Temperature-dependent excitonic superfluid plasma frequency evolution in an excitonic insulator, Ta$_2$NiSe$_5$

Yu-Seong Seo$^1$, Man Jin Eom$^2$, Jun Sung Kim$^2$, Chang-Jong Kang$^2$, Byung Il Min$^2$ & Jungseek Hwang$^1$

An interesting van der Waals material, Ta$_2$NiSe$_5$ has been known one of strong excitonic insulator candidates since it has very small or zero bandgap and can have a strong exciton binding energy because of its quasi-one-dimensional crystal structure. Here we investigate a single crystal Ta$_2$NiSe$_5$ using optical spectroscopy. Ta$_2$NiSe$_5$ has quasi-one-dimensional chains along the a-axis. We have obtained anisotropic optical properties of a single crystal Ta$_2$NiSe$_5$ along the a- and c-axes. The measured a- and c-axis optical conductivities exhibit large anisotropic electronic and phononic properties. With regard to the a-axis optical conductivity, a sharp peak near 3050 cm$^{-1}$ at 9 K, with a well-defined optical gap ($\Delta_{op}^{EI} \approx 1800$ cm$^{-1}$) and a strong temperature-dependence, is observed. With an increase in temperature, this peak broadens and the optical energy gap closes around $\sim 325$ K ($T_{c}^{EI}$). The spectral weight redistribution with respect to the frequency and temperature indicates that the normalized optical energy gap ($\Delta_{op}^{EI}(T)/\Delta_{op}^{EI}(0)$) is $1 - (T/T_{c}^{EI})^2$. The temperature-dependent superfluid plasma frequency of the excitonic condensation in Ta$_2$NiSe$_5$ has been determined from measured optical data. Our study may pave new avenues in the future research on excitonic insulators.

Excitonic insulators (EI), proposed in the 1960s$^{1-3}$, are novel materials exhibiting correlated electronic phases and have attracted the interest of several experimental and theoretical condensed matter physics groups. An EI has a condensation phase of excitons (or electron-hole pairs) as its ground state for a specific condition ($E_b > E_g$)$^3$, where $E_b$ and $E_g$ are the binding energy and bandgap, respectively. In the EI phase, superfluidity of neutral electron-hole pairs occurs$^4$. EI systems are either semiconductors with small bandgaps or semi-metals with small overlaps between the conduction and valence bands$^3$. The excitonic condensation in semiconductors occurs through a Bose-Einstein condensation process, while the condensation in semi-metals occurs through the Bardeen-Cooper-Schrieffer (BCS) process$^5$.$^6$. Typically, chalcogenide compounds are known to form one group of EIs. Several studies have been performed on Ta$_2$NiSe$_5$, which is one of transition metal chalcogenides$^{7-16}$. Ta$_2$NiSe$_5$ has quasi-one-dimensional chains along the a-axis$^7$.$^8$. An angle-resolve photoemission (ARPES) study on Ta$_2$NiSe$_5$ showed that the top of the valence band at the $\Gamma$-point flattened at temperatures below its structural transition temperature ($T_{c}^{Str} = 325$ K), and this flat band was interpreted as an excitonic insulating ground state of condensed electron-hole pairs of Ta 5 d-electrons and Ni 3 d- and Se 4 p-holes$^9$. A recent study also shows that Ta$_2$NiSe$_5$ is a zero-gap semiconductor, with a transitions to an EI occurring near 326 K (referred as the onset temperature ($T_{c}^{EI}$))$^{12}$. There was another very recent ellipsometry spectroscopic study on Ta$_2$NiSe$_5$; the authors claimed that exciton-phonon complexes in Ta$_2$NiSe$_5$ and Ta$_2$NiSe$_5$ are confirmed and their observation agrees with the hypothesis of an excitonic insulator ground state. In this article, we provide a new set of anisotropic optical data of Ta$_2$NiSe$_5$ obtained using a different optical spectroscopy technique from the ellipsometry technique. We observed the temperature-dependent evolution of the excitonic insulator energy gap (or excitonic condensation gap) of Ta$_2$NiSe$_5$ Furthermore, we extracted a very important physical quantity, the excitonic superfluid plasma frequency, of Ta$_2$NiSe$_5$ from the measured optical data.

$^1$Department of Physics, Sungkyunkwan University, Suwon, Gyeonggi-do, 16419, Republic of Korea. $^2$Department of Physics, Pohang University of Science and Technology, Pohang, 37673, Republic of Korea. Correspondence and requests for materials should be addressed to J.H. (email: jungseek@skku.edu)
Anisotropic reflectance spectra

We present the temperature-dependent anisotropic optical properties of single crystal Ta$_2$NiSe$_5$, recorded along two different crystal orientations (a- and c-axes) using a conventional optical spectroscopic technique. (refer to the Method) Fig. 1(A and B) show the measured reflectance spectra of a single crystal Ta$_2$NiSe$_5$ along the a- and c-axes respectively. There was a significant difference in the electronic and phononic properties along the two different crystal axis orientations (a- and c-axes) as we expected. For Ta$_2$NiSe$_5$, the quasi-one-dimensional chains are along the a-axis. Several sharp peaks were observed in the a-axis reflectance spectra at low temperatures, with similar strong temperature-dependent behaviors. The reflectance below $\sim$2700 cm$^{-1}$ increases gradually with temperature and above the frequency a peak centered near 3200 cm$^{-1}$ grows with lowering the temperature. This behavior is a typical signature of optical gap formation. The phonon modes seem to be screened at high temperatures above 300 K. The inset in Fig. 1(A) depicts the crystal structure of Ta$_2$NiSe$_5$, which has a layered structure with the b-axis as the stack axis. In contrast to the a-axis reflectance spectra, the c-axis reflectance spectra displays a rather monotonic temperature-dependence, with the reflectance being gradually suppressed over a wide spectral range from 80 to $\sim$15,000 cm$^{-1}$ with the lowering of the temperature. A set of peaks with weak intensity and narrow spectral widths appear at low temperatures. The physical origin of these new set of peaks are not clear yet. The experimentally measured dc resistivity of the ac-plane of Ta$_2$NiSe$_5$ is displayed in the inset of Fig. 1(B). An anomaly in the dc resistivity associated with the structural phase transition temperature ($T_{\text{Str}}$) was observed close to 322 K. Below the $T_{\text{Str}}$, we also observed the splitting of a phonon mode centered around 160 cm$^{-1}$, which indicates that the structural phase transition clearly takes place.

Anisotropic optical conductivity

Figure 2(A and B) depict the optical conductivity for the a- and c-axes of the Ta$_2$NiSe$_5$ sample, respectively. The optical conductivities were obtained from the measured reflectance using the well-developed Kramers-Kronig analysis. In Fig. 2(A), the optical conductivity of 9 K shows a strong and sharp interband transition (or peak) near 3050 cm$^{-1}$ with an optical gap on the low frequency side of the peak. As the temperature increases, the spectral weight of the peak shifts towards the low frequency region, thereby filling up the optical gap. This temperature-dependent behavior of the peak is similar to a typical signature of an optical gap formation. A detailed discussion and analysis on this optical gap and the temperature-dependence of the 3050 cm$^{-1}$ peak will be covered in the following section. This peak centered near 3050 cm$^{-1}$ seems to be closely related to the flat valence band (or the proposed excitonic condensation feature) near the $\Gamma$-point in the Brillouin zone, which was observed via ARPES studies, since its temperature-dependent behavior and energy scale are similar to those of the flat...
The same sharp interband transition has been reported in a recent study of Ta$_2$NiSe$_5$ probed using spectroscopic ellipsometry$^{15,16}$. Interestingly, we also observe some more sharp peaks in the optical conductivity (associated with interband transitions) in a higher energy region above 5000 cm$^{-1}$, with these peaks displaying a temperature-dependence behavior similar to that of the 3050 cm$^{-1}$ peak. The similar temperature-dependence behavior will also be discussed later (refer to Fig. 3(B) and adjoining discussion). We have also extracted the dc resistivity from the optical conductivity by extrapolation to $\omega = 0$. The extracted dc resistivity for both $a$- and $c$- axes of Ta$_2$NiSe$_5$ single crystal is displayed in the inset of Fig. 2(B). The temperature-dependence profile and relative values of the extracted dc resistivity are consistent with those reported ones in recent literature$^{15}$. The optical conductivity of the Ta$_2$NiSe$_5$ single crystal along the $c$-axis (depicted in Fig. 2(B)) displays a monotonic temperature-dependence. A strong interband transition peaked near $\sim 15,000$ cm$^{-1}$ was observed, with an energy corresponding to the $d$-$d$ transition between the valence Ni-$d$ and conduction Ta-$d$ orbitals$^{19}$. There was also a significant absorption below this transition, which is not the focus of this article.

First-principles calculations were performed to compute the anisotropic optical properties of Ta$_2$NiSe$_5$. (refer to the Method). The inset in Fig. 2(A) displays the electronic dispersion along the X-$\Gamma$-X direction, which is chosen to compare with the ARPES study results$^{10,13}$. The Fermi energy ($E_F$) is set to the top of the valence band. The Ni-$d$ and Ta-$d$ orbitals account for the majority of the valence and conduction bands, respectively, as evident from the inset of Fig. 2(A). The results obtained with the mBJ functional were similar to those found with PBE, although the bandgap is twice that obtained with PBE. In general, the results are consistent with those reported by Kaneko et al.$^{11}$. We calculated the optical conductivity from the dielectric function obtained using the random phase approximation (RPA)$^{20}$ and our first-principles calculation results. The calculated optical conductivity ($\sigma_{\alpha-\omega}$ and $\sigma_{\beta-\omega}$) for the $a$- and $c$- axes are displayed as dashed black lines in Fig. 2(A and B), respectively. The difference between the two theoretical conductivity spectra is due to the effect of Ta-NiSe-Ta chains along the $a$-axis$^{24}$. The calculated $\sigma_{\alpha-\omega}$ agrees reasonably with the measured conductivity of the $c$-axis in its overall shape. However, the calculated $\sigma_{\beta-\omega}$ shows some discrepancy in the low frequency region below 5000 cm$^{-1}$; the theoretical conductivity shows a higher energy gap and a much smaller spectral weight as compared to the measured one at 9 K. We speculate that this discrepancy occurs due to the non-inclusion of electron-hole interactions in our calculations. Therefore, this result may indicate that the sharp interband transition near 3050 cm$^{-1}$, is closely related to the excitonic excitations. Our observation is in line with a previous report on carbon nanotubes$^{21}$.

Figure 2. Anisotropic optical conductivity of Ta$_2$NiSe$_5$ along $a$- and $c$- axes. The experimentally optical conductivities of Ta$_2$NiSe$_5$ along $a$- and $c$-axes are depicted in (A) and (B), respectively. The optical conductivities were obtained with the Kramers-Kronig analysis on the measured reflectance spectra for the different temperatures (within the range of 9 to 350 K). The inset of (A) shows the band dispersion diagrams obtained via the PBE functional and the partial densities of states, which were obtained from the first-principles calculations. The inset in (B), shows the extracted dc resistivity (along $a$- and $c$- axes) from extrapolations of the optical conductivity to zero frequency. The dashed black lines correspond to the theoretical optical conductivities for $a$- and $c$- axis orientations obtained from the first-principles calculations.
wherein a similar set of calculations (with and without including electron-hole interactions) yielded a similar difference between two results. It is important to note that it is not easy to include electron-hole interactions in the electronic structure calculations for a complex system like Ta$_2$NiSe$_5$.

**Temperature-dependent optical excitonic insulator gap and interband transitions**

Figure 3(A) displays the temperature-dependent optical EI gap ($\Delta_{op}^{EI}$) of Ta$_2$NiSe$_5$, obtained from the optical conductivity. The red dashed line is a guide to the eye. The inset shows the procedure by which the optical EI gap was obtained. (B) A schematic diagram of the temperature-dependent evolution of the optical EI gap in Ta$_2$NiSe$_5$, above and below the transition temperature ($T_{c}^{EI}$). The intraband transitions are denoted with red arrows. The upward blue arrow denotes the interband transition between the two parabolic bands near the Fermi level. The double direction blue arrows denote the transitions between the two flat bands, which form the optical EI gap. The other interband transitions involving bands near the Fermi level are depicted with green arrows.

**Figure 3.** Excitonic insulator energy gap and temperature-dependent interband transitions. (A) The temperature-dependent optical EI gap ($\Delta_{op}^{EI}$) of Ta$_2$NiSe$_5$, obtained from the optical conductivity. The red dashed line is a guide to the eye. The inset shows the procedure by which the optical EI gap was obtained. (B) A schematic diagram of the temperature-dependent evolution of the optical EI gap in Ta$_2$NiSe$_5$, above and below the transition temperature ($T_{c}^{EI}$). The intraband transitions are denoted with red arrows. The upward blue arrow denotes the interband transition between the two parabolic bands near the Fermi level. The double direction blue arrows denote the transitions between the two flat bands, which form the optical EI gap. The other interband transitions involving bands near the Fermi level are depicted with green arrows.
Temperature-dependent accumulated spectral weight and excitonic superfluid plasma frequency

In general, an optical gap formation results in spectral weight redistributions in the optical conductivity. We studied the spectral weight redistribution of the first interband transition peaked near 3050 cm$^{-1}$ with respect to both frequency and temperature. The accumulated spectral weight ($SW$) is a useful physical quantity for studying the spectral weight redistribution and can be defined as $SW(\omega, T) \equiv \int_0^\omega \sigma_1(\omega', T)d\omega'$. In Fig. 4(A), $SW(\omega)$ of the Ta$_2$NiSe$_5$ sample are displayed at various temperatures in a frequency range up to 5000 cm$^{-1}$. All the accumulated spectral weights were observed to be more or less parallel to one another above $\sim 4000$ cm$^{-1}$ while a small amount of suppression in the accumulated spectral weight occurred below $\sim 4000$ cm$^{-1}$, for temperatures below the transition temperature ($T^{EI}_c$). In the inset, $SW(\omega)$ for a wider spectral range up to 20000 cm$^{-1}$ in log-log scales is displayed.

In Fig. 4(B), $SW(\omega)$ at 200 cm$^{-1}$ as a function of temperature is shown. We chose a low frequency of 200 cm$^{-1}$, well below the full optical EI gap (1800 cm$^{-1}$) to study only the thermal excitation effect, excluding other absorptions at high frequencies. It is important to note that we have subtracted 10000 $\Omega^{-1}$ cm$^{-2}$ from the obtained $SW(200$ cm$^{-1}, \ T)$ to exclude contributions from the low frequency phonons. We show an exponential fit (red dashed line) to the data; the equation employed in the fit is $SW(T) \equiv SW_0 \exp{\left[\frac{(\omega^{EI} - \Delta_0)}{T}\right]}$. Here, $SW_0$ is the spectral weight up to 200 cm$^{-1}$ at $T = 0$ K. Since this accumulated spectral weight at low frequency is proportional to the charge carrier concentration due to a predominant thermal effect, it can be written as $SW(T) \simeq SW_0 \exp{\left[-\frac{\Delta^{EI}(T) - \Delta_0}{T}\right]}$, where $\Delta^{EI}(T)$ is an excitonic insulator (EI) energy gap and $\Delta_0 \equiv \Delta^{EI}(0)$. By combining these two equations, we obtain $\Delta^{EI}(T)/\Delta_0 = 1 - T^{EI}/(\Delta_0 \alpha) = 1 - \left(\frac{T}{T^{EI}_c}\right)^2 \geq 0$, where $T^{EI}_c = \sqrt{\Delta_0 \alpha}$ is the onset temperature of the gap. If we consider $\Delta_0$ as the full optical EI gap ($\approx 1800$ cm$^{-1}$) and $\alpha = 44.26$ K (from the exponential fit), then the onset temperature ($T_c^{EI}$) is 338 K. In Fig. 4(C), we plot the EI energy gap, $\Delta^{EI}(T)$, with the red dashed line along with the optical EI gap, $\Delta^{opt}(T)$, which was obtained directly from the optical conductivity (refer to Fig. 3(A)). From the figure, it is evident that these two results are in good agreement with each other.

Furthermore, from the accumulated spectral weight, we can calculate an interesting physical quantity, the superfluid plasma frequency of the excitonic condensation. In Fig. 4(D), we present a differential quantity, $\Delta SW(\omega, T) = SW(\omega, 350$ K) $- SW(\omega, T)$ at various temperatures. This quantity seems to consist of two components: one is unrecovered spectral weight near 5000 cm$^{-1}$ (or the missing spectral weight) due to the excitonic condensation marked with the red arrow and the other is the peak near 2600 cm$^{-1}$ due to the thermal broadening effects, which may come from two different temperatures of the two different phases (here, the most pronounced peak between 9 K and 350 K). We present a more detailed discussion on this quantity ($\Delta SW(\omega, T)$), comparing it with that of the superconductors, in the following section. The superfluid spectral weight ($SW_\alpha$) can be related to the superfluid plasma frequency ($\Omega_\alpha$) as $\Omega_\alpha(T) \equiv \sqrt{\frac{120}{\pi}} \frac{SW_\alpha(T)}{\Omega_\alpha}$. We note that the numerical factor $\pi/120$ is the unit conversion factor; here $\Omega_\alpha$ and $SW_\alpha$ are in cm$^{-1}$ and $\Omega^{-1}$ cm$^{-2}$ units, respectively. We display the superfluid plasma frequency (blue solid squares) as a function of temperature in Fig. 4(E). $\Omega_\alpha$ is gradually decreasing with increasing the temperature and then eventually going to zero near the EI onset temperature, $T^{EI}_c$. Therefore, the onset temperature of the superfluid condensation seems to be the same as that of the EI energy gap. It is worthwhile to note that up to now we used the spectral weight at 350 K as the reference spectral weight for getting the differential spectral weight at various temperatures since we do not have data closer to the transition temperature. If we use a linear interpolated spectral weight (at 325 K) between 300 K and 350 K as the reference spectral weight we will have slightly lower excitonic condensation plasma frequencies than the values obtained using the spectral weight at 350 K as the reference spectral weight, as displayed in Fig. 4(E) with red open circles.
Discussion: Excitonic insulators and superconductors

It is worthwhile to compare the condensation in the EI with that in a superconductor. In Fig. 5(A–H), we compare the two material systems: s-wave superconductors (SC) and EI schematically. We depict the transition from a normal metal (NM) to a SC and a zero-gap semiconductor (ZGSC) to an EI, as the temperature is lowered from above to below the transition temperatures ($T_c^{SC}$ and $T_c^{EI}$), respectively, through spectral weight redistributions. Figure 5(A) shows the density of states (DOS's) of the normal metal and the superconductor, 5(B) shows the corresponding optical conductivities ($\sigma(\omega)$), 5(C) shows the accumulated spectral weights ($SW(\omega)$), and 5(D) shows the differential spectral weights ($\Delta SW(\omega, T) \equiv SW(\omega, T) - SW(\omega, T < T_c^{SC})$). In the superconductor, the superfluid spectral weight of condensed Cooper (or electron-electron) pairs appears as a delta function at zero frequency, which is marked with a thick red vertical arrow in Fig. 5(B); the hatched area below the superconducting gap ($\Delta_{op}^{SC}$) seems to have disappeared\cite{23}. Therefore, this area is termed as the missing spectral weight. At high frequencies well above the SC gap, the accumulated spectral weights of NM and SC will differ by the missing spectral weight, as shown in Fig. 5(C). When the condensed Cooper pairs are broken by thermal or other...
processes, the missing spectral weight reappears back in a finite frequency region. The differential spectral weight ($\Delta SW(\omega)$) in the high frequency region will clearly show the missing spectral weight, as depicted in Fig. 5(D), where $SW_{sf}$ stands for the superfluid spectral weight.

We also sketch the corresponding four physical quantities (DOS's, $\sigma_1(\omega)$, $SW(\omega)$, and $\Delta SW(\omega)$) for both the ZGSC and the EI in Fig. 5(E–H). In the EI, there is a superfluid spectral weight associated with the condensed electron-hole pairs; however, the neutral excitonic superfluid will be located at zero frequency with zero spectral weight since the neutral excitons cannot contribute to the electrical conductivity. The electrons involved in the condensation will be disappeared in the EI states as in the SC state; this also causes a missing spectral weight. However, the electrons in the EI state do not appear anywhere in the whole frequency range while the electrons in the SC state will appear at zero frequency as a delta function. Therefore, in the EI state the optical sum rule seems to be violated; the missing spectral weight (or missing electron density) still remains in the sample but is just optically invisible. The EI has singularities at the bottom of the conduction band and on the top of the valence band, similar to the superconductor, as evident in Fig. 5(E). Here we assume that both ZGSC and EI phases are at the absolute zero temperature. The resulting accumulated spectral weight in Fig. 5(G) looks analogous to what was observed in our measured accumulated spectral weights in Fig. 4(A), for frequencies below 5000 cm$^{-1}$. However, they appear to be different in the high frequency region well above the EI gap. The accumulated spectral weights of ZGSC and EI flatten and are parallel to each other at the high frequency region while the measured ones are still parallel to each other but keep increasing. This difference at the high frequency region can be explained by considering other interband absorptions occurring at higher frequencies. If we include the other interband absorption bands at higher frequencies, the results will show a continuous parallel increase at high frequencies, as in the measured data (refer to Fig. 4(A)). In Fig. 5(H) we display the differential spectral weight ($\Delta SW(\omega)$), where $SW_{sf}$ stands for the superfluid spectral weight. We do not see the peak, which was observed in the experimental differential spectral weight (refer to Fig. 4(D)). If we take the thermal broadening effects, which may come from the temperature difference between ZGSC and EI phases, into account we will have the peak in the $\Delta SW(\omega)$.

Figure 5. Comparison of excitonic insulators with superconductors. (A) The densities of states (DOS's) of normal metal (NM) and superconductor (SC). (B) The corresponding optical conductivities ($\sigma_1(\omega)$). The thick red vertical arrow indicates the superfluid spectral weight condensed at zero frequency. (C) The accumulated spectral weights ($SW(\omega)$) of NM and SC. (D) The differential spectral weight ($\Delta SW(\omega)$) between NM and SC. (E) DOS's of zero-gap semiconductor (ZGSC) and excitonic insulator (EI); the red (electrons) and blue (holes) dashed horizontal lines show the thermal excitations, (F) $\sigma_1(\omega)$; the black (for ZGSC) and red (for EI), (G) $SW(\omega)$, and (H) $\Delta SW(\omega)$. The red arrow shows the missing (or superfluid) spectral weight, which is closely related to the excitonic superfluid plasma frequency.
Conclusion
In conclusion, we observed a strong and sharp peak around 3050 cm$^{-1}$ in the optical conductivity (along the $a$-axis) of Ta$_2$NiSe$_5$ at low temperatures along with a well-defined optical gap on the low frequency side of the peak. This peak corresponds to an interband transition, which shows a characteristic strong temperature-dependence, a behavior previously attributed to that of the flat valence band in observations made of Ta$_2$NiSe$_5$ with ARPES.$^{15,16}$

The results of our first-principles calculations were in good agreement with the overall experimental optical data for both $a$- and $c$-axes except for the strong and sharp peak in the $a$-axis conductivity. We speculate that this discrepancy between experiment and theory arises from the fact that the electron-hole interactions in Ta$_2$NiSe$_5$ were not included in the theoretical calculations. This result probably indicates that the strong and sharp peak results from the electron-hole interactions for this system. Furthermore, the spectral weight redistribution analysis demonstrates that the excitonic condensation of electron-hole pairs can occur below the onset temperature of the optical gap and the temperature-dependent excitonic superfluid plasma frequency can be obtained from the measured optical data. We also found that the optical sum rule can be violated in the EI phase. These interesting findings illustrate the new opportunities for further investigations on Ta$_2$NiSe$_5$, and other excitonic insulators.

Experiments and analysis
A high-quality single crystal Ta$_2$NiSe$_5$ sample was grown by a chemical vapor transport method. The detailed crystal growth method can be found in a literature.$^{14}$ The crystal structure and chemical compositions of the Ta$_2$NiSe$_5$ sample were characterized using x-ray diffraction and energy-dispersive x-ray spectroscopy. Our optical study was performed on the sample with an area of 2 $\times$ 2 mm$^2$ and a thickness of 0.5 mm. A commercial FTIR-type spectrometer (Vertex 80 v, Bruker) and a continuous flow liquid helium cryostat were used to obtain $a$- and $c$-axis reflectance spectra over a wide spectral range (80–20,000 cm$^{-1}$) at various selected temperatures between 9 and 350 K. We used linear polarized beam to get anisotropic optical spectra with an incident angle on the sample of 10°. We also used an in-situ metallization method to obtain accurate reflectance spectra.$^{24}$ In this method we used the coated 200 nm thick gold for mid- and far-infrared (or alumina and near-infrared and visible) film on the sample as the reference reflectance. Furthermore, we corrected the measured reflectance with respect to the gold (or aluminum). The optical conductivity is obtained from the measured reflectance ($R(\omega)$) using the Kramers-Kronig relation between the amplitude ($\sqrt{R(\omega)}$) and phase ($\phi(\omega)$) of the reflection coefficient$^{17}$, the Fresnel formula, and well-known relationships between the optical constants.$^{25}$

First-principles calculation
We adopted the full-potential linearized augmented plane wave (FP-LAPW) implemented in Wien2K$^{26}$ to calculate the band structure with a number of exchange-correlation functionals, including the generalized gradient approximation (GGA), GGA+U, van der Waals force correction (vdW)$^{27}$, and their hybrid functionals. We obtained insulating ground-states when we used two GGAs: Perdew, Burke, and Ernzerhof (PBE)$^{28}$ and modified Becke-Johnson (mBJ)$^{29}$. We found that the electronic ground state was semi-metallic when the experimental lattice constants were used; therefore, we fully relaxed the crystal structure using the PBE and then used the relaxed geometry in further calculations for the band structure and optical conductivity. Note that the volume of our relaxed structure is nearly 14% larger than the experimental volume. This difference due to the distance between layers ($b$ lattice constant) as shown in the inset of Fig. 1(A): (i) the relaxed $b$ lattice constant is 14.5 Å, which is nearly 13% larger than the experimental one. (ii) the $a$ and $c$ lattice constants are 3.509 Å (±0.4%) and 15.732 Å (+0.6%), respectively. The relaxed structure was chosen because our calculated electronic properties are similar to previous ab-initio properties found using the experimentally determined lattice constants.$^{31}$ The reciprocal space integration was approximated by sampling the Brillouin zone with a 28 $\times$ 6 $\times$ 28 mesh of the Monkhorst-Pack scheme.

References
1. Mott, N. F. The transition to the metallic state. Philosophical Magazine 6, 287–309 (1961).
2. Knox, R. Solid State Physics. (Academic press, New York, 1963).
3. Jérome, D., Rice, T. M. & Khon, W. Excitonic Insulator. Physical Review B 105, 145101 (1997).
4. Kozlov, A. N. & Maksimov, L. A. The metal-dielectric divalent crystal phase transition. Physical Review B 81, 205117–11 (2010).
5. Pan, V.-N., Becker, K. W. & Fehske, H. Spectral signatures of the BCS-BEC crossover in the excitonic insulator phase of the extended Falicov-Kimball model. Physical Review B 81, 205117–11 (2010).
6. Zener, K., Ille, D., Bronold, F. X. & Fehske, H. Electron-hole pair condensation at the semimetal-semiconductor transition: A BCS-BEC crossover scenario. Physical Review B 85, 121102–5 (2012).
7. Sunshine, S. A. & Ibers, J. A. Structure and Physical of the New Layered Ternary Chalcogenides Ta$_2$NiS$_5$ and Ta$_2$NiSe$_5$. Inorganic Chemistry 24, 3611–3614 (1985).
8. Di Salvo, F. J. et al. Physical and structural properties of the new layered compounds Ta$_2$NiS$_5$ and Ta$_2$NiSe$_5$. Journal of the Less-Common Metals 116, 51–61 (1985).
9. Wakisaka, Y. et al. Excitonic Insulator State in Ta$_2$NiSe$_5$ Probed by Photoemission Spectroscopy. Physical Review Letters 103, 026402–4 (2009).
10. Wakisaka, Y. et al. Photoemission Spectroscopy of T$_2$NiSe$_5$. Journal of Superconductivity and Novel Magnetism 25, 1231–1234 (2012).
11. Kaneko, T., Toriyama, T., Konishi, T. & Ohta, Y. Electronic structure of Ta$_2$NiSe$_5$ as a candidate for excitonic insulators. Journal of Physics: Conference Series 400, 032035–5 (2012).
12. Kaneko, T., Toriyama, T., Konishi, T. & Ohta, Y. Orthorhombic-to-monoclinic phase transition of Ta$_2$NiSe$_5$ induced by the Bose-Einstein condensation of excitons. Physical Review B 87, 035121–5 (2013).
13. Seki, K. et al. Excitonic Bose-Einstein condensation in Ta$_2$NiSe$_5$ above room temperature. Physical Review B 90, 155116–7 (2014).
14. Kim, S. Y. et al. Layer-confined excitonic insulating phase in ultrathin Ta$_2$NiSe$_5$ crystals. ACS Nano 10, 8888 (2016).
15. Lu, Y. et al. Zero-gap semiconductor to excitonic insulator transition in Ta$_2$NiSe$_5$. Nat. Comm. 8, 14408 (2017).
16. Larkin, T. I. et al. Giant exciton fano resonance in quasi-one-dimensional Ta$_2$NiSe$_5$. Phys. Rev. B 95, 195144 (2017).
17. Wooten, F. Optical Properties of Solids. (Note: Key material on page 176) (Academic, New York, 1972).
18. Hwang, J., Yang, J., Timusk, T. & Chou, F. C. Infrared conductivity of Na$_x$CoO$_2$: Evidence of gapped states. *Phys. Rev. B* **72**, 024549 (2005).
19. Lee, J. S., Kim, M. W. & Noh, T. W. Optical excitations of transition-metal oxides under the orbital multiplicity effects. *New J. Phys.* **7**, 147 (2005).
20. Ambrosch-Draxl, C. & Sofo, J. O. Linear optical properties of solids within the full-potential linearized augmented plane wave method. *Computer Physics Communications* **175**, 1–14 (2006).
21. Spataru, C. D., Ismail-Beigi, S., Benedict, L. X. & Louie, S. G. Excitonic effects and optical spectra of single-walled carbon nanotubes. *Phys. Rev. Lett.* **92**, 077402 (2004).
22. London, R. One-dimensional hydrogen atom. *Am. J. Phys.* **27**, 649 (1959).
23. Glover, R. E. & Tinkham, M. Transmission of superconducting films at millimeter-microwave and far infrared frequencies. *Phys. Rev.* **104**, 844 (1956).
24. Hones, C. C., Reedy, M., Cradles, D. A. & Timusk, T. Technique for measuring the reflectance of irregular, submillimeter-sized samples. *Applied Optics* **32**, 2976–2983 (1993).
25. Hwang, J., Timusk, T. & Gu, G. D. Doping dependent optical properties of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$. *J. Phys.: Condens. Matter* **19**, 125208 (2007).
26. Blaha, P., Schwarz, K., Madsen, G. K. H., Kavasnicka, D. & Luitz, J. WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties. (Karlsruhe University, Germany, 2001).
27. Tkatchenko, A. & Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Physical Review Letters* **102**, 073005–4 (2009).
28. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **77**, 3865–3868 (1996).
29. Tran, F. & Blaha, P. Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential. *Physical Review Letters* **102**, 226401–4 (2009).

**Acknowledgements**

J.H. acknowledges financial support from the National Research Foundation of Korea (NRF-2017R1A2B4007387). Y.S.S acknowledges financial support from the National Research Foundation of Korea (NRF-2016R1A6A3A11933016). M.E. and J.K. acknowledge support from the NRF through SRC (Grant No. 2011-0030785) and the Max Planck POSTECH/KOREA Research Initiative (Grant No. 2011-0031558) Programs, and also from IBS (No. IBSR014-D1-2014-a02). J.H. gratefully acknowledges Yunkyu Bang, Hyoung Joon Choi, Han-Jin Noh, and Sung-Sik Lee for helpful discussions.

**Author Contributions**

J.H. and Y.S. analyzed the measured optical spectra and wrote the main manuscript, Y.S. took the optical spectra. M.E. and J.K. grew the single crystal. M.E. got the dc resistivity data. C.K. and B.M. performed the theoretical calculations. All authors reviewed the manuscript.

**Additional Information**

**Competing Interests:** The authors declare no competing interests.

**Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018