Pressure suppression of the excitonic insulator state in Ta$_2$NiSe$_5$ observed by optical conductivity

H. Okamura$^1$, T. Mizokawa$^1$, K. Miki, Y. Matsui, N. Noguchi, N. Katayama$^2$, H. Sawa$^3$, M. Nohara$^3$, Y. Lu$^4$, H. Takagi$^5,6$, Y. Ikemoto$^7$, and T. Moriwaki$^7$

Department of Applied Chemistry, Tokushima University, Tokushima 770-8506, Japan
$^1$Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan
$^2$Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan
$^3$Department of Quantum Matter, Hiroshima University, Higashi-Hiroshima 739-8503, Japan
$^4$College of Materials Science and Engineering, National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, China
$^5$Department of Physics, University of Tokyo, Tokyo 113-0013, Japan
$^6$Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany
$^7$Japan Synchrotron Radiation Research Institute, Sayo 679-5198, Japan

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The layered chalcogenide Ta$_2$NiSe$_5$ has recently attracted much interest as a strong candidate for the long sought excitonic insulator (EI). Since the physical properties of an EI are expected to depend sensitively on the external pressure, it is important to clarify the pressure evolution of microscopic electronic state in Ta$_2$NiSe$_5$. Here we report the optical conductivity [$\sigma(\omega)$] of Ta$_2$NiSe$_5$ measured at high pressures to 10 GPa and at low temperatures to 8 K. With cooling at ambient pressure, $\sigma(\omega)$ develops an energy gap of about 0.17 eV and a pronounced excitonic peak at 0.38 eV, as already reported in the literature. Upon increasing pressure, the energy gap becomes narrower and the excitonic peak is broadened. Above a structural transition at $P_c \simeq 3$ GPa, the energy gap becomes partially filled, indicating that Ta$_2$NiSe$_5$ is a semimetal after the EI state is suppressed by pressure. At higher pressures, $\sigma(\omega)$ exhibits metallic characteristics with no energy gap. The detailed pressure evolution of $\sigma(\omega)$ is presented, and discussed mainly in terms of a weakening of excitonic correlation with pressure.

I. INTRODUCTION

Excitonic insulator (EI) is an unconventional insulator in which the attractive correlation between electrons and holes results in a collective condensation of electron-hole ($e$-$h$) pairs (excitons) and an energy gap at the Fermi level ($E_F$). EI was first predicted theoretically in $^1$1960$^2$ with a phase diagram schematically shown in Fig. 1. The starting material for EI can be either semimetal ($E_g < 0$) or semiconductor ($E_g > 0$), where $E_g$ indicates the one-particle band gap in the absence of $e$-$h$ correlation. An EI state is expected in the vicinity of $E_g$=0 below the transition temperature $T_c$, if the exciton binding energy $E_b$ is larger than $|E_g|$. Another feature of the EI is a characteristic flattening of the bands indicated in Fig. 1.

Despite the theoretical interest on EI, only a few compounds had been considered as candidates for EI, including TmSe$_1$-$x$Te$_x$ and 17-TiSe$_2$. In 2009, Wakisaka et al. suggested that Ta$_2$NiSe$_5$ should be an EI on the basis of angle-resolved photoemission spectroscopy (ARPES) data. Ta$_2$NiSe$_5$ has a layered crystal structure, and exhibits a structural phase transition at $T_c$=328 K, where the crystal symmetry changes from orthorhombic to monoclinic with decreasing temperature ($T$). Below $T_c$, the resistivity increases rapidly with cooling, indicating energy gap of about 0.2 eV. The ARPES study at 1 $T$ found an unusually flat dispersion at the top of valence band, which was regarded as strong evidence for an EI. Further ARPES study and band calculation indicated that the flat band feature persisted even above $T_c$, and suggested the low-$T$ phase of Ta$_2$NiSe$_5$ to be an EI in the strong coupling regime caused by a condensation of preformed excitons. It was pointed out that above $T_c$...
by symmetry. It was also suggested that the structure change below \( T_c \) was mainly driven by the exciton condensation, rather than by a structural instability due to electron-lattice (e-l) coupling.\(^{23,24}\) Lu et al. reported transport and optical data of \( \text{Ta}_2\text{Ni(Se,S)}_5 \) and \( \text{Ta}_2\text{Ni(Se,Te)}_5 \) where the chemical substitution and external pressure were used to control \( E_g \) of \( \text{Ta}_2\text{NiSe}_5 \). The optical conductivity \( \sigma(\omega) \) of \( \text{Ta}_2\text{NiSe}_5 \) at low \( T \) clearly exhibited \( \varepsilon \) pronounced peak of excitonic origin at about 0.4 eV and an energy gap of about 0.16 eV. An experimental phase diagram of \( \text{Ta}_2\text{NiSe}_5 \) was constructed from the transport data, which was indeed consistent with the predicted one depicted in Fig. 1 and strongly suggested \( \text{Ta}_2\text{NiSe}_5 \) to be an EI.\(^{24} \) Detailed \( \sigma(\omega) \) data\(^{24,25} \) were analyzed by a theoretical study\(^{24} \) which again suggested that \( \text{Ta}_2\text{NiSe}_5 \) should be an EI in the strong coupling regime below \( T_c \), and it should be a semiconductor \( (E_g > 0) \) above \( T_c \).\(^{24,25} \)

Many more works on \( \text{Ta}_2\text{NiSe}_5 \) have also been reported, including ARPES\(^{12,26} \) optical conductivity\(^{26,27} \) Raman scattering,\(^{24,28} \) ultrafast laser spectroscopy,\(^{26,27} \) resonant inelastic X-ray scattering,\(^{25,28} \) high pressure studies,\(^{25,28,29} \) scanning tunneling spectroscopy,\(^{26} \) and theoretical analyses.\(^{20,36,37} \) While many of these works support that the transition at \( T_c \) is driven by exciton condensation, some of them question such scenario.\(^{20,33,36} \) For example, a semimetallic \( (E_g < 0) \) band dispersal around \( E_F \) has been reported by an ARPES study above \( T_c \).\(^{26} \) Theoretically, it has been shown that a flat valence band may be obtained by a band calculation without \( e-l \) correlation,\(^{28} \) and that there can be a sizable \( \sim 0.1 \) eV hybridization with the mirror symmetry breaking below \( T_c \) but without \( e-h \) correlation.\(^{36} \)

Following the above development, it is important to carefully evaluate effects of both the \( e-h \) correlation and \( e-l \) coupling in \( \text{Ta}_2\text{NiSe}_5 \). An important aspect is the response of \( \text{Ta}_2\text{NiSe}_5 \) to changes in the ratio \( E_b/E_g \), since the physical properties of \( \text{EI} \) should sensitively depend on \( E_b/E_g \). In this regard, photo-excited experiments, which are probed by either ARPES\(^{12,14} \) or laser,\(^{29,31} \) have the advantage of being able to tune the carrier density, and hence to control \( E_b \), through the Coulomb screening of \( e-h \) attraction. In fact, photo-induced gap closing and semimetallic states in \( \text{Ta}_2\text{NiSe}_5 \) have been observed and analyzed.\(^{32-34,38} \) Another effective way of tuning an EI state is the application of external pressure \( (P) \) since an applied pressure usually broadens the conduction and valence bands, and increases (reduces) their overlap (separation). Detailed high-\( P \) studies\(^{23,24} \) have been performed on the crystal structure, resistivity \( (\rho) \), Hall coefficient, and \( \sigma(\omega) \) of \( \text{Ta}_2\text{NiSe}_5 \). They revealed a rich \( P-T \) phase diagram of \( \text{Ta}_2\text{NiSe}_5 \) as depicted in Fig. 2. Above the first order structural transition at \( P_s \approx 3 \) GPa, the \( ac \) plane becomes flat with a less rippling of \( ac \) plane along the \( c \) axis.\(^{23,34} \) \( \rho(T) \) is reduced with increasing \( P \), showing a crossover from semiconducting \( T \) dependence below \( P_s \) to a completely metallic one well above \( P_s \), with quite large and dramatic change of \( \rho(T) \) around \( P_s \). A superconductivity with \( T_c \) \( \approx 2 \) K appears at about 8 GPa. Above \( P_s \), from \( \rho(T) \) and \( \sigma(\omega) \) data, it has been shown that \( \text{Ta}_2\text{NiSe}_5 \) is a semimetal with a partial energy gap, in contrast to the full energy gap below \( P_s \). It has been suggested that the electronic transition at \( T^* \) to the low-\( T \) semimetallic state is caused by \( e-l \) coupling, while that at \( T_c \) below \( P_s \) is caused by both excitonic correlation and \( e-l \) coupling.\(^{23} \)

In this paper, we present a full account of the \( \sigma(\omega) \) and reflectance data of \( \text{Ta}_2\text{NiSe}_5 \) at high \( P \) and low \( T \), which have been obtained at the \( (P,T) \) points indicated in Fig. 2. The data reveal how the well-developed energy gap and excitonic peak at \( P=0 \), which have been taken as evidence for an EI, are suppressed as the applied pressure reduces the excitonic correlation.

![Figure 2: Temperature (T) vs Pressure (P) phase diagram of Ta2NiSe5 reproduced from Matsubayashi et al.\(^{24} \) Tc, T*, and Pc indicate the structural transition temperatures and pressure, and Tc the superconducting transition temperature. The green arrows and dots indicate the (P,T) paths and points where \( \sigma(\omega) \) was measured in this work.](image)

### II. EXPERIMENTAL

The samples of \( \text{Ta}_2\text{NiSe}_5 \) used were single crystals grown with the chemical vapor transport method as reported previously.\(^{24} \) The reflectance spectrum at zero external pressure \( (R_0(\omega)) \) was measured at 0.015-4.5 eV photon energy range on an as-grown, specular surfaces. \( \sigma(\omega) \) was derived from the measured \( R_0(\omega) \) using the standard Kramers-Kronig (KK) analysis.\(^{39} \) Below the measured energy range, \( R_0(\omega) \) was extrapolated by the Hagen-Rubens function or a constant, depending on the data.\(^{39} \) Above the measured range, it was extrapolated by a function of the form \( \omega^{-d} \) \( T \) dependence of \( R_0(\omega) \) were measured below 1.4 eV, and above 1.4 eV the \( R_0(\omega) \) at 295 K was connected. Reflectance spectra at high \( P \) were measured using a diamond anvil cell (DAC)\(^{41} \).
IIa diamond anvils with a 0.8 mm culet diameter and stainless steel gasket were used to seal the sample with KBr as the pressure transmitting medium. An as-grown surface of a sample was directly attached on the culet surface of the diamond anvil, and the reflectance at the sample/diamond interface \( [R_d(\omega)] \) was measured. A gold film was also sealed with the sample as the reference off reflectance. The pressure in the DAC was measured with the ruby fluorescence method \( R_d(\omega) \) at high \( P \) and low \( T \). The measured \( R_d(\omega) \) at high \( P \) and low \( T \) were measured at photon energies between 0.025 and 1.1 eV, using synchrotron radiation as a bright infrared source \( \omega \) at the beamline BL43IR of Spring-8. The measured \( R_d(\omega) \) were connected to the \( R_0(\omega) \) at 295 K and the refractive index of diamond \( \eta \). Then the connected \( R_d(\omega) \) were used to obtain \( \sigma(\omega) \) by a modified KK analysis \( \sigma \). Moro details of the high pressure infrared experiments are reported elsewhere \( \sigma \).

III. RESULTS AND DISCUSSIONS

In the crystal structure of Ta₂NiSe₅, the (-Ta-Se-) and (-Ni-Se-) chains extend along the \( a \) axis in the \( a-c \) layers stacked along the \( b \) axis. Therefore, characteristic optical responses of EI are expected with \( E \parallel a \) polarization where \( E \) is the electric field of the incident light. \( R_0(\omega) \) and \( \sigma(\omega) \) spectra of Ta₂NiSe₅ measured at ambient pressure \( (P=0) \) are indicated in Figs. 3(a) and 3(b), respectively. In the \( E \parallel a \) data, with cooling, \( R_0(\omega) \) exhibits large \( T \) dependences. \( \sigma(\omega) \) develops a clear energy gap with the onset at about 0.17 eV, as indicated by the broken line in Fig. 3(b), and a pronounced peak centered at \( \sim 0.38 \) eV. The sharp spikes below 0.05 eV are due to optical phonons and the periodic oscillations below 0.1 eV are due to interference caused by internal reflections from the rear surface of the sample. In contrast, in the \( E \parallel c \) data, both \( R_0(\omega) \) and \( \sigma(\omega) \) are much lower than those in the \( E \parallel a \) data, and their \( T \) dependence is much smaller. At 8 K, the onset of \( \sigma(\omega) \) appears to be located around 0.3 eV, with only a gradual increase of \( \sigma(\omega) \) above the onset. These results are very similar to previously reported \( P=0 \) data in the literature \( \sigma \). The development of the energy gap and the pronounced peak with \( E \parallel a \) have been interpreted as the result of EI state formation below \( T_c \). The peak at 0.38 eV is an excitonic peak, as already discussed in Introduction, and its origin can be basically understood in terms of a band flattening as illustrated in Fig. 3(c). In a conventional insulator, the optical excitation between the band edges lead to the increase of \( \sigma(\omega) \) above the band gap, as indicated by the green curves in Fig. 3(c). The spectrum in this case is actually similar to that measured with \( E \parallel c \) in Fig. 3(b). In the case of EI, in contrast, the band edges are flattened by excitonic correlation. This results in a larger density of states (DOS) at the band edges, which should cause an enhancement in \( \sigma(\omega) \) as shown by the red curves in Fig. 3(c). The spectrum in this case is very similar to that observed with \( E \parallel a \) in Fig. 3(b). The \( T \) evolution of \( \sigma(\omega) \) in Ta₂NiSe₅ has also been discussed in terms of exciton-phonon Fano effect\( \sigma \) and exciton-superfluid formation \( \sigma \). The shifts of the onset and the transfer of spectral weight in \( \sigma(\omega) \) will be discussed later.

Pressure evolution of \( R_d(\omega) \) and \( \sigma(\omega) \) at 295 K with \( E \parallel a \) is shown in Figs. 4(a)-4(c). Upon applying pressure, both \( R_d(\omega) \) and \( \sigma(\omega) \) below 0.2 eV exhibit large increases. In particular, \( \sigma(\omega) \) below \( \sim 0.2 \) eV, which is reduced by the energy gap at \( P=0 \), rapidly increases with \( P \). In addition, the excitonic peak is broadened and red-shifted with \( P \), and is almost suppressed at 3 GPa and above. This is more clearly seen in Fig. 4(c) where the spectra are vertically offset. The large spectral change
The red shift of the excitonic peak below 23 GPa is almost coincident with the structural transition at $\sigma(\omega)$ below 0.23 eV, as shown in (d)-(f) and (g)-(j). The broadening and red shift of the excitonic peak below $P_s$ probably indicate the weakening of excitonic correlation even within the EI phase below $P_s$. As discussed in Appendix, Raman spectra of Ta$_2$NiSe$_5$ at high $P$ were also measured, using the same DAC and sample condition. The Raman spectra (Fig. 7) exhibit a sudden shift and disappearance of phonon peaks around 3 GPa, which should result from the first order structural transition at $P_s$. This Raman result further supports that the observed spectral changes in $\sigma(\omega)$ indeed result from the structural transition at $P_s$. With increasing $P$ above 3 GPa, $\sigma(\omega)$ further increases and shows metallic characteristics with a rising (Drude) component toward zero energy.

Temperature dependent $R_d(\omega)$ spectra at $P=2.5$, 3.5 and 6.5 GPa are indicated in Figs. 4(d)-(f), and the corresponding $\sigma(\omega)$ spectra in Figs. 4(h)-4(j). First, note that the large $T$ dependences of $R_d(\omega)$ and $\sigma(\omega)$ observed at $P=0$ are progressively reduced with increasing $P$. Accordingly, both the energy gap and excitonic peak at low $T$ are progressively suppressed with $P$. At 2.5 GPa, $\sigma(\omega)$ develops a clear energy gap with cooling [Fig. 4(h)], but the onset of $\sigma(\omega)$ at 8 K is located at 0.062 eV, which is much smaller than that at $P=0$ [Fig. 4(g)]. Namely, a clear energy gap still exists at $P=2.5$ GPa, but its width is significantly reduced from that at $P=0$. At 3.5 GPa, $\sigma(\omega)$ below 0.2 eV is still strongly reduced with cooling, but unlike those at $P=0$ and 2.5 GPa, it is not completely depleted even at 8 K. A rising component toward zero energy is observed at 8 K, which should be a Drude component due to free carriers. The thermal energy $k_BT$, where $k_B$ is the Boltzmann constant, is about 0.7 meV at 8 K, while the tail of the Drude component at 8 K extends to much higher energy, $\sim 50$ meV. Therefore, the electronic state at 3.5 GPa and 8 K is difficult to understand as a semiconductor with thermally excited free carriers. Instead, it should be a semimetal with a band overlap of the order of 50 meV. Accordingly, the energy gap at 3.5 GPa should be a partial one, which is open only in certain portions of the Brillouin zone. At 6.5 GPa, the spectra show only minor $T$ dependences, and $\sigma(\omega)$ below
FIG. 5: Low-energy portion of $\sigma(\omega)$ in $E \parallel a$ polarization at (a) $P=0$ and (b) $P=2.5$ GPa. The broken lines indicate extrapolations to the linear-in-energy portion of the spectra, and the vertical arrows indicate the onset given by the zero crossing. (c) The onset energy in (a) and (b) plotted as a function of temperature ($T$). The broken curves indicate $\Delta(T) = \Delta(0) \left\{ 1 - \left( T/T_c \right)^\alpha \right\}$ with the indicated values of $\alpha$. $\Delta(0)=0.175$ eV and $T_c=328$ K are used for $P=0$, and $\Delta(0)=0.062$ eV and $T_c=170$ K for $P=2.5$ GPa.

0.4 eV is almost unchanged from 295 to 8 K. Clearly, at 6.5 GPa there is no energy gap in Ta$_2$NiSe$_5$ and its electronic structure is quite metallic.

To examine more closely the variations of energy gap with $P$ and $T$, the low-energy portion of $\sigma(\omega)$ at $P=0$ and 2.5 GPa are displayed in Figs. 5(a) and (b), respectively. The broken lines are extrapolations to the linear-in-energy portion in $\sigma(\omega)$. Their zero crossings, marked with the vertical arrows, indicate the onset of $\sigma(\omega)$. Here we regard the onset energy as the gap width $\Delta$, following a previous $\sigma(\omega)$ work on Ta$_2$NiSe$_5$ (Ref. [22]) and other optical studies on strongly correlated electron systems. At $P=0$ [Fig. 5(a)], the extrapolation crosses zero at 295 K and below, but not at 320 K. Namely, the gap in $\sigma(\omega)$ becomes fully open at 295 K and below, which is reasonable since the gap formation starts below $T_c=328$ K and the gap is not well developed yet at 320 K. The $T$ dependence of the onset energy is plotted in Fig. 5(c). The result is similar to that previously reported by Ref. [22], which reported a $T$ dependence of the form $\Delta(T) = \Delta(0) \left\{ 1 - \left( T/T_c \right)^\alpha \right\}$ with $\alpha=2$. For comparison, in Fig. 5(c) we also plot this function with $T_c=328$ K and $\alpha=2$, 2.5, and 3. It is seen that the present data is close to $\alpha=2.5$, but cannot be well described by a single exponent. At 2.5 GPa [Fig. 5(b)], the extrapolation crosses zero at 160 K and below, but not at 200 K. Namely, the gap becomes fully open at 160 K and below, which is much lower than $T_c \approx 290$ K at 2.5 GPa. This is in contrast to the $P=0$ case above, where the gap in $\sigma(\omega)$ is already open at 295 K which is below but still close to $T_c=328$ K. Namely, it seems that the $P$ dependence of the energy gap in $\sigma(\omega)$ is different from that of $T_c$. The $T$ dependence of the onset at 2.5 GPa is also plotted in Fig. 5(c). It is similar to that at $P=0$, but to fit with the form $\Delta(T) = \Delta(0) \left\{ 1 - \left( T/T_c \right)^\alpha \right\}$, $T_c \approx 170$ K and $\alpha \approx 2.5$ are required as shown by the broken curve in Fig. 5(c). Note that the use of this functional form is only phenomenological, and not based on a microscopic model for EI. The much stronger suppression of energy gap by pressure than that of $T_c$ will be discussed again later.

To analyze the spectral weight (SW) transfer in $\sigma(\omega)$ with $P$ and $T$, the effective electron number $N^*(\omega)$ per formula unit (fu) of Ta$_2$NiSe$_5$, expressed as:

$$N^*(\omega) = \frac{n}{m^*} \sigma(\omega) = \frac{2m_0 \pi e^2 N_0}{\hbar} \int_0^\infty \sigma(\omega') d\omega',$$

is plotted in Fig. 6. Here, $n$, $m^*$ and $e$ are the electron density, effective mass in units of the rest mass $m_0$, and the elementary charge. $N_0$ is the number of fu’s per unit volume, which was calculated using the high $P$ crystal structure data. At $P=0$, $N^*(\omega)$ can be regarded as the number of electrons that contribute to $\sigma(\omega)$ between 0 and $\omega$, therefore it directly reflects the SW transfer up to $\omega$. At all $P$ and $T$ in Fig. 6, $N^*(\omega)$ at 1 eV is of the order of 1 fu$^{-1}$, which is reasonable compared with the total DOS within 1 eV from $E_F$ given by band calculations. At $P=0$, $N^*(\omega)$ varies with $T$ over a wide energy range. The $N^*(\omega)$ spectra at different temperatures do not converge even at 1 eV, showing that the electronic structure reconstruction in the EI phase occurs over a wider energy scale than the gap width (0.17 eV) and the excitonic peak energy (0.4 eV). At 2.5 and 3.5 GPa, however, $N^*(\omega)$ varies with $T$ only up to about 0.6 eV, indicating the SW transfer is complete within 0.6 eV. At 6.5 GPa, $N^*(\omega)$ is almost independent of $T$. These results show that both the amount and energy range of the SW transfer are progressively suppressed by $P$, which is closely related with the suppression of energy gap.

As discussed in Introduction, it has been pointed out that the gap formation in Ta$_2$NiSe$_5$ below $P_s$ may be partly due to $e$-$l$ coupling, rather than being solely due to $e$-$h$ (excitonic) correlation. If their relative contribu-

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The text is a detailed explanation of the low-energy portion of the conductivity ($\sigma(\omega)$) in the crystal Ta$_2$NiSe$_5$, focusing on the behavior of the gap width ($\Delta$) as a function of temperature ($T$) and pressure ($P$). The authors compare their data with theoretical predictions and discuss the implications of the observed phenomena on the electronic structure of the material. The text is rich with scientific details and references, illustrating the complex interplay between experimental observations and theoretical models in the study of strongly correlated electron systems.
tions do not change with \( P \), and if both the structural transition at \( T_c \) and the gap opening below \( T_c \) are driven by a common mechanism, then one would naively expect that \( \Delta \) and \( T_c \) should have similar \( P \) dependences. This is in contrast to the present results, in which the reduction of \( \Delta \) by pressure is much greater than that of \( T_c \). This would naturally lead to a stronger suppression of \( \Delta \) than \( T_c \) by pressure, since the \( e-h \) correlation is likely more reduced by pressure than the \( e-l \) coupling as long as the structure does not change. An understanding of these \( P \) dependences based on a specific microscopic model is beyond the scope of the present study. It is hoped that effects of both the \( e-h \) correlation and the \( e-l \) coupling with symmetry breaking-induced hybridization are both included in a microscopic model to understand the pressure evolution of electronic states in Ta\(_2\)NiSe\(_5\).

IV. SUMMARY

\( \sigma(\omega) \) spectra of Ta\(_2\)NiSe\(_5\), a strong candidate for an EI, have been measured at high pressures and at low temperatures. A clear energy gap of about 0.17 eV and a marked excitonic peak at 0.38 eV at \( P=0 \) are suppressed with increasing \( P \), which is especially marked across the structural transition at \( P_s=3 \) GPa. At 2.5 GPa (\(< P_s \)), the gap is still clearly open with a reduced width of 0.062 eV, but at 3.5 GPa (\( > P_s \)), the gap is partially filled, indicating that the ground state above \( P_s \) is semimetallic. At 6.5 GPa, \( \sigma(\omega) \) shows very metallic characteristics with no energy gap. These results have been discussed in terms of a progressive weakening of excitonic correlation with pressure. Also, it is noted that the reduction of energy gap with pressure is much greater than that of \( T_c \). This result may suggest that the relative importance of \( e-h \) correlation and \( e-l \) coupling in the gap formation changes with pressure.

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Appendix: Raman spectra at high pressures

Raman scattering spectra of Ta\(_2\)NiSe\(_5\) measured at high pressures and at 295 K are shown in Fig. 7. The measurement was made under a back scattering geometry on an as-grown sample surface containing the \( ac \) plane. A standard micro-Raman apparatus was used with a 532 nm laser source polarized along the \( a \) axis. High pressures were applied using the same DAC as that used for the \( \sigma(\omega) \) studies, with exactly the same procedure for sample loading. In Fig. 7, the Raman peaks are due to optical phonons. As indicated by the broken lines in Fig. 7, the peak near 100 cm\(^{-1}\) is blue shifted and the peak near 125 cm\(^{-1}\) disappears in the spectra at 3.1 GPa and above. These sudden changes should result from the first-order structural phase transition at \( P_s \) (Fig. 2), where the rippling of the \( ac \) plane along \( c \) axis is reduced above \( P_s \).
FIG. 7: Raman spectra of Ta$_2$NiSe$_5$ measured at high pressures ($P$) and at 295 K. The spectra are vertically offset for clarity. The excitation was made at 532 nm with $E \parallel a$ polarization. The broken lines are guide to the eye, emphasizing the sudden changes at around 3 GPa.

* Electronic address: ho@tokushima-u.ac.jp

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