Mapping the unoccupied state dispersions in Ta$_2$NiSe$_5$ with resonant inelastic x-ray scattering

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The transition metal chalcogenide Ta$_2$NiSe$_5$ undergoes a second-order phase transition at $T_c = 328 \text{ K}$ involving a small lattice distortion. Below $T_c$, a band gap at the center of its Brillouin zone increases up to about 0.35 eV. In this work, we study the electronic structure of Ta$_2$NiSe$_5$ in its low-temperature semiconducting phase, using resonant inelastic x-ray scattering (RIXS) at the Ni L$_3$ edge. In addition to a weak fluorescence response, we observe a collection of intense Raman-like peaks that we attribute to electron-hole excitations. Using density functional theory calculations of its electronic band structure, we identify the main Raman-like peaks as interband transitions between valence and conduction bands. By performing angle-dependent RIXS measurements, we uncover the dispersion of these electron-hole excitations that allows us to extract the low-energy boundary of the electron-hole continuum. From the dispersion of the valence band measured by angle-resolved photoemission spectroscopy, we derive the effective mass of the lowest unoccupied conduction band.

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I. INTRODUCTION

The interplay of electronic correlations and structural instabilities can lead to complex phase transitions involving both the electronic and lattice degrees of freedom. In that context, the low-dimensional compound Ta$_2$NiSe$_5$ has stimulated large interest in the last decade because of its small lattice distortion. Below $T_c$, a band gap at the center of its Brillouin zone increases up to about 0.35 eV. In this work, we study the electronic structure of Ta$_2$NiSe$_5$ in its low-temperature semiconducting phase, using resonant inelastic x-ray scattering (RIXS) at the Ni L$_3$ edge. In addition to a weak fluorescence response, we observe a collection of intense Raman-like peaks that we attribute to electron-hole excitations. Using density functional theory calculations of its electronic band structure, we identify the main Raman-like peaks as interband transitions between valence and conduction bands. By performing angle-dependent RIXS measurements, we uncover the dispersion of these electron-hole excitations that allows us to extract the low-energy boundary of the electron-hole continuum. From the dispersion of the valence band measured by angle-resolved photoemission spectroscopy, we derive the effective mass of the lowest unoccupied conduction band.

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GROUND STATE WITH SOME IT POSSIBLE TO CONTROL THE SIZE OF THE BAND GAP IN TA2NiSe5, an INSULATOR GROUND STATE AT LOW TEMPERATURE [14,19–22]. IT HAS PUMP–PROBE TECHNIQUES SUPPORT THE EXISTENCE OF AN EXCITONIC BAND GAP IN TA2NiSe5, MEASURED AT THE Ni \( (\sigma) \) EDGE. RIXS SPECTROSCOPIES (ADRESS) BEAMLINE [23,24] OF THE SWISS LIGHT SOURCE, PAUL SCHERRER INSTITUT, USING THE SUPER-ADVANCED \( \sigma \)-POLARIZED INCIDENT LIGHT [PERPENDICULAR TO THE SCATTERING PLANE; SEE FIG. 1(a)]. THE COMBINED ENERGY RESOLUTION WAS 150 MEV AT THE Ni L3 EDGE (\( \sim 850 \) eV). TA2NiSe5 SINGLE CRYSTALS WERE CLEAVED IN SITU [WITH A SURFACE IN THE (001) DIRECTION] AT A PRESSURE OF ABOUT \( 1 \times 10^{-8} \) mbar. TA2NiSe5 SINGLE-CRYSTAL SAMPLES WERE PREPARED BY REACTING THE ELEMENTAL NICKEL, TANTALUM, AND SELENIUM WITH A SMALL AMOUNT OF IODINE IN A EVACUATED QUARTZ TUBE. THE TUBE WAS SLOWLY HEATED AND KEPT WITH A TEMPERATURE GRADIENT FROM 950 °C TO 850 °C FOR 7 DAYS, FOLLOWED BY SLOW COOLING. SINGLE-CRYSTAL SAMPLES WITH A TYPICAL SIZE OF \( 0.04 \times 10 \times 10 \) mm\(^2\) WERE OBTAINED IN THE COOLER END. DENSITY FUNCTIONAL THEORY AND THE PROJECTOR AUGMENTED WAVE METHOD IMPLEMENTED IN VASP [25–30] WERE USED FOR BAND STRUCTURE CALCULATIONS IN THE MONOCLINIC PHASE WITH EXPERIMENTALLY DETERMINED STRUCTURAL PARAMETERS [31]. THE KINETIC ENERGY CUTOFF OF THE PLANE-WAVE BASIS WAS 500 eV, AND THE BRILLIOUN ZONE INTEGRATION WAS PERFORMED USING A 11 \( \times \) 11 \( \times \) 5 k-POINT GRID. THE EXCHANGE–CORRELATION EFFECTS WERE INCLUDED WITHIN THE STRONGLY CONFINED APPROXIMATION.

FIG. 1. (a) Schematic description of the experimental geometry generated with the VESTA software [15]. (b) XAS spectrum of Ta2NiSe5, measured at the Ni L3 edge by total fluorescence yield with \( \sigma \)-polarized incident light at 30 K and for specular geometry (\( Q_{\perp} = 0 \)). The Brillouin zone of the low-temperature monoclinic phase of Ta2NiSe5 is shown in the inset.

The difficulty of classifying its electronic structure arises from the small size of the band gap at the Fermi level and the occurrence of fluctuations of the low-temperature phase [7], potentially hiding the true semimetallic nature of Ta2NiSe5 [16]. In a configuration interaction picture, Ta2NiSe5 has been shown to be a negative charge transfer material, and its Ni site has a mainly \( d^9L^2 \) ground state with some \( d^{10}L^2 \) contribution [2]. In parallel, studies based on density functional theory (DFT) calculations disagree on its capability to capture the normal state of Ta2NiSe5, notably due to the difficulty of finding an appropriate functional for describing this material [11,12,17,18]. In addition, time-resolved studies based on pump-probe techniques support the existence of an excitonic insulator ground state at low temperature [14,19–22]. It has been notably shown that this correlated ground state makes it possible to control the size of the band gap in Ta2NiSe5, depending on the excitation density [14]. However, so far, no momentum-resolved data on the unoccupied states of Ta2NiSe5 have been published.

In this paper, we present a RIXS study at the Ni L3 edge of Ta2NiSe5 at low temperature in the monoclinic phase. RIXS spectra are measured as a function of incident photon energy, and they show both fluorescence and Raman-like spectral components. We focus on the Raman-like components, which we interpret as interband electron-hole excitations in the semiconducting electronic configuration of this material at low temperature. A comparison with DFT calculations permits us to identify most of the low-energy RIXS peaks with specific interband transitions. By varying the in-plane component of the transferred momentum of light in the RIXS process, we map its electron-hole continuum in both energy and momentum. This allows us to extract the low-temperature band gap value of Ta2NiSe5, as well as the effective mass of the lowest conduction band, thanks to a comparison with existing ARPES data.

II. METHODS

RIXS experiments were performed at the advanced resonant spectroscopies (ADRESS) beamline [23] of the Swiss Light Source, Paul Scherrer Institut, using the super-advanced x-ray emission spectrometer (SAXES) [24]. A scattering angle of 130° was used, and all the spectra presented here were measured with linearly \( \sigma \)-polarized incident light [perpendicular to the scattering plane; see Fig. 1(a)]. The combined energy resolution was 150 meV at the Ni L3 edge (\( \sim 850 \) eV). Ta2NiSe5 single crystals were cleaved in situ [with a surface in the (001) direction] at a pressure of about \( 1 \times 10^{-8} \) mbar. Ta2NiSe5 single-crystalline samples were prepared by reacting the elemental nickel, tantalum, and selenium with a small amount of iodine in a evacuated quartz tube. The tube was slowly heated and kept with a temperature gradient from 950 °C to 850 °C for 7 days, followed by slow cooling. Single-crystalline samples with a typical size of \( 0.04 \times 10 \times 10 \) mm\(^2\) were obtained in the cooler end. Density functional theory and the projector augmented wave method implemented in VASP [25–30] were used for band structure calculations in the monoclinic phase with experimentally determined structural parameters [31]. The kinetic energy cutoff of the plane-wave basis was 500 eV, and the Brillouin zone integration was performed using a 11 \( \times \) 11 \( \times \) 5 k-point grid. The exchange–correlation effects were included within the strongly constrained and appropriately normed [32] metageneralized gradient approximation.

III. RESULTS AND DISCUSSION

In Fig. 1(a), the geometry adopted for this study is depicted. The scattering plane (defined by the incoming and outgoing x-ray beams) is parallel to the \( a-b \) planes of Ta2NiSe5 and perpendicular to the \( c \) axis of Ta2NiSe5. In this geometry, the transferred momentum of light \( \bar{Q} \) has a component both along the \( a \) axis (parallel to the direction of Ni and Ta chains and to the \( \Gamma X \) direction in reciprocal space), \( Q_{\perp} \), and along the \( b \) axis, \( Q_{\parallel} \). The in-plane \( \Gamma Z \) and \( \Gamma X \) distances are about 0.2 and 0.9 Å\(^{-1}\), respectively, and the out-of-plane \( \Gamma \) distance is about 0.24 Å\(^{-1}\). We first discuss the x-ray absorption spectroscopy (XAS) data of Ta2NiSe5 measured at the Ni L3 edge in total fluorescence yield at 30 K, reported in Fig. 1(b). The main structure lies in the range of energies 852 to 856 eV and consists of two peaks, with the most intense one being at 854.5 eV and the second one making a shoulder at about 853.7 eV.

In Fig. 2, we show our RIXS data obtained at 30 K with \( \sigma \)-polarized incoming light for incident energies \( h\omega_{\text{inc}} \) varying along the XAS spectrum at the Ni L3 edge. The RIXS map in Fig. 2(a) consists mainly of two structures: an intense broad peak centered at about \( h\omega_{\text{inc}} \approx 854.4 \) eV and a weaker peak which disperses like fluorescence from \( h\omega_{\text{inc}} \approx 853 \) eV up to \( h\omega_{\text{inc}} \approx 860 \) eV. In Fig. 2(b), we show particular RIXS spectra acquired in the low incident energy region, up to \( h\omega_{\text{inc}} \approx 854 \) eV. In this range of incident photon energies, several peaks at low energy loss display a Raman behavior, i.e., appear at fixed energy loss for varying incident energies. In contrast to this, the broad fluorescence structure disperses from 3 to 4 eV energy loss. We now focus on the low energy loss Raman-like peaks and their interpretation. At low temperature, in the monoclinic phase, Ta2NiSe5 exhibits a semiconducting electronic structure with a direct gap, displaying bands dispersing on about 1 eV within \( \pm 0.5 \) Å\(^{-1}\) around \( \Gamma \) [6,11]. For these reasons, we interpret the broad peaks between 0
and 2 eV energy loss in Ta$_2$NiSe$_5$ as interband electron-hole excitations conserving the transferred momentum and energy of light in the scattering event of the RIXS process, in the same way as demonstrated for the semimetal TiSe$_2$ [4]. In particular, we observe that the spectra acquired for lower incident photon energies display more spectral weight at low energy loss and therefore seem to be more sensitive to low-energy electron-hole excitations.

To better interpret this, we look at the band structure of Ta$_2$NiSe$_5$ calculated with DFT in the low-temperature monoclinic phase, displayed in Fig. 3(a). There have been various DFT studies of Ta$_2$NiSe$_5$ since 2012, and mainly two difficulties were encountered for this complicated material. First, the description of its normal phase band structure above $T_c$ is delicate because the electronic structure of Ta$_2$NiSe$_5$ is close to being either a semimetal or a semiconductor, depending on the fine details of the DFT calculation, especially the choice of an appropriate functional for describing this material [11,12,17,18,33]. Second, the evaluation of the band gap in the low-temperature semiconducting phase is a difficult task because it is a combination of a hybridization band gap due to the low-symmetry monoclinic phase and a correlation gap due to the excitonic insulator phase. The evaluation of the hybridization gap within DFT results in a value between 30 and 140 meV [11,12,33]. The correlation gap in the excitonic insulator phase has been approached so far by model Hamiltonians [3,7,16,17]. In this context, our calculated band structure agrees well with the literature, giving a hybridization gap in the monoclinic phase of about 70 meV and band dispersions similar to recent studies [11,12,33].

Based on our band structure calculation [Fig. 3(a)], we attempt to attribute specific interband transitions involving occupied and unoccupied bands to the peaks and shoulders observed in the RIXS spectrum near $Q_\parallel \sim 0$ below 3-eV energy loss. We display in Fig. 3(b) such a RIXS spectrum taken at $h\omega_{in} = 853.3$ eV in near-specular geometry $(Q_\parallel = 0.06 \text{ Å}^{-1})$. At this low incident energy (with respect to the main peaks in the XAS spectrum), the structures in the RIXS spectrum are the clearest, and we also expect to probe electron-hole excitations close to the extrema of the valence and conduction bands. The comparison between the calculated band structure and the RIXS spectrum is rendered in Fig. 3 by the colored arrows. The horizontal (energy) positions of the vertical arrows in Fig. 3(b) are positioned approximately at the energy loss corresponding to the interband transitions in Fig. 3(a). The agreement on this assignment is good and highlights possible vertical $(Q_\parallel \sim 0)$ transitions that are expected to involve a large number of states in the band structure because of relatively flat bands. We stress here that we show in Fig. 3(a) only a few possibilities and that this should be generalized to the whole Brillouin zone of Ta$_2$NiSe$_5$ since all interband transitions fulfilling momentum and energy conservation are expected to contribute to the RIXS signal [34].

In this approach, we make three assumptions. (i) We neglect the effect of band dispersions perpendicular to the surface, along $\Gamma Y$ (i.e., we neglect any influence of $Q_\perp$). This is verified in the DFT band structure plot of Fig. 3(a), for which dispersions along $\Gamma Y$ are mostly below 0.2 eV [much smaller than the energy loss scale of the RIXS spectrum in Fig. 3(b)]. (ii) We assume that the position of the peaks and shoulders in the RIXS spectrum at lowest energy loss for $Q_\parallel = 0$ is representative of direct transitions in the DFT band structure plot of Fig. 3(a). Indeed, the number of possible direct transitions between two parabolic dispersions of opposite effective mass tends to increase as the energy loss (energy difference for the electron-hole excitation) increases. As a consequence, the resulting peak in RIXS becomes asymmetric on the higher energy loss side (see Fig. 3(b) in Ref. [4]). Again, looking at the DFT band structure plot of Fig. 3(a), most dispersions near $\Gamma$ and $Z$ are parabolic. (iii) We neglect any RIXS matrix elements modulating the intensity, as well as the orbital character of the involved states. This is an audacious assumption, but to overcome this assumption, one would need a state-of-the-art RIXS calculation for a

![FIG. 2. (a) RIXS map as a function of incident photon energy, measured at the Ni $L_3$ edge with $\sigma$-polarized incident light at 30 K and in near-specular geometry ($Q_\parallel = 0.06 \text{ Å}^{-1}$). The XAS spectrum of Fig. 1(b) is recalled on the vertical axis as a red curve. (b) RIXS spectra at selected incident photon energies, shown in the legend. The dashed lines indicate the main fluorescence and Raman-like structures.](image)

![FIG. 3. (a) Calculated band structure of Ta$_2$NiSe$_5$ along the main high-symmetry directions [see the inset of Fig. 1(b) for a description of the high-symmetry points]. (b) RIXS spectrum in near-specular geometry ($Q_\parallel = 0.06 \text{ Å}^{-1}$) for $h\omega_{in} = 853.3$ eV measured with $\sigma$-polarized incident light at 30 K. The colored arrows indicate fine structures in the RIXS spectrum that we attribute to specific interband transitions in the band structure of (a). The inset shows a possible extraction of the minimum gap by extrapolating the low-energy cutoff of the RIXS spectrum down to the baseline.](image)
multi-orbital dispersive material like Ta$_2$NiSe$_5$, which goes beyond the present study.

It is instructive to note that the low-energy interband transitions resonate when the incident photon energy is tuned to the shoulder in the Ni $L_3$-edge XAS of Ta$_2$NiSe$_5$ at around 853.7 eV (see Fig. 2). When the photon incident energy is tuned to the main peak of the XAS, the RIXS spectra display mainly an intense peak at about $-2$ eV energy loss, which by analogy can be traced back to interband transitions involving the dense flat bands at around 2 eV above the Fermi level in Fig. 3(a) (these states have a significant Ni character [17]). This interpretation suggests that the two-peak structure of the XAS of Ta$_2$NiSe$_5$ mostly reflects the unoccupied DOS of this material, implying that the core-hole potential of the Ni $2p$ states does not have a strong effect on the XAS final states.

Having determined that RIXS effectively measures electron-hole excitations in Ta$_2$NiSe$_5$, we next vary the in-plane momentum $Q_\parallel$ by rotating the sample with respect to the (fixed) incoming and outgoing light beams [in practice, this is done by varying the incident angle $\theta$ in Fig. 1(a)]. For negligible dispersions perpendicular to the sample surface, as confirmed above, this procedure permits us to map electron-hole excitations in a momentum-resolved way. The RIXS spectra, taken at 30 K, are shown in Fig. 4(a), and the corresponding false-color map is shown in Fig. 4(b). Clear dispersions of the Raman-like peaks are observed, especially below 2 eV energy loss. However, it is difficult to extract all momentum-resolved contributions because there are many overlapping peaks. We therefore focus on the low-energy edge of the RIXS spectra (below 1 eV energy loss). In our picture, it is related to the edge of the electron-hole continuum of Ta$_2$NiSe$_5$ and is therefore the result of the momentum- and energy-resolved convolution of the highest valence band and the lowest conduction band [4]. To extract the dispersion of this continuum edge, we perform a second derivative (in the direction of the energy loss) of the smoothed RIXS spectra. An example is shown in Fig. 4(c) for $Q_\parallel = 0.06$ Å$^{-1}$. We attribute the pronounced minimum with the lowest energy loss (apart from the elastic line) to the continuum edge. From the position of the lowest-energy peak for the RIXS spectra measured in near-specular geometry ($Q_\parallel \sim 0$), we find that the first-electron-hole excitation starts at about 0.38 eV. This value corresponds to the size of the charge gap in Ta$_2$NiSe$_5$ at 30 K, as determined from our RIXS study, and is in good agreement with the charge gap estimated from scanning tunneling spectroscopy measurements (at 78 K) [12] or from a symmetric band behavior around the Fermi level in photoemission [6]. At first glance, it is substantially larger than the gap of 0.16 to 0.22 eV obtained from recent optical studies that probe $Q = 0$ interband transitions [8,9,13]. However, applying the same analysis method and extrapolating the low-energy cutoff of the RIXS spectrum down to the intensity baseline [see the inset of Fig. 3(b)] provides us with a gap of 0.17 eV, in very good agreement with optical data.

Extending the second-derivative analysis to all RIXS spectra, we extract the dispersion of the continuum edge, which is plotted as open red circles in Fig. 4(b). Fitting this dispersion with a parabola, we find that the effective mass of the continuum edge is about $m_{\text{tot}} = 1.7 m_e$ with $m_e$ being the electron mass in vacuum. The edge of the electron-hole continuum is a convolution of the dispersions of the highest valence band and lowest conduction band. For approximate parabolic bands of effective masses $m_{\text{VB}}$ and $m_{\text{CB}}$ along the $\Gamma X$ direction, the effective mass of the convoluted dispersion measured in RIXS is $M_{\text{tot}} = m_{\text{VB}} + m_{\text{CB}}$. In their ARPES study of Ta$_2$NiSe$_5$, Wakisaka et al. found that the effective mass of the occupied valence band along $\Gamma X$ is about $m_{\text{VB}} = 0.4 m_e$ at low temperature, based on a parabolic fit of its top part [6]. This value of $m_{\text{VB}}$ is most likely a lower bound since the parabolic fit does not account for the flat top part of the valence band and is limited to a small energy range ($\sim 0.3$ eV). Therefore, from the data of Wakisaka et al. [6], we estimate a higher bound for $m_{\text{VB}} = 0.8 m_e$ using a larger energy and momentum range for a parabolic fit since the electron-hole continuum under consideration here is measured over an energy range of about 1 eV. Using these extreme values, we find that the lowest conduction band must have an effective mass $m_{\text{CB}}$ between 1.5$m_e$ and 0.9$m_e$.

The observation of clear dispersive electron-hole excitations in direct RIXS for low-dimensional materials is still quite exceptional since it has been observed only in TiSe$_2$ [4] and Ta$_2$NiSe$_5$ so far. This is in contrast to cuprate and nickelate materials, which have attracted much attention in the last decade in the RIXS community. Especially on the under-doped side of their phase diagram, cuprates show prominent Raman-like crystal field excitations, called $dd$ excitations, that hardly disperse, except in the case of exotic orbiton physics [35–37]. In these strongly correlated systems, Eisbitt and Eberhardt have already stressed that the weakly screened...
core hole at the $L$ edge gives rise to strong excitonic effects and opens channels for relaxation of the excited electron in the intermediate state, thus making the interpretation of RIXS spectra in terms of band mapping difficult or even impossible [38]. For TiSe$_2$ and Ta$_2$NiSe$_5$, the screening of the core hole is larger. In this case, the dispersive electron-hole excitations can be seen as dispersive $dd$ excitations (or crystal field excitations), in the sense that they are the result of energy- and momentum-conserving transitions between electronic bands split by the crystal field (and by their dispersion due to transfer integrals). However, electron-hole excitations appear on the overdoped side of cuprates, and their modeling with the charge susceptibility [39–41] (or more evolved theoretical approaches [42,43]) tends to attest to a picture similar to the one described in this work.

In that framework, it is remarkable that such dispersive electron-hole excitations are not observed in iron pnictides [44–51]. The main difference in that respect is that pnictides are semimetals with a rather large density of states near the Fermi level, contrary to Ta$_2$NiSe$_5$ and TiSe$_2$ (which is a semimetal with a very small density of states near the Fermi level). Additionally, magnetic excitations are dominant in RIXS for pnictides at low energy, while both Ta$_2$NiSe$_5$ and TiSe$_2$ are nonmagnetic materials. We believe that the presence of many charge carriers near the Fermi level makes it easy for the excited valence electron in the intermediate state of the RIXS process to scatter due to electron-electron interaction, leading to a loss of momentum conservation between the excited electron and hole in the final state of the RIXS process. This is described as $k$-unselective processes (or sometimes incoherent processes) [38]. It would therefore be very interesting to extend these momentum-resolved measurements of dispersive electron-hole excitations to semiconducting materials with large band gaps to better determine the necessary conditions for (coherent) $k$-selective processes.

IV. CONCLUSIONS

In summary, we have measured the quasi-one-dimensional material Ta$_2$NiSe$_5$ with resonant inelastic x-ray scattering at the Ni $L_3$ edge at low temperature. In addition to a fluorescence component, we observe Raman-like excitations up to 2-eV energy loss for incident photon energies tuned to a preedge shoulder in the x-ray absorption spectrum. They are interpreted as interband electron-hole excitations in this dispersive material and are identified as specific transitions between bands calculated with density functional theory. Focusing on these interband excitations, we have acquired RIXS spectra as a function of parallel momentum along the most dispersive axis of Ta$_2$NiSe$_5$. In this way, the momentum- and energy-resolved electron-hole continuum of Ta$_2$NiSe$_5$ is mapped. This allows us to estimate the band gap of this semiconductor and also to extract the effective mass of the lowest conduction band from the edge of the dispersive electron-hole continuum. We hope that our experimental work will serve as a benchmark for a delocalized and weakly correlated material and will stimulate a state-of-the-art RIXS calculation like the new dynamical mean-field theory based method recently proposed by Hariki et al. [52].

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