like structure in $\mathcal{D}(E)$ at the low- T limit is presumably driven by strong correlation effects, the persistence of a finite $\mathcal{D}(E_F)$ 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 \mathcal{D} on T displayed in Fig. 3 shows that the gap-like structure disappears over a relatively narrow temperature range of ≈ 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 gap-like structure in the single-particle excitation spectra. At lower temperatures, however, 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 change-over with temperature, as suggested by the slow change of $\mathcal{D}(E_F)$ 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 non-trivial 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 $\mathcal{D}(E_F)$ 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 non-stoichiometry 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 [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, $M\text{S}_2$, with $M = \text{Mn-Zn}$ [18]. The unusually expanded lattice of NiS_2 is expected to lead to a reduction of the bandwidth, driving bulk NiS_2 insulating, in contrast to the metallic ground states of CoS_2 and CuS_2 . This point of view is supported by the fact that bulk NiS_2 turns metallic at a pressure of 46 kbar [19]. Given this relation between the lattice parameters and the metallic character of

bulk NiS₂, a reduction of the lattice parameters at the surface could lead to an altered surface electronic structure of NiS₂ with the tendency towards a more metallic character. And in fact, preliminary *ab initio* full-potential calculations of the surface electronic structure of NiS₂ [20] indicate a reduction of the lattice parameters and consequently an increase in d bandwidth at the surface for several crystallographic surfaces.

To summarize, we propose the following scenario: Lattice relaxation near the surface region of NiS₂ and related compounds tends to drive the surface metallic, which, however, is inhibited by the 2D nature of the surface layer; instead Anderson localization leads to an insulating ground state of the surface layer. At higher temperatures, crossover towards a metallic behavior occurs, as evidenced by the transport properties. This crossover is characterized by the disappearance of the gap-like feature in the electronic structure around E_F and by a rapid increase in $\mathcal{D}(E_F)$, driven by a decrease of the effective Coulomb interaction strength as well as of the disorder potential due to screening by a larger number of thermally excited electrons. However, the narrow temperature range, in which this strong change in the electronic structure occurs, is remarkable and requires further theoretical explanation.

The authors thank S. Das Sarma, H.R. Krishnamurthy, and P. Mahadevan for fruitful discussions. The work was supported by the Deutsche Forschungsgemeinschaft, Sfb-290, TPA 06, and the Deutsches Zentrum für Luft- und Raumfahrt e.V., Project INI-012-99, as well as by the Department of Science and Technology and Board of Research in Nuclear Sciences, Government of India. D.D.S. thanks the Freie Universität Berlin and the University of Tokyo for hospitality. C.M. acknowledges financial support by the Alexander von Humboldt Foundation.

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Figure Captions

Fig. 1. PE spectra of NiS₂ from (a) single-crystalline and (b) polycrystalline samples at the given temperature. The inset illustrates the normalization procedure over a larger range of binding energies.

Fig. 2. PE spectra of polycrystalline NiS₂, recorded at various temperatures. Insets: corresponding spectra for polycrystalline Ag and polycrystalline NiS.

Fig. 3. T dependence of $\mathcal{D}(E_F)$ of NiS₂, extracted from the spectra of Fig. 2; data for NiS_{1.6}Se_{0.4} are included. Inset: $\mathcal{D}(E)$ at various temperatures, obtained as described in the text.

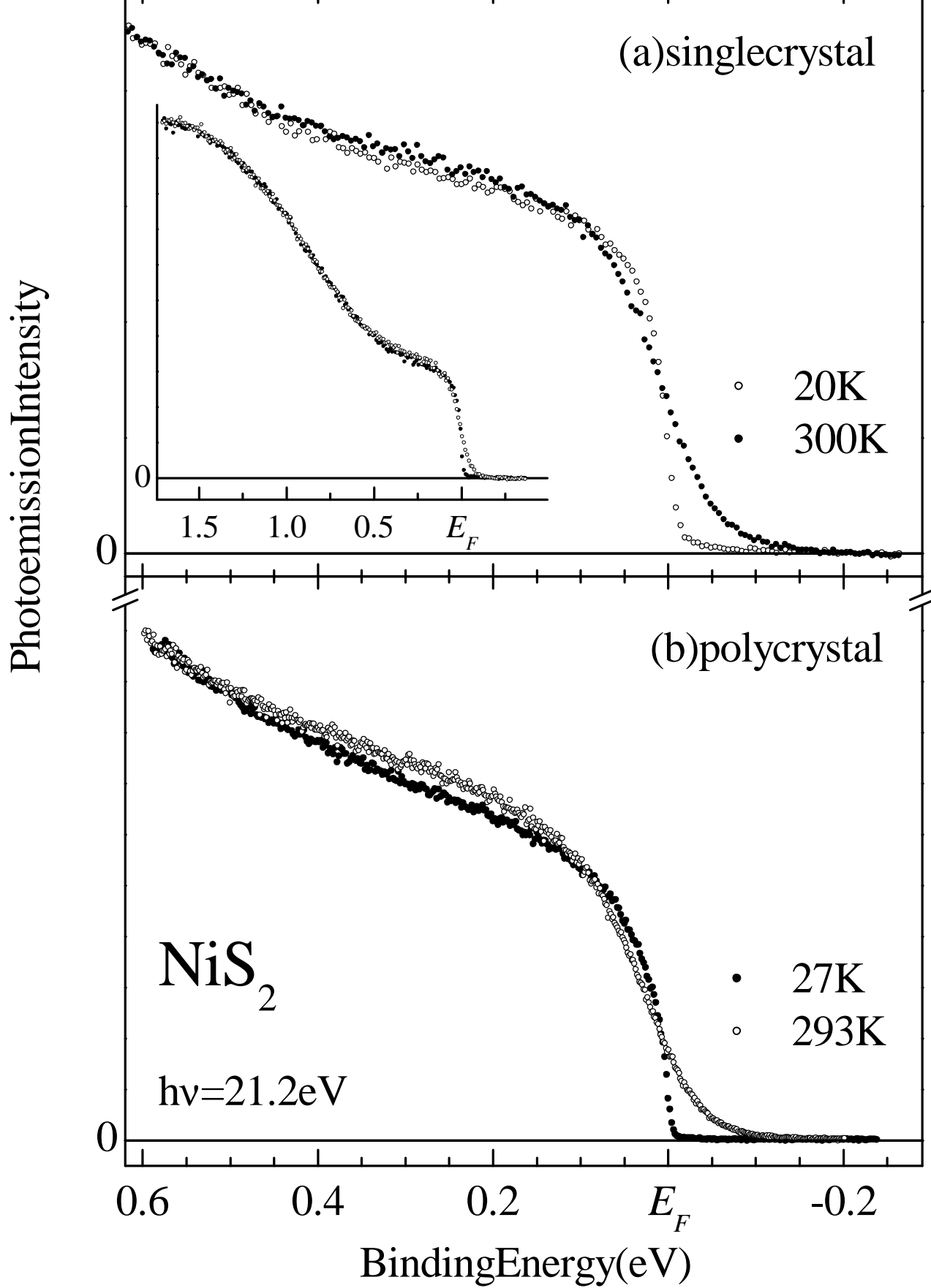
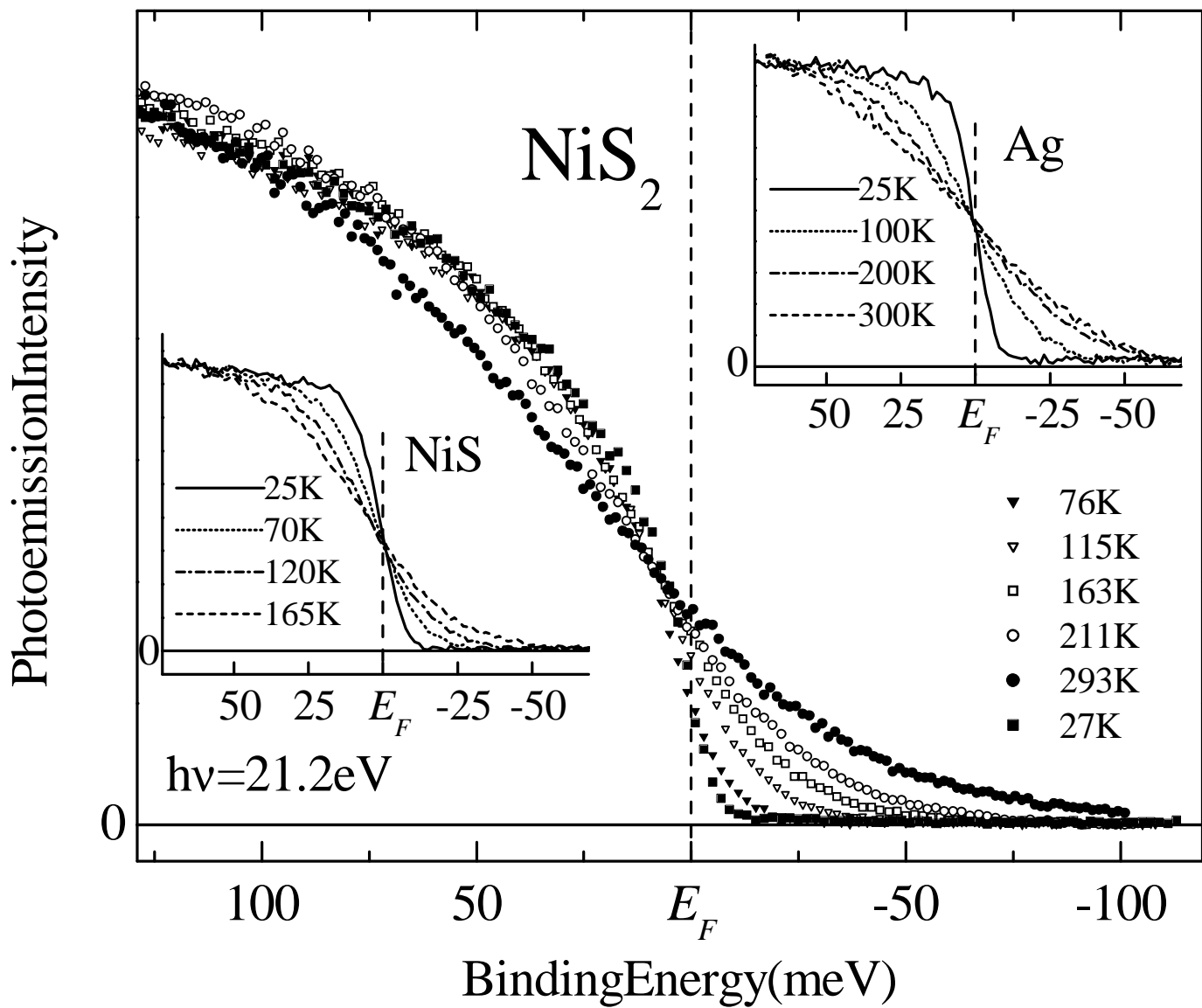


Fig. 1, Sarma et al.



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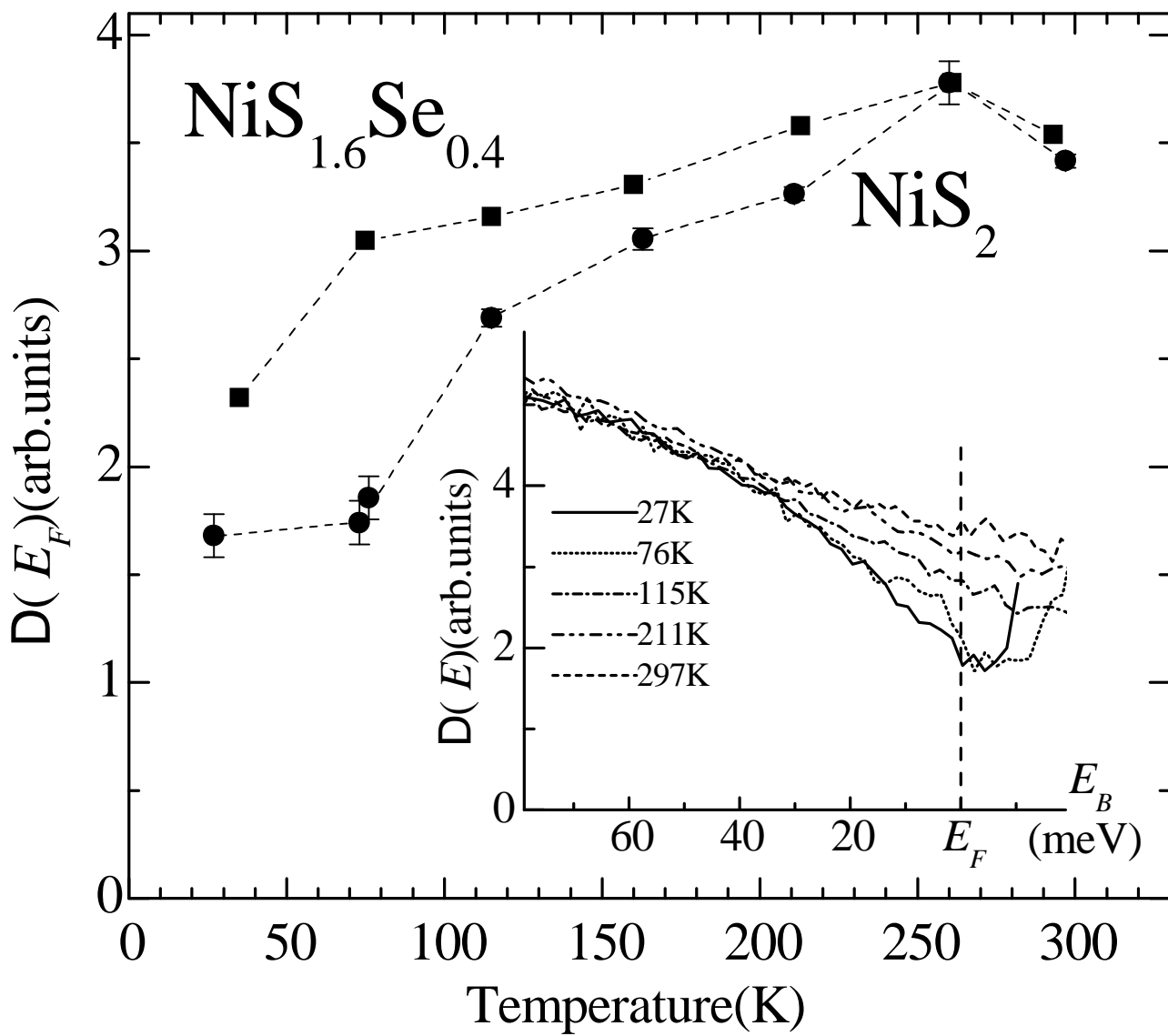


Fig.3,Sarmaetal.