Transient band gap enhancement of the photoexcited excitonic insulator phase in quasi-1D Ta_2NiSe_5

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Electronic correlations can lead to exotic electronic properties that a single-particle theory cannot explain. Among these is the strong electron-hole interaction in small gap semiconductors and semimetals, which may lead to a spontaneous formation of excitons resulting in a phase transition (PT) to an excitonic insulator (EI) [1]. The ternary chalcogenide Ta_2NiSe_5 (TNS) has been proposed as a possible candidate for such semiconductor-to-EI transition occurring at $T_c \approx 328$ K in combination with a structural change from orthorhombic to monoclinic symmetry [2]. In order to unveil how the monoclinic/EI phase stabilizes in TNS, we investigate the photoinduced dynamics by means of time-resolved photoemission and optical spectroscopy and we interpret the complex relaxation processes in the framework of strong electron-hole correlations in EI systems.

Time-resolved photoemission in the monoclinic/EI phase shows a strong depletion of the valence band as a function of the excitation density, until a saturation of the PE intensity occurs above a critical fluence F_{sat}. This effect is reflected in a saturation threshold of the overall transient optical response in the near-IR, resonantly probing the energy gap of TNS. A coherent phonon at 4 THz, which is characteristic of the monoclinic/EI phase, persists above $F_{sat,}$ indicative of a hindered photoinduced phase transition. Excitation density dependence at different temperatures in the EI phase shows that F_{sat} decreases as the sample temperature approaches T_c. This effect is interpreted as an enhanced resonance condition for the pump photon energy, which is consistent with the thermally-driven shifting of the valence band maximum towards lower binding energy observed by ARPES [3].

Time-resolved photoemission in the monoclinic/EI phase reveals a band gap shrinking below F_{sat}, which we assign to free-carrier-enhanced screening of Coulomb interaction. We note that this process persists away from Γ point of the Brillouin zone even above F_{sat}. However, at Γ and for strong excitation above F_{sat}, these dynamics compete with a delayed band gap widening that we attribute to further localization of the photoexcited excitons due to repulsive interaction, as expected in a weakly interacting Bose gas. After ~ 1.5 ps, excess energy is transferred to the lattice and the band gap shrinking is driven quasi thermally.

Thus, time-resolved photoemission of the occupied band structure proves that the saturation in the optical response is due to a depopulation of the valence band with consequent photobleaching of pump pulse absorption that precludes the possibility of a photoinduced gap closing in TNS. Furthermore, under strong excitation the band structure at Γ is likely affected by dynamical change of the exciton binding energy that compete with free-carrier screening of electron-hole Coulomb interaction, such that the excitonic band gap can be transiently enhanced. This supports the key role of exciton correlation as origin of the EI phase in TNS.

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