Metal-insulator transition and nature of the gap in NiS$_{2-x}$Se$_x$

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The origin of the gap in NiS$_2$ as well as the pressure and doping induced metal-insulator transition in the NiS$_{2-x}$Se$_x$ solid solutions are investigated both theoretically by the first-principles bandstructures combined with the dynamical mean-field approximation for the electronic correlations and experimentally by means of infrared and X-ray absorption spectroscopy. The bonding–anti-bonding splitting in the S-S (Se-Se) dimer is identified as the main parameter controlling the size of the charge gap. The implications for the metal-insulator transition driven by pressure and Se doping are discussed.

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I. INTRODUCTION

The metal-insulator transition (MIT) due to electronic correlations has been subject of intense research for several decades. The NiS$_{2-x}$Se$_x$ series provided an important model system exhibiting a MIT controlled by varying the Se content $x$, temperature $T$ or pressure $P$. Particularly interesting is the similarity of the $x-T$ and $P-T$ phase diagrams to that of the Hubbard model in the infinite dimension limit, consisting in the presence of the phase transition between paramagnetic metal and paramagnetic insulator at intermediate temperatures, existence of the high-temperature crossover regime, and the possibility of driving a metal insulating, in a certain range of $x$, by increasing the temperature. Consequently, the MIT has been commonly attributed to broadening of the Ni-$d$ bands. Despite a large volume of available experimental data, the microscopic origin of the MIT in NiS$_{2-x}$Se$_x$ is poorly understood and a satisfactory material-specific theory is missing.

NiX$_2$ (X=S,Se) can be viewed as NiO with the O atom replaced by an X$_2$ dimer. Strong hybridization between the $X-p$ orbitals pointing along the $X-X$ dimer, $p_{\sigma}$ orbitals, leads to a formation of split bonding and anti-bonding bands (the latter ones are referred to as $p_{\sigma}^*$), which accommodate two holes leading to an $X^2_{\sigma}p_{\sigma}$ valence state. Numerous photoemission (PES) studies complemented by cluster calculations revealed a similarity between the NiX$_2$ and NiO valence band (VB) spectra, supporting this analogy. The bandstructure calculations in the local density approximation (LDA) rendered NiS$_2$ a metal with a partially filled $e_g$ band and empty $p_{\sigma}^*$ orbitals. By analogy to NiO it was speculated that local $d-d$ correlations open a gap between the S-$p$ band and the upper Hubbard band of Ni-$d$ $e_g$ character, leading to the classification of NiS$_2$ as a charge-transfer (CT) insulator in the Zaanen-Sawatzky-Allen (ZSA) scheme, although in the original ZSA paper NiS$_2$ was classified as 'p-type metal were it not for the gap between the S $p_x$ and the rest of the p band'.

We have combined theoretical calculations with new experimental data in order to address the following questions: i) Why is NiS$_2$ an insulator and NiSe$_2$ a metal? ii) How do NiX$_2$ respond to external pressure?, iii) Are the effects of pressure and varying Se content equivalent?, iv) What is the mechanism of the MIT in NiS$_{2-x}$Se$_x$?

The electronic structure of NiX$_2$ is studied numerically, using a combination of the ab initio bandstructure and the approximation of the dynamical mean-field theory (LDA+DMFT). The infrared (IR) reflectivity is measured on samples with various Se concentrations under applied pressure to investigate the evolution of the optical gap and the spectral weight transfer. The x-ray absorption spectroscopy (XAS) at S K-edge is used to elucidate the orbital character of features in the single-particle spectrum of NiS$_2$.

II. COMPUTATIONAL METHOD

Our computations proceed as follows. First, we perform paramagnetic LDA calculations and minimize the total energy to find the equilibrium S(Se) positions. Next, we represent the one-particle Hilbert space of the hybridized Ni-$d$ and S(Se)-$p$ bands in Wannier basis (44 orbitals per unit cell) and calculate the parameters of the on-site $d-d$ interaction with the constraint LDA approach. We found only moderately different $U_{\text{NiS}_2} = 5$ eV and $U_{\text{NiSe}_2} = 4.7$ eV and used $J$ of 1 eV throughout the study. Finally, we construct a multi-band
Hubbard Hamiltonian
\begin{equation}
\hat{H} = \sum_k \hat{a}_k^\dagger H_k \hat{a}_k - \varepsilon_{d_c}(n_d) \hat{N}_d + \sum_{i \in \text{Ni}} \hat{n}_i^d U^{dd} \hat{n}_i^d, \tag{1}
\end{equation}

and compute the single-particle spectra using the DMFT approximation. Here, $H_k$ is the LDA Hamiltonian, $44 \times 44$ matrices (four NiX$_2$ units) in the basis of Ni-$d$ and X-$p$ Wannier orbitals, on a uniform $k$-mesh in the first Brillouin zone.$^{12}$ The second term is the double-counting correction amounting to a constant shift applied to Ni-$d$ site energies.$^{12}$ The last term is the two-particle interaction at the Ni sites in the density-density approximation. The DMFT equations are solved on the Matsubara contour. The continuous time quantum Monte-Carlo impurity solver$^{20}$ is employed to solve the auxiliary multi-orbital impurity problem. Single-particle spectral densities are obtained by analytic continuation of Monte-Carlo data using the maximum entropy method$^{21}$.

III. EXPERIMENTAL DETAILS

Single crystals, grown by vapor transport technique, were slightly polished in order to obtain a clean, mirror-like surface. Near-normal incidence reflectivity was measured with a casegrainian-based IR microscope coupled to a Michelson interferometer. The NiS$_2-x$Se$_x$ series ($x=0, 0.3, 0.5, 0.7$) was studied at ambient conditions.

A clamp diamond anvil cell (Diacell cryoDAC-Mega) equipped with type IIa diamonds was employed to perform pressure dependent studies. A small piece of NiS$_2$ (NiS$_{1.7}$Se$_{0.3}$) was cut and placed together with CsI (as hydrostatic medium) inside a 400 $\mu$m hole drilled in a 90 $\mu$m thick CuBe gasket. The pressure was evaluated in situ, by the standard ruby-fluorescence technique.$^{22}$ Measurements were carried out partly at the University of Augsburg and partly at the IR1 beamline in ANKA, so to exploit the high brilliance of synchrotron radiation in the far-IR range. We recall that due to the small size of the samples inside the diamond anvil cell measurements as a function of pressure were performed for $\omega > 250$ cm$^{-1}$. The measurement procedure, as well as the data processing to extract the optical conductivity $\sigma_1(\omega)$ are carefully described in Refs. 24,25.

The sulfur 1s X-ray absorption spectra (XAS) spectra which provides information about vacant S 3p-states were measured at the soft X-ray microcharacterization beamline (SXRMB) at the Canadian Light Source. The spectra were measured in total electron yield (TEY) mode. Additional measurements were taken in total fluorescence (TFY) mode using a channel-plate detector, and partial fluorescence (PFY) mode using a silicon drift detector with a resolution of about 100 eV. Both the PFY and TFY measurements showed the same features as the TEY measurements, indicating that the surface of the samples was clean. The TEY measurements were used for the analysis because they had a better signal-to-noise ratio than the TFY or PFY measurements, and did not suffer from the self-absorption effects present in the fluorescence measurements. An Si(111) crystal was used in the monochromator, and the experimental resolution (E/E) was about 10000.

IV. RESULTS AND DISCUSSION

We start the exposition of our results with a brief review of the non-interacting LDA bandstructures, which agree with those published previously.$^{8,12,13}$ The Ni-$d$ orbitals form narrow $t_{2g}$ and broader, Ni-X anti-bonding, $e^\pi_g$ bands due to octahedral coordination of Ni with the chalcogen X. The deviations from an exact octahedral symmetry at the Ni sites lead to further splitting of the $t_{2g}$ bands into an $e^\pi_g$ doublet and an $a_{1g}$ singlet. This splitting plays no discernible role in our investigation. The characteristic feature of the chalcogen bands is a large bonding–anti-bonding splitting of the $p$-orbitals pointing along the X-X dimer (Fig. 1). Due to the S-S-Ni angle being close to the right angle ($\approx$104 deg in NiS$_2$) the dimer states hybridize only weakly with the Ni $e^\pi_g$ states.

The Ni-X and X-X dimer distances as function of the lattice constant were obtained by minimization of the LDA total energies (see Fig. 1). At ambient pressure the calculated NiS$_2$ bond lengths agree well with experimental observations. Compression leads to shortening of the Ni-S distance while the S-S dimer behaves as a rigid object. The situation is less clear in NiSe$_2$. While the calculated ambient pressure Ni-Se bond length reproduces the experimental value, the length of the Se-Se dimer is substantially overestimated. Under pressure our
FIG. 2: (color online) The calculated pressure dependence of the equilibrium Ni-X and X-X distances. The isolated points mark the experimental values of Refs. [11] (star) and [27] (cross).

calculations yield an initial increase of the Se-Se indicating that the Ni-Se bond becomes stronger relative to the Se-Se bond and suggesting that Se-Se dimer cannot be viewed as a molecular unit. We will discuss later on how the behavior of the bond lengths affects the electronic properties.

A. Single-particle spectra

1. NiS$_2$

In this section we present orbitally resolved spectral densities obtained at ambient pressure with the LDA+DMFT method. In Fig. 3 we show the NiS$_2$ spectra, which exhibit a small charge gap in agreement with experimental observations. The valence band (VB) resembles that of NiO$^{26}$ with the characteristic distribution of the Ni-d spectral weight between $d^7$ (around -6 eV) and $d^{10}$ excitations (at low binding energy), the result of a strong $p - e_g^*$ hybridization. Overall, a good correspondence between positions of the main features in the experimental x-ray photoemission spectra (XPS) and their theoretical counterparts can be stated. Particularly important for the further discussion is the high-energy shoulder at -7 eV, which is dominated by the S-p density in agreement with the observation of Ref. [10].

The absence of an obvious gap in the experimental spectra shown in Fig. 3 is due to the experimental resolution.

The calculated conduction band (CB) spectrum consists of two peaks: (a) $p^*_g$ band with a large resonant $e_g^*$ contribution at 1 eV, and (b) the upper Hubbard band of pure $e_g^*$ character at 3.5 eV. The identification of $b$ with the upper Hubbard band is based on the observation of its shift upon increasing the interaction strength (see the inset of Fig. 3) and the absence of $p$ character. The experimental CB spectrum, obtained with the Bremsstrahlung isochromat spectroscopy (BIS) of Ref. [11], exhibits three distinct features: a sharp low-energy peak at 1 eV, a high-energy peak at 3.5 eV and a broad band (c) starting around 5.5 eV. The 5.5 eV band is not spanned by the Hamiltonian (1) and thus the corresponding contribution is missing in Fig. 3. The orbital character of the other two peaks is of key importance for understanding the nature of the charge gap. The question can be formulated simply as: ‘is the upper Hubbard band located below or above the $p^*_g$ band?’ The authors of Ref. [11] interpreted the 1 eV as Ni-d upper Hubbard band and the 3.5 eV peak as $S\ p^*_g$ band, which is a clear contraindication to our result.

In order to resolve this issue we have measured the XAS at the K-edge of sulfur, which can be directly compared to the calculated S-p spectral density as shown in Fig. 4. The theoretical high energy spectrum was obtained by projecting out the S-p contribution from the LDA bands not included in the Hamiltonian (1). The identification of peak $a$ with $p^*_g$ is corroborated by its position with respect to the X-ray emission (XES) spectrum as well as by its distance from the high energy (5 eV) XAS band. Although the calculated onset of the high energy band is misplaced by about 1 eV with respect to the experiment, the overall agreement is very good. We point out that the experimental XAS $a$ and $c$ peaks match their
FIG. 4: The calculated S-p spectral density obtained from LDA+DMFT (full line), augmented with the S-p contribution from the high energy LDA bands (dashed line), compared to experimental XES spectral of Ref. 28 (circles) and XAS (diamonds) spectra of this work.

FIG. 5: (color online) The calculated (U=4.5 eV, T=580 K) orbital resolved spectra of NiSe₂ compared to the experimental XPS+BIS spectra. (the same notation as in Fig. 3) The position of the calculated high band is marked with the dotted line. The left inset shows the eσ densities for various interaction strengths U (eV). In the right inset the effect of reducing the Se-Se distance (Å) on the spectra (U=4.5 eV) is shown.

B. Origin of the charge gap

To analyze the behavior of the p∗σ band we have calculated the bare p bandstructures, obtained by decoupling the Ni-d states. This can be done conveniently by removing the Ni-centered orbitals from the LDA basis set [Fig. 6(c),(d)], or rigorously using the p−p block of the Hamiltonian in Wannier basis [Fig. 6(a),(b)] with qualitatively similar results. The p-bands form a broad manifold bounded by dimer bonding bands at the bottom and a distinct anti-bonding p∗σ band complex at the top, separated by a (pseudo)gap. The key difference between NiS₂ and NiSe₂ is the size of this gap separating the p∗σ band from the rest of the p-manifold controlled by the length of the dimer. The gap in NiS₂ is large enough to sustain the coupling to the correlated Ni-d orbitals, while the NiSe₂ gap is too small and the coupling to d orbitals closes it completely.

Next, we consider the effect of applied pressure. The LDA+DMFT calculations for pressures up to 13 GPa show the closing of the charge gap (Fig. 7). This is a result of the combination of the rigidity of the S-S dimer and an overall band broadening. As a consequence of the former the bonding – anti-bonding splitting is insensitive to pressure. On the other hand, the widths of the individual p-bands, controlled by the reduced inter-dimer distances, increase with pressure thus reducing the bare p gap. Together with increasing p−d hybridization this leads to the metal-insulator transition. Noteworthy the LDA results showed an elongation of the Se-Se dimer at moderate pressures, suggesting that the pressure-induced
closing of the charge gap proceeds faster in compounds with higher Se content.

### C. IR reflectivity

To verify the theoretical conclusions and to obtain further information about the electronic properties of NiS$_{2-x}$Se$_x$ we have measured the infrared properties of the NiS$_{2-x}$Se$_x$ series ($x$=0; 0.3; 0.5; 0.7) at ambient conditions, shown in Fig. 8b). For NiS$_2$, $R(\omega)$ slightly increases with increasing frequency, showing a broad maximum in the mid-infrared and two narrow phonon absorption in the far-IR. As Se is chemically substituted in the compound, $R(\omega)$ increases its absolute value at low frequency, partially shielding the phonon lines and eventually becoming metallic-like (i.e. decreasing with increasing $\omega$) for $x=0.7$. The corresponding optical conductivities $\sigma_1(\omega)$ clearly show how the transition from an insulator (NiS$_2$) to a metal (NiS$_{1.3}$Se$_{0.7}$) takes place: A well-defined gap followed by an absorption band is found for NiS$_2$. As Se is introduced the absorption band moves towards lower energies, progressively closing the gap.

A similar behavior is found as pressure is applied: as shown in Fig. 8b) it is again the red-shift of the absorption band that closes the gap. A closer inspection at the curve at 5 GPa for NiS$_2$ shows the coexistence of two distinct terms at low-frequency. As it was also shown in recent IR measurements$^{13}$, our data can be fitted at low frequency with two distinct features: a Drude-like term and a Lorentz peak.

Our aim is to follow and compare the gap-closure by chemical alloying and external pressure. We define the experimental optical gap as the frequency at half-height of the absorption band and report its values in Fig. 9 for NiS$_2$ and NiS$_{1.7}$Se$_{0.3}$ under pressure. This definition of the gap leads to a similar pressure dependence as obtained by linearly extrapolating the steepest rise of $\sigma_1(\omega)$ or by considering the maximum of the absorption peak obtained with Drude-Lorentz fitting$^{22}$. We remark that strong phonon absorptions of the diamond prevent to have (fully) reliable data between 1700-2500 cm$^{-1}$. To overcome this problem and unambiguously define the gap value, the data analysis was performed as follows: reflectivity data are fitted with a Drude-Lorentz model in order to extrapolate the missing parts of the spectra. The KK transformations are performed, followed by a simultaneous fitting of R and sigma. This process is carried out iteratively until the $\sigma_1(\omega)$ is stable with respect to the extrapolation used in the KK transformations.
Comparing the conductivity spectra we find that
the qualitatively similar effect of pressure on NiS
and S substitution by Se follows the scaling relation
P[GPa]≈x/0.15 proposed in Ref. [4]. The pressure dependence
of the optical gaps for pure NiS and NiS$_1$$_x$S$_{0.3}$ is shown in Fig 8), with an horizontal off-set according to
the scaling relation. Our experimental results show that
in the Se-doped compound pressure is more efficient in
closing the gap, in accord with the previous theoretical
reasoning.

Next we discuss the metallic phase. To quantify
the ‘metallicity’ we use the spectral weight (SW) transfer relative to the ambient pressure
NiS$_2$ data. ∆SW=SW(x, P)−SW(x=0, P=0),
where SW(ω)=∫$^{ω'}_0$ dω$^\prime$ R(ω). Recalling that at low frequency
there is the coexistence of two terms we can infer
that with applied pressure a large part of the spectral
weight is transferred to the mid-IR region first, while
the appearance of Drude-like peak occurs upon further
pressure increase [see Fig. 8(b)]. Without making a
quantitative connection we point out that a qualitatively
similar behavior is observed in the DMFT results: As
pressure is applied to NiS$_2$, due to the rigidity of the
S-S dimers the transition occurs mainly due to band
broadening not corresponding at first instance to the
formation of a Drude term. Instead, when the Se-Se
distance is varied we expect a fast response of the low-
energy electrodynamics (right inset of Fig. 5). Following
the scaling relation we compare NiS$_2$ at 5 GPa with
NiS$_1$$_x$S$_{0.7}$ at ambient pressure in Fig. 9). Although a
similar amount of SW is transferred below 4000 cm$^{-1}$,
NiS$_1$$_x$S$_{0.7}$ exhibits a higher SW transfer at lower
frequencies (<2000 cm$^{-1}$) pointing to a more intense
Drude-like term, also supporting our conclusion about
the faster onset of metallicity with Se substitution.

V. CONCLUSIONS

Using the LDA+DMFT approach we have reproduced
the paramagnetic phases of NiS$_2$ (insulator) and NiSe$_2$
(metal) and provide the following answers to the
questions posed in the introduction: i) The presence of the
charge gap in NiS$_2$ in contrast to NiSe$_2$ is a consequence
of a larger gap in the bare p-bandstructure (p-gap) of
NiS$_2$ resulting from stronger bonding within the S-S
dimer. ii) The pressure reduces the p-gap by broadening
the individual p-bands, while the Se substitution reduces
the p-gap due to smaller bonding–anti-bonding splitting.
iii) The MIT is controlled by varying the size of the p-gap.
We find both computationally and experimentally that
the pressure driven MIT is accelerated by the Se substitu-
tion. The conceptual picture of NiS$_2$$_x$S$_{1-x}$ is provided
by a periodic Anderson model with a variable gap in the
conduction electron bath rather than the charge-transfer
insulator model.

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