

## Ultrafast Electronic Band Gap Control in an Excitonic Insulator

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We report on the nonequilibrium dynamics of the electronic structure of the layered semiconductor Ta<sub>2</sub>NiSe<sub>5</sub> investigated by time- and angle-resolved photoelectron spectroscopy. We show that below the critical excitation density of  $F_C = 0.2 \text{ mJ cm}^{-2}$ , the band gap *narrows* transiently, while it is *enhanced* above  $F_C$ . Hartree-Fock calculations reveal that this effect can be explained by the presence of the low-temperature excitonic insulator phase of Ta<sub>2</sub>NiSe<sub>5</sub>, whose order parameter is connected to the gap size. This work demonstrates the ability to manipulate the band gap of Ta<sub>2</sub>NiSe<sub>5</sub> with light on the femtosecond time scale.

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Semiconductor materials are intensively studied due to their technological importance, for instance, in the field of photovoltaics or data processing. The free carriers and charge redistributions generated across the band gap, for instance by light absorption, modify the screening properties and electrostatic (Hartree) energies, which may lead to a shifting of the conduction (CB) and valence band (VB) toward each other and hence a narrowing of the band gap. This process is referred to as band gap renormalization [1–8]. In addition, due to the attractive Coulomb interaction (CIA) between electrons and holes, bound states, called excitons, may form after electrons and holes relax toward the band extrema.

When, for example, in small gap semiconductors with low dielectric constant, the exciton binding energy  $E_B$  exceeds the band gap  $E_g$ , the formation of excitons can occur without any external stimulus, resulting in a total energy gain. A macroscopic condensation of excitons has been predicted to occur in small gap semiconductors and to stabilize in a new ground state, the excitonic insulator (EI) phase [9–11]. This EI phase is characterized by a wider band gap  $E_g + 2\Delta$ , where  $\Delta$  is the energy difference between the parabolic (semiconductor) and flat upper (excitonic insulator) VB maxima [see Fig. 1(b)], which is related to the exciton condensate density and hence to the order parameter of the phase transition [9]. A few materials have been suggested to exhibit a *ground state* EI phase, like Ta<sub>2</sub>NiSe<sub>5</sub> (TNS) [12,13], TiSe<sub>2</sub> [14,15], and TmSe<sub>0.45</sub>Te<sub>0.55</sub> [16,17].

The quasi-one-dimensional TNS shows a second-order phase transition at a critical temperature of  $T_C = 328 \text{ K}$ , accompanied by a structural distortion [12,18]. Above  $T_C$ ,

TNS exhibits a direct band gap at  $\Gamma$ , which increases up to approximately 0.3 eV with decreasing the temperature below  $T_C$  [19–21]. Simultaneously, an anomalous flattening and broadening of the VB occurs, which has been interpreted as a signature of the formation of an EI phase in TNS [12,13,21,22]. Contrary to the indirect band gap material TiSe<sub>2</sub> [23,24], the EI phase of TNS is not coupled to a charge density wave [25,26].

In this work, we study the ultrafast, nonequilibrium dynamics of the occupied electronic structure of TNS using time- and angle-resolved photoelectron spectroscopy (trARPES). We show that, at modest near-infrared (NIR) excitation densities ( $< F_C = 0.2 \text{ mJ cm}^{-2}$ ), the occupied electronic structure exhibits an abrupt shift towards the Fermi energy,  $E_F$ . These dynamics are indicative of a transient *narrowing* of the band gap induced by free-carrier screening of the CIA and Hartree shifts. However, above  $F_C$ , the direct band gap of TNS is transiently *enhanced* on the time scale of 200 fs. As this behavior is opposite to that of ordinary semiconductors, we argue, on the basis of Hartree-Fock calculations, that it is a direct consequence of the transient enhancement of the order parameter of the exciton condensate. We demonstrate that we can either increase or decrease the size of the band gap in TNS by tuning the NIR excitation density, the proof of principle of ultrafast electronic band gap control in a semiconductor.

The electronic structure of TNS and the experimental scheme [27] are illustrated in Fig. 1(a). From the upper VB, two electronic transitions can be optically excited by an ultrashort NIR laser pulse with a photon energy of

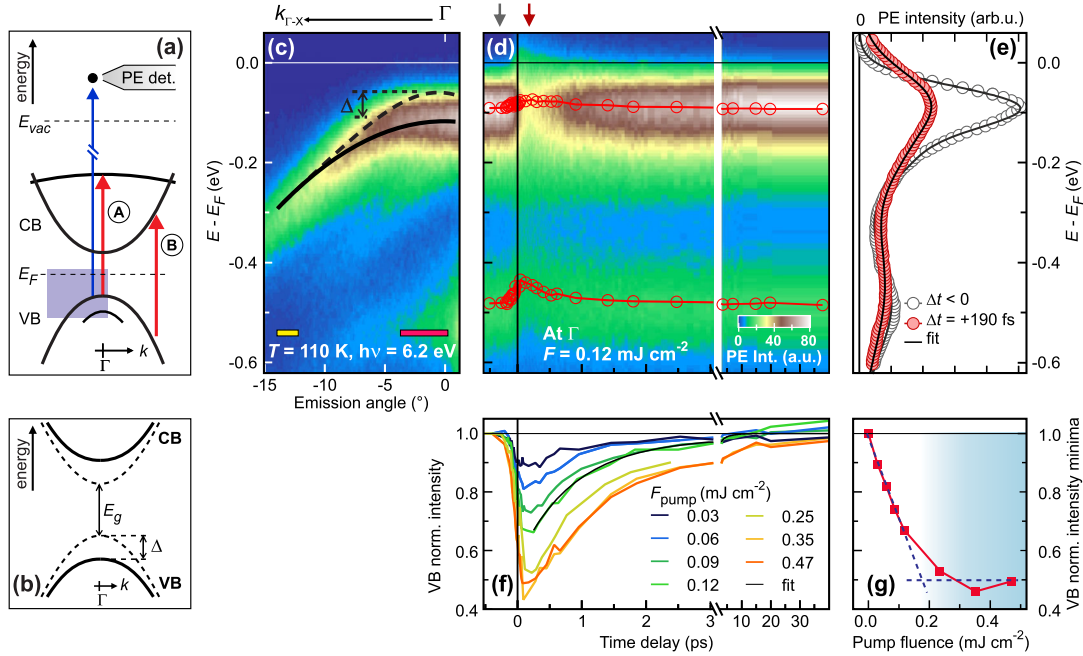


FIG. 1. (a) Schematic band structure of TNS at low temperature (see main text for details). (b) Schematic EI (solid) and semiconductor (dashed) band structures.  $E_g$  is the semiconductor band gap and  $\Delta$  the enhancement of the band gap due to the transition to the EI phase. (c) PE spectrum of the TNS occupied electronic structure around  $\Gamma$  at 110 K. The red and yellow bars indicate the momentum intervals of integration for the extracted EDCs at  $\Gamma$  and at  $k \neq 0$ , respectively. (d) PE intensity at  $\Gamma$  as a function of electron binding energy with respect to  $E_F$  (left axis) and pump-probe time delay (bottom axis) at 110 K. Markers indicate the transient energetic position of the two VBs. (e) EDCs at equilibrium (empty gray circles) and 190 fs after photoexcitation (solid red circles). (f) Transient population of the upper VB at  $\Gamma$ . (g) Minima from (f) as a function of pump fluence: Above  $F_C \approx 0.2 \text{ mJ cm}^{-2}$ , the VB depopulation saturates at  $\sim 50\%$ . Dashed lines are linear fits.

$h\nu_{\text{pump}} = 1.55 \text{ eV}$ : (A) to the flat unoccupied  $d$  band at  $\Gamma$  (i.e.,  $k = 0$ ), and (B) to the lowest CB, but at larger  $k$  vectors. The occupied electronic band structure indicated by the blue-shaded region and its nonequilibrium dynamics are monitored by trARPES using  $h\nu_{\text{probe}} = 6.2 \text{ eV}$ . The energy resolution is 86 meV and the upper limit for the time resolution is 110 fs [27].

At  $T = 110 \text{ K}$  and at equilibrium, i.e., without laser excitation, TNS exhibits, as shown in Fig. 1(c), two VBs with maxima at  $E - E_F \approx -0.5$  and  $-0.1 \text{ eV}$ , respectively, which is consistent with previous angle-resolved photoelectron spectroscopy results [12]. Considering the optical gap of 0.3 eV [19,20], the sample appears to be slightly  $p$  doped [27]. Figure 1(d) shows the temporal evolution of the photoelectron (PE) intensity at  $\Gamma$  and  $T = 110 \text{ K}$  in false color after moderate photoexcitation [29]. The data reveal a rapid response to the optical excitation at  $\Delta t = 0 \text{ fs}$ : a massive suppression of PE intensity within the first 500 fs, and an energy shift of both VBs towards  $E_F$ . This is further illustrated by two energy distribution curves (EDCs), before (empty gray circles) and 190 fs after (solid red circles) NIR photoexcitation, in Fig. 1(e). For a quantitative analysis of the monitored electronic structure dynamics, we fit such EDCs at various pump-probe time delays [27] and obtain the transient amplitude of the spectral function and

energetic position at  $\Gamma$  for each band. Two exemplary fits are shown in Fig. 1(e) (solid lines). The resulting peak positions are depicted in panel (d) (red circles), confirming that both VBs show an abrupt upward shift upon photoexcitation, which is more pronounced for the lower band. It should be noted that the general trend of the peak shift is visible by eye in the normalized data and robust against the choice of fit function [27].

Figure 1(f) displays the temporal evolution of the flat top VB integrated intensity at  $\Gamma$  for different incident pump fluences: the VB is increasingly depopulated by the increasing excitation density and its occupation recovers, on average, within  $870 \pm 210 \text{ fs}$  via interband carrier thermalization, likely assisted by scattering with phonons [30]. The population minima scale linearly with the pump fluence up to a critical value  $F_C \approx 0.2 \text{ mJ cm}^{-2}$  above which the VB depopulation saturates at  $\sim 50\%$ , as shown in Fig. 1(g). It seems likely that this behavior results from an absorption saturation [31]. We also observe this saturation effect in time-resolved reflectivity measurements [32].

In Fig. 2, we focus on the shifts observed for the upper VB at  $k \neq 0$  and the lower VB at  $k = 0$ , which are expected to remain largely unaffected by photoinduced changes to the exciton condensate. Different trace colors correspond to

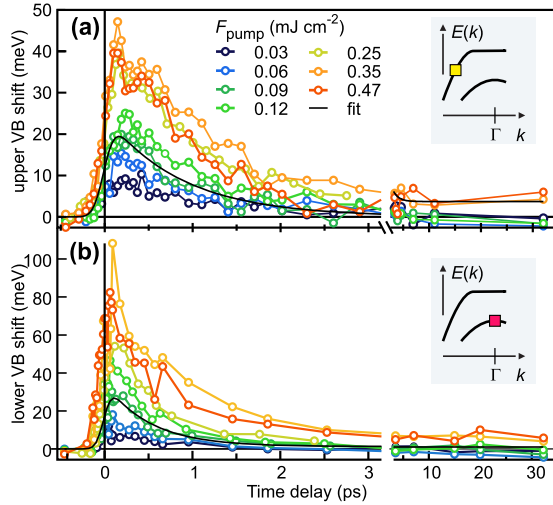


FIG. 2. (a) Shift of the upper VB at  $k \neq 0$  as a function of pump-probe time delay for different excitation densities. (b) Same analysis for the lower VB at  $\Gamma$ . Black lines in (a) and (b) are single exponential fits to the data convolved with the envelope of the laser pulses.

different excitation densities. In both cases, the bands shift abruptly toward lower binding energy, i.e., toward  $E_F$ . We quantify these dynamics by fitting a single exponential decay convoluted with the envelope of the laser pulses [27] as exemplarily shown by the black curves in Fig. 2. At all fluences and for both VBs the fits yield comparable recovery times (of about 1 ps). This is in good agreement with the timescale observed for the population dynamics of the photoinduced carriers at  $\Gamma$ ; see Fig. 1(f). Moreover, the band shift becomes stronger with increasing excitation density up to the same critical fluence  $F_C$  at which the absorption saturation of the flat top VB occurs. Since we do not observe a rigid spectrum shift, nor changes of the low-energy cutoff [27], the measured shifts and saturation cannot be due to surface photovoltage effects. Thus, we interpret the upward shift as the fingerprint of a *transient shrinking* of the band gap following the photoexcitation. Our findings strongly suggest that the abrupt band gap narrowing is a consequence of the photocarriers generated by photoexcitation (A) from the flat top VB.

The photoinduced shift of the flat top VB at  $\Gamma$  is shown in Fig. 3. For  $F < F_C$  (blue to light green traces), the dynamics resemble the trend observed at  $k \neq 0$  [see Fig. 2(a)], although less pronounced at the respective fluences. The same fit function (solid black) as in Fig. 2 is used to quantify these early dynamics. However, for larger fluences (orange and red traces), we observe a shift in the *opposite* direction, delayed by  $\sim 200$  fs, such that the flat top VB maximum transiently lies at *higher* binding energies than its equilibrium position. After approximately 1 ps, this effect relaxes by an upward shift of the band that even “overshoots” the equilibrium position. The delayed downshift of the flat top VB is sufficiently pronounced to

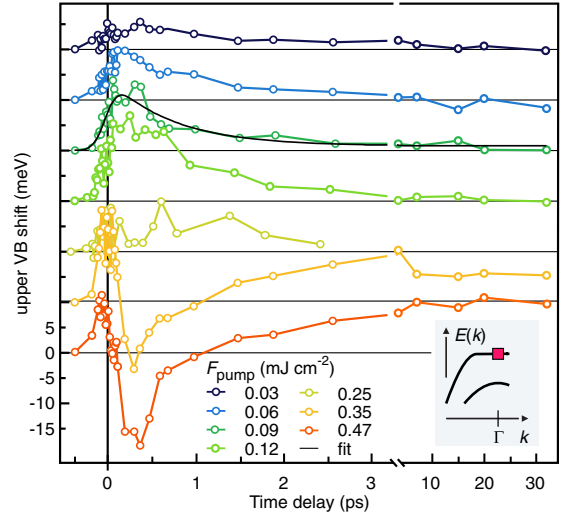


FIG. 3. Shift of the upper VB at  $\Gamma$  as a function of pump-probe time delay for different excitation densities.

be directly seen in the raw PE data [27]. These results demonstrate that the band gap of TNS is transiently *enhanced* by strong photoexcitation.

Figure 4(a) summarizes the observed different VB shifts at three points in the TNS electronic structure as a function of the incident fluence. Clearly, the upward shift occurring in the upper VB at  $k \neq 0$  (yellow) and in the lower VB at  $\Gamma$  (green) is enhanced with increasing excitation density and exhibits a slope change at the same critical fluence  $F_C$  as the VB depopulation threshold shown in Fig. 1(f). The transient shift of the flat top VB at  $\Gamma$  follows, on the contrary, a nonmonotonic curve, revealing that two competing phenomena are at play: While, for  $F < F_C$ , the flat top VB qualitatively follows the trend of the yellow and green curves, a *time-delayed* process counteracts this band gap narrowing for  $F > F_C$ . This is reflected in a shift away from  $E_F$  with respect to the equilibrium position and, consequently, a transient widening of the band gap at  $\Gamma$ .

Both effects are illustrated by the insets in Fig. 4(a). As the upward shift saturates at  $F_C$ , we conclude that it must be connected to the transient free carrier density that is generated by excitation (A) [cf. Fig. 1(a)] where carriers from the flat top VB are transferred to the upper CB, a process that saturates at a population redistribution of  $\sim 50\%$ . The upward shift is, thus, driven by a band gap renormalization that is caused by transiently enhanced free carrier screening, as expected for a semiconductor under optical excitation [1–8]. The extraordinary behavior of the *downward* shift of the flat top VB is analyzed with regard to the presence of an exciton condensate in the following.

In particular, we show that, in the presence of an exciton condensate, nonthermal carrier distributions and an electrostatic shift of the underlying band structure can lead to an enhancement of the condensate density and a corresponding enhancement of the band gap at  $\Gamma$ . To demonstrate this,

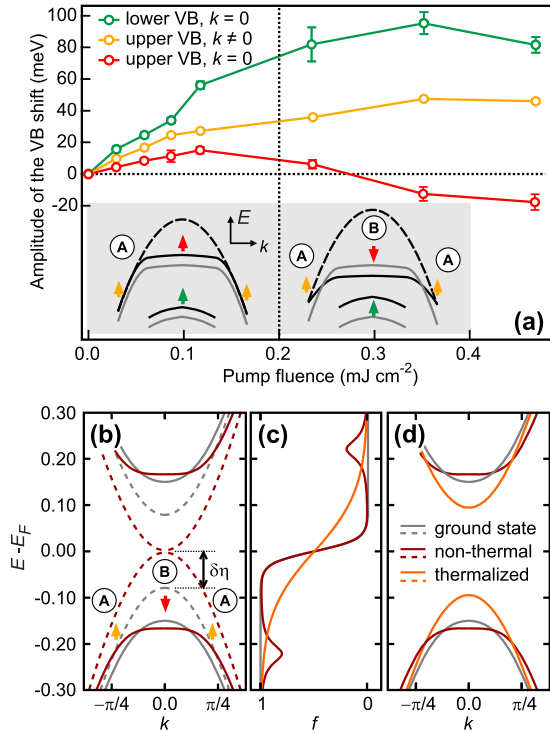


FIG. 4. (a) The fit amplitude of the shift of the lower VB at  $\Gamma$  (green) and of the upper VB at  $k \neq 0$  (yellow) and at  $\Gamma$  (red) as evaluated for a delay of 255 fs [see Fig. 3] as a function of the incident pump fluence. In the inset, the band structure dynamics are schematized for two excitation regimes, below (left) and above (right)  $F_C$ , respectively. (b) Dispersion relation for the ground state (gray) and a nonthermal distribution function (dark red), obtained from the Hartree-Fock calculations. The dashed lines show the bare semiconducting dispersion (with Hartree shift included). (c) Distribution functions corresponding to the dispersion relations in panel (b) and (d). (d) Comparing the dispersions of the thermal state at elevated temperature (orange) with that of the ground state and the photoexcited nonthermal state.

we perform a Hartree-Fock calculation for the simplified case of a one-dimensional two-band system, representing the upper VB and lower CB [33]. We emphasize that the mechanism proposed in the following does not depend on the dimensionality of the system, and its effect would most likely be further enhanced by including higher lying orbitals in the model, due to additional Hartree shifts. The bands are shown in Fig. 4(b), where the dashed (solid) curves represent the noninteracting (interacting) case. We now distinguish two essential effects resulting from the photoexcitation. (i) The formation of a nonthermal carrier distribution, which is *explicitly* included in the calculation as shown in Fig. 4(c) (dark red). This effect leads to an electrostatic reduction of the splitting between the bare semiconductor VB and CB. (ii) The generation of additional free charge carriers that involves also other bands in the experiment and enhances the screening in the semiconductor.

We mimic this effect by an additional reduction of the bare band splitting. The total shift of the bare dispersion is denoted by  $\delta\eta$  in Fig. 4(b). Clearly, we observe that the interplay of (i) and (ii) in the interacting case can lead to an enhancement of the band gap at  $\Gamma$  while the bands shift towards each other at larger  $k$  [compare solid dark red and grey lines in Fig. 4(b)] as observed in the experiment.

The Hartree-Fock calculations suggest that the enhancement of the band gap is related to an increase of the exciton condensate density (and, hence, of the order parameter of the EI phase), which relies on two effects. On the one hand, one finds that for a given value of the CIA the equilibrium condensate density increases if the (noninteracting) conduction and valence bands are shifted closer together, because then excitons are formed from more resonant states. The electrostatic effect of a photoexcited electron density  $n_{\text{ex}}$  (i.e., the Hartree contribution to the interaction) can produce such a shift, and thus tends to enhance the density of condensed pairs [34]. On the other hand, a large  $n_{\text{ex}}$  weakens the condensate, similar to a thermal population of quasiparticle states. The crucial observation is that this potentially detrimental effect of the photoexcited population on the order parameter can be much weaker in a nonthermal state than in a thermal one: for the parameters of Fig. 4(b) and an excitation density of  $n_{\text{ex}} = 0.02$ , we use the nonthermal carrier distribution displayed in panel (c) (dark red). In this situation the exciton condensate is enhanced. The effect is robust for a broad range of nonthermal distribution functions [27], while in the fully thermalized state [solid orange in Fig. 4(d)] the temperature would be above the melting temperature of the condensate. Therefore, as thermalization occurs, we expect a band gap reduction, as indeed observed in the experiments after about 1 ps [cf. Fig. 3].

In conclusion, the present experimental and theoretical work reports and analyzes a transient band gap enhancement in the layered semiconductor  $\text{Ta}_2\text{NiSe}_5$  upon photoexcitation due to the existence of an excitonic insulator phase in this material. We propose that the strengthening of the condensate in the perturbed state is a consequence of the low-energy electronic structure of this material, which provides different channels for resonant excitation and the possibility of significant Hartree shifts and nonthermal quasiparticle distributions. A critical photoexcitation density is observed, which separates regimes in which the band gap can be either increased or decreased. This work not only provides new insights about the *nonequilibrium* properties of excitonic insulators but also proves the possibility of controlling the band gap of such materials by tuning the photoexcitation fluence.

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- [34] We define  $n_{\text{ex}} = n_{\text{ex}}^{\text{nonth}} - n_{\text{ex}}^{\text{ini}}$  as the difference of the integrated weight for the occupied density of states above the Fermi level between the nonthermal  $n_{\text{ex}}^{\text{nonth}}$  and the initial state  $n_{\text{ex}}^{\text{ini}}$ .