

Collective modes and Raman response in Ta₂NiSe₅Banhi Chatterjee¹,[✉] Jernej Mravlje^{1,2},[✉] and Denis Golež^{1,2}¹*Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*²*Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*

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We explore the collective response in an excitonic insulator phase in Ta₂NiSe₅ using a semirealistic model including relevant lattice and electronic instabilities. We calculate order-parameter susceptibility and Raman response within a time-dependent Hartree-Fock approach. Contrary to the standard expectations, the amplitude mode frequency does not coincide with the single-particle gap but has a higher frequency. We find a phase mode that is massive because the excitonic condensation breaks a discrete symmetry only and that becomes heavier as the electron-lattice coupling is increased. These features are expected to apply to generic realistic excitonic insulators. We discuss scenarios under which the phase mode does not appear as a sharp in-gap resonance.

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Introduction. In semimetals and narrow-band semiconductors, the electron-hole attraction can lead to an excitonic insulator (EI) phase [1–3], characterized by excitonic condensation that hybridizes conduction and valence bands. The EI transition has similarities with the superconducting one but with an order parameter that is not charged. Textbook EIs involve the spontaneous breaking of U(1) symmetry associated with separate conservation of charge in valence/conduction orbitals and are realized in heterostructure/bilayer systems [4–9]. In bulk materials, the charge in orbital subspace is not conserved even prior to excitonic condensation and determining the broken symmetry is more nuanced [10]. Prominent candidates for bulk EI are 1T-TiSe₂ [11–13], Sb nanoflakes [14], Ta₂Pd₃Te₅ [15–18], and Ta₂NiSe₅ [19].

Ta₂NiSe₅ exhibits a resistivity anomaly at $T_c = 325$ K, where the material undergoes a transition from a semimetal to a small-gap $\Delta \sim 0.15$ eV semiconductor [20–23]. Simultaneously, a structural transition occurs from a high-temperature orthorhombic phase to a low-temperature monoclinic phase. The structural change is small with the monoclinic angle deviating from the high-symmetry configuration by a mere 0.7° [24].

Photoemission studies observed a flat valence band and argued that it arises from a gap opening due to excitonic condensation [19,25,26]. Additionally, short timescales and peculiar fluence dependencies observed in pump-probe time-resolved studies [27–33] as well as the vanishing of thermopower at low temperatures [34] have been interpreted in terms of electronic degrees of freedom and argued to point to an excitonic ground state. A realistic theoretical investigation [10] identified excitonic order parameter ϕ with a B_{2g} pattern of hybridization between Ni- and Ta-based orbitals, breaking

discrete (mirror) symmetries of the orthorhombic phase. This study aligns with earlier considerations of excitonic phases obtained using simpler models [35,36].

Another line of research highlights structural aspects [37–39] and argues the transition is due to freezing of an unstable B_{2g} mode corresponding to a structural order parameter X . Some pump-probe angle-resolved photoemission spectroscopy (ARPES) studies [40] argue against the presence of excitonic effects. Importantly, in equilibrium, ϕ and X have the same symmetry. A nonvanishing X activates real electronic hybridizations of the same kind as ϕ . This implies that the monoclinic distortion can explain the flatness of the bands or the vanishing of thermopower [34], challenging purely excitonic scenarios.

Electron-phonon coupling plays an important role [22,23,28,40–42]. Raman spectroscopy [43–46] reveals a strongly asymmetric shape of the B_{2g} mode, with some studies suggesting softening [43], but all observing significant broadening of this phonon mode and hybridization with a strong electronic background as the temperature is lowered toward T_c . This broadening suggests that the coupling between electronic and lattice degrees of freedom above T_c will manifest in some manner also below T_c . Several recent studies have taken a balanced perspective, emphasizing the relevance of both excitonic and structural aspects [47–49]. A very recent nonequilibrium Raman study [48] found a nonequilibrium state without a gap but with monoclinic distortion.

A crucial but so far poorly addressed question is that of the collective response [50,51]. In this paper, we evaluate the excitonic order parameter susceptibility and Raman response in a minimal six-band model [10] that we extend by coupling to the relevant phonon mode with B_{2g} symmetry. We find several surprising features. The amplitude mode is not pinned to the lower edge of the single-particle gap but has a larger energy. We find a strong phase mode at a finite frequency that stiffens further when the electron-phonon coupling is introduced. While our study focuses on Ta₂NiSe₅, its findings

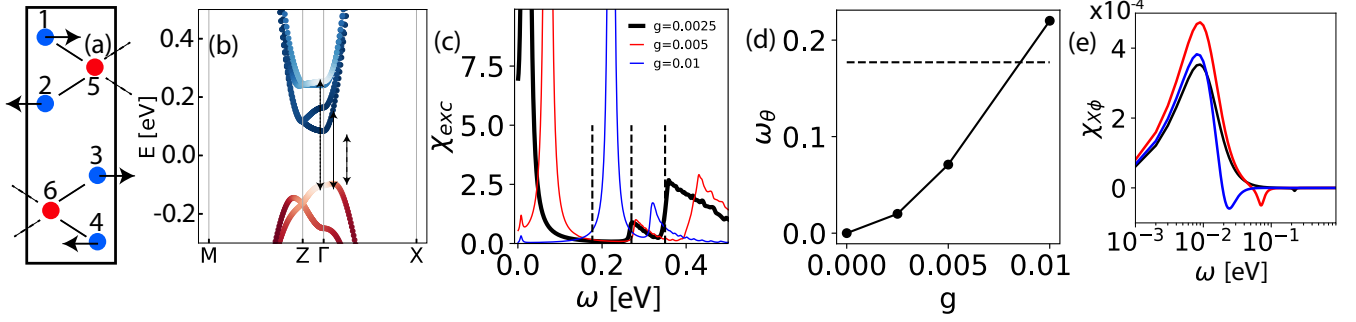


FIG. 1. (a) Unit cell with Ta (blue) and Ni (red) atoms. Arrows indicate B_{2g} distortion. The full (dashed) lines mark the positive (negative) value of the hybridization between Ta and Ni orbitals. (b) Band structure in the symmetry-broken state where blue (red) shading encodes the weight of Ta (Ni) orbitals. (c) Excitonic susceptibility χ_{exc} for a kick coupling to order parameter amplitude for different electron-phonon interactions g . The vertical dashed lines indicate energies marked in (b). (d) The mass of the phase mode ω_θ versus g . The dashed line marks the edge of the single-particle continuum. (e) Cross-correlation function between excitonic and lattice order parameters for several g from (c). We have fixed the single-particle gap for all examples by adjusting the nearest-neighbor electronic interactions; see SM [52] for details. Parameters: $\beta = 100$, damping $\eta = 0.003$.

concerning collective behavior in the presence of multiple bands, order parameter with symmetry lower than U(1), and coupling to phonon modes apply to other EI candidates, e.g., $\text{Ta}_2\text{Pd}_3\text{Te}_5$ [15–18].

Model and methods. Ta_2NiSe_5 is a layered compound. Within each layer in the ac plane, one encounters Ta-Ni-Ta chains that form a quasi-one-dimensional structure. We follow Ref. [10] by retaining the low-energy bands spanned by one Wannier orbital per each Ta and Ni atom and using the unit cell depicted in Fig. 1(a). In the orthorhombic phase, the material has an inversion $\mathcal{I}$ and four reflection symmetries for planes parallel and perpendicular to the Ta-Ni-Ta chain ($\sigma_{\parallel,\perp}^{A/B}$), and the latter are broken as we enter the monoclinic phase [10,38].

The kinetic part of the Hamiltonian is represented in the tight-binding form

$$\hat{H}_{\text{kin}} = \sum_{\mathbf{R}\delta} \hat{\Psi}_{\mathbf{R}+\delta\sigma}^\dagger T(\delta) \hat{\Psi}_{\mathbf{R}\sigma}, \quad (1)$$

where the sum is taken over all unit cells $\mathbf{R}$ and neighboring cells δ as parametrized by the matrix of tight-binding hopping elements T , see SM [52] for details. We have introduced the spinor $\hat{\Psi}_{\mathbf{R}\sigma} = \{\hat{c}_{1\sigma\mathbf{R}}, \dots, \hat{c}_{6\sigma\mathbf{R}}\}$ and $\hat{c}_{i\sigma\mathbf{R}}$ is the annihilation operator in unit cell $\mathbf{R}$, orbital i and spin σ ; see Fig. 1(a). The electronic interaction energy is given by

$$\begin{aligned} \hat{H}_{\text{int}} = & U \sum_{\mathbf{R}i} \hat{n}_{i\uparrow\mathbf{R}} \hat{n}_{i\downarrow\mathbf{R}} + V \sum_{\substack{i \in \{1,2\} \delta_i \\ \mathbf{R}\sigma\sigma'}} \hat{n}_{i\sigma\mathbf{R}+\delta_i} \hat{n}_{5\sigma'\mathbf{R}} \\ & + V \sum_{\substack{i \in \{3,4\} \delta_i \\ \mathbf{R}\sigma\sigma'}} \hat{n}_{i\sigma\mathbf{R}+\delta_i} \hat{n}_{6\sigma'\mathbf{R}}, \end{aligned} \quad (2)$$

where the first term represents the on-site Hubbard interaction for all atoms. The second and third terms are the nearest-neighbor interactions, with δ_i indicating nearest neighbors.

The electronic order parameters measure the amount of breaking of the four reflection symmetries, namely, $\sigma_{\parallel,\perp}^{A/B}$. It is convenient to define operators corresponding to the electronic order parameter as $\hat{\phi}_{\mathbf{R}} = \{\hat{\phi}_{15\mathbf{R}}, \hat{\phi}_{25\mathbf{R}}, \hat{\phi}_{36\mathbf{R}}, \hat{\phi}_{46\mathbf{R}}\}$, where $\hat{\phi}_{ij\mathbf{R}} = \sum_{\sigma} \hat{c}_{i\sigma\mathbf{R}}^\dagger \hat{c}_{j\sigma\mathbf{R}} + \hat{c}_{i\sigma\mathbf{R}\pm a}^\dagger \hat{c}_{j\sigma\mathbf{R}}$ and a is the

unit-cell displacement in the x direction. We choose $+$ ($-$) for $\{ij\} = 15, 25$ ($36, 46$), respectively. The electronic order parameter is then defined as the thermal expectation value of the operator $\phi_{\mathbf{R}} = \langle \hat{\phi}_{\mathbf{R}} \rangle$ and, in equilibrium, all its components are real. In the following, we will focus on the experimentally relevant phase where expectation values have the same magnitude and their sign alternates as $\phi_{\mathbf{R}} = \phi_0 \{1, -1, -1, 1\}$ breaking $\sigma_{\parallel,\perp}^{A/B}$ symmetries consistent with the monoclinic distortion.

A key issue, often overlooked in previous realistic simulations of the material, is an equal footing description of the competition between lattice and excitonic symmetry breaking. We will consider the coupling between electrons and lattice distortion corresponding to optical shearing mode with a frequency of 2 THz, see Fig. 1(a), modeled as an Einstein phonon $\hat{H}_{\text{ph}} = \frac{\omega_0}{2} \sum_{\mathbf{R}} (\hat{X}_{\mathbf{R}}^2 + \hat{\Pi}_{\mathbf{R}}^2)$, where $\hat{X}_{\mathbf{R}}$ ($\hat{\Pi}_{\mathbf{R}}$) are the lattice distortions (momentum) in the unit cell $\mathbf{R}$. The order parameter transforms according to the B_{2g} irreducible representation of the orthorhombic structure symmetry group and therefore it may linearly couple to a B_{2g} lattice mode $X_{\mathbf{R}}$. A similar conclusion can be obtained by considering a Peirls-type coupling, where larger (smaller) nuclei distance leads to a smaller (larger) absolute value of the hopping matrix element, see SM [52]. For the distortion marked in Fig. 1(a), it is easy to show that the electron-lattice coupling reduces to

$$\hat{H}_{\text{el-ph}} = g \sum_{\mathbf{R}} \hat{X}_{\mathbf{R}} (\hat{\phi}_{15\mathbf{R}} - \hat{\phi}_{25\mathbf{R}} - \hat{\phi}_{36\mathbf{R}} + \hat{\phi}_{46\mathbf{R}}), \quad (3)$$

where we will treat the electron-phonon interaction g as a free parameter. The system will lower its energy by forming an intertwined lattice and electronic order in the ground state [36,53].

We solve the problem within the Hartree-Fock theory for the electron-electron and electron-lattice interaction within the symmetry-broken state and assume a homogenous solution ($\phi = \phi_{\mathbf{R}}$ and $X = X_{\mathbf{R}}$). We focus on the dynamical two-particle susceptibilities $\chi_{AB}(\omega)$ and consider three types of susceptibilities. The excitonic susceptibility χ_{exc} is given by the order parameter autocorrelation function with $\hat{A} =$

$\hat{B} = \hat{\phi}_{15} - \hat{\phi}_{25} - \hat{\phi}_{36} + \hat{\phi}_{46} + \text{H.c.}$ and measure the collective response of the excitonic order for a kick coupling to its amplitude direction (real part of order parameter; out of equilibrium, ϕ becomes complex valued). Furthermore, we can define the mixed lattice-exciton correlation function $\chi_{X\phi}$ with $\hat{A} = \hat{\phi}_{15} - \hat{\phi}_{25} - \hat{\phi}_{36} + \hat{\phi}_{46} + \text{H.c.}$ and $\hat{B} = \hat{X}$, which is a measure of correlations between the excitonic and lattice excitations. Finally, the electronic Raman response is determined using

$$\hat{A} = \hat{B} = \sum_{\mathbf{R}\sigma ij} T_{ij}(\mathbf{R})(\mathbf{R}_{ij} \cdot \mathbf{e}_1)(\mathbf{R}_{ij} \cdot \mathbf{e}_2) e^{-i\mathbf{R} \cdot \mathbf{k}} \hat{c}_{i\sigma\mathbf{k}}^\dagger \hat{c}_{j\sigma\mathbf{k}}, \quad (4)$$

where $\mathbf{R}_{ij} = \mathbf{R} + \mathbf{r}_i - \mathbf{r}_j$ with $\mathbf{r}_i$ being the position of atomic orbital i in the unit cell. The polarization of the Raman pulse is set by $\mathbf{e}_i$, and we will focus on the ac channel, namely, $\mathbf{e}_1 = \{1, 0\}$ and $\mathbf{e}_2 = \{0, 1\}$; see SM [52] for details. We take $k_B = \hbar = 1$ and use eV as the unit of energy when not explicitly written otherwise. We further confirmed that the inclusion of the fluctuation effects beyond Hartree-Fock leads to only quantitative corrections, while the qualitative physics discussed in the following remains the same, see SM [52].

Results. We set the intraband interaction $U = 2.5\text{eV}$ and the interband interaction $V = 0.785\text{eV}$ and consider the system at a low temperature with $\beta = 1/T = 100$ at which the system is in the excitonic phase; see also Ref. [10]. Figure 1(b) depicts the corresponding band structure and the excitonic hybridization opens a gap of 160 meV, which is close to the experimental values [21,22,26]. The orbital character of the bands is depicted with color. One sees a strong admixture of Ta character in the valence bands close to the Γ point. Remarkably, the excitonic hybridization does not strongly affect the lowest pair of conduction bands. Rather, it strongly affects the two higher conduction bands, namely, only an odd combination of Ta chains couples to excitonic order parameter and the effect of this hybridization is lowering of the valence band and raising of the odd conduction bands, whereas the even conduction bands are nonbonding with respect to exciton and are unaffected; see SM [52] for more details.

This observation has important consequences for the collective response. In Fig. 1(c), we depict excitonic susceptibility $\chi_{\text{exc}}(\omega)$ for different electron-lattice couplings g , where we adjusted the nearest-neighbor electronic interaction V to fix the single-particle gap. For the weakest coupling $g = 0.0025$, there are three dominant features: Around $\omega \approx 350$ meV, there is a strong shoulder whose energy matches the energy difference between highly hybridized bands marked in Fig. 1(b) by a long arrow, a weaker shoulder at 270 meV, and at very low energies $\omega \approx 20$ meV a dominant peak. By comparison with the real-time evolution of the order parameter, we attribute the high energy peak to the amplitude mode and the low energy resonance to the phase mode [54]. However, due to the broken $U(1)$ symmetry, the two modes are coupled [55]. The weak shoulder is not associated with the collective response. Its energy matches the transition between the top valence band and flat region on the second conducting band close to the Γ point (van Hove singularity).

Four interesting observations distinguish the realistic EI from the ideal $U(1)$ symmetry-breaking one. First, the phase mode that is massless in the ideal EI acquires a finite mass ω_θ due to interchain hoppings that violate $U(1)$ symmetry [10]. Its mass grows further with the electron-lattice coupling, see Fig. 1(d), and can exceed the single-particle gap. While it is difficult to determine the exact frequency of the massive phase mode due to the uncertainties in the microscopic parameters, we can estimate its lower boundary from the response in the purely electronic case, which gives a value of order tens of the meV. Note that the origin of the finite mass is distinct from the case of superconductors, where the phase mode acquires a large mass due to the Anderson-Higgs mechanism. Second, the amplitude mode is seen to oscillate with a frequency of 350 meV, which is larger than the single-particle gap (in contrast to the standard case where one finds the amplitude mode pinned to the single-particle gap [54]). This comes from the fact that the lowest conduction band is almost unaffected by the excitonic hybridization. Third, the phase and the amplitude mode are coupled, which is different than in ideal $U(1)$ symmetric case [55] or in superconductors [56]. The response occurs in both modes following a kick coupling to the amplitude of the electronic order. Finally, for stronger electron-lattice coupled systems, e.g., $g \geq 0.005$, there is also a visible resonance at the phonon energy $\omega_0 = 8$ meV; see Fig. 1(c).

One can directly study the exciton-lattice coupling by considering the corresponding cross-correlation $\chi_{X\phi}$; see Fig. 1(e). For all examples studied, there is a strong correlation between high-energy excitonic and low-energy lattice modes despite an order of magnitude different energy scales. Any distortion of the electronic order at high energies would strongly distort the lattice mode. We believe this is a natural explanation of recent optical pump-THz probe experiments on Ta_2NiSe_5 [51,57] observing a strong THz amplification of reflectivity.

Phenomenologically, we can understand the above response within the time-dependent Landau theory for lattice coupled with the real part of the electronic order parameter [58],

$$F[\phi] = m|\dot{\phi}|^2 + a|\phi|^2 + b|\phi|^4 - c(g)X|\phi| \cos(\theta) - d \cos \theta + F_{\text{ph}},$$

where we have written the order parameter with amplitude and phase $\phi = |\phi|e^{-i\theta}$ (θ may differ from 0 in time-dependent solution), a, b, c, d, m are phenomenological parameters, and F_{ph} is the contribution of the free energy coming from the lattice. The coupling between the order parameters is described by $c(g)$, which monotonously increases with electron-lattice coupling strength g , see Ref. [58] for explicit relations, and d describes breaking of the $U(1)$ symmetry on the purely electronic level [10]. We see that the stronger the electron-lattice coupling, the larger the lattice distortion becomes, see also Fig. 2(d), and the more the phase mode stiffens. Furthermore, the distortion of the excitonic amplitude mode acts as a force term on the lattice distortion, explaining the cross-correlation across large energy scales.

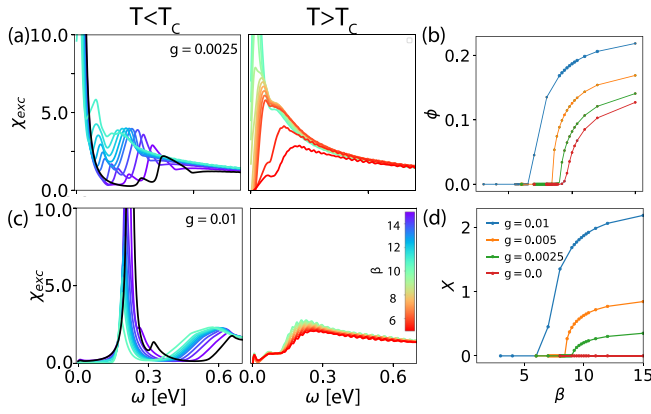


FIG. 2. (a), (c) The temperature dependence of the excitonic susceptibility χ_{exc} below (left) and above T_c (right) for weak $g = 0.0025$ (a) and strong $g = 0.01$ electron-lattice coupling (c). (b), (d) Temperature dependence of the electronic order parameter ϕ and lattice distortion X (in the units of X_0), respectively. Damping parameter $\eta = 0.01$.

Further intuition is obtained by studying the excitonic susceptibility shown in Fig. 2. Panels (b) and (d) show the temperature dependence of ϕ and X , respectively. Due to the linear coupling, the two quantities vanish at the same T_c . The dimensionless lattice distortion X is measured in $X_0 = \sqrt{\hbar/(2M\omega_0)} = 0.07\text{\AA}$ (setting M to reduced mass of Ta and Ni ions) and by comparison with experimental distortion of $X_{0,\text{exp}} = 0.04\text{\AA}$ one infers electron-lattice coupling is small, e.g., $g = 0.0025$. For such g , the excitonic susceptibility above T_c shows a clear softening of the excitonic response, see Fig. 2(a), and for $T < T_c$ there is a gradual hardening of the amplitude and phase mode. On the contrary, for large $g = 0.01$ [Fig. 2(c)], the excitonic susceptibility does not show any softening above critical temperature $T > T_c$, and as we lower the temperature both the phase and the amplitude modes harden and the former gets substantially sharper. According to Ref. [46], the experimental Raman data is consistent with the former scenario.

We have evaluated the Raman response within the Peierls approximation; see SM [52] for details. The data shown in Fig. 3 exhibit similar behavior as the order parameter susceptibility with a strong and rather broad amplitude mode above the single-particle gap, which gradually stiffens with decreasing temperatures and the phase mode, whose mass

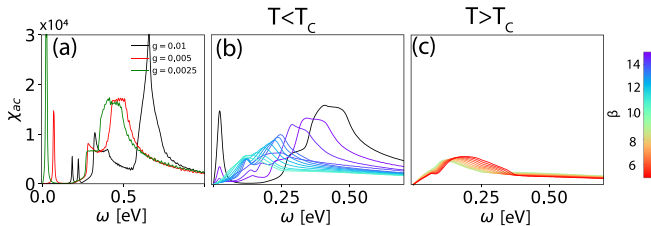


FIG. 3. (a) Raman spectrum in the B_{2g} channel χ_{ac} for several electron-lattice interactions g in the low-temperature state at $\beta = 100$. Temperature dependence of the Raman spectrum for $g = 0.0025$ below (b) and above T_c (c).

grows with increasing g . Like in the excitonic susceptibility, one sees a softening of the electronic response as we approach T_c from above and the hardening of the phase and amplitude mode as one approaches the ground state. The Raman scattering operator in the ac channel contains terms that are proportional to the order parameter operator, hence that channel probes fluctuations of the order parameter, which explains similarity between the two response functions. The finding of amplitude mode above the single-particle gap is consistent with Raman experiments that do find a peak at about 400 meV [45]. The agreement of the amplitude mode energy and lattice displacement with experiments gives confidence that the electron-lattice interaction is in a reasonable parameter range. Despite the amplitude mode being a rather broad resonance due to coupling with the continuum, we can still observe several coherent oscillations in the real-time signal (not shown) and its strong sensitivity on the buildup of the order; see Fig. 2. Our identification of the amplitude mode energy opens a promising perspective for probing it via nonlinear spectroscopy [59], in analogy to superconductors [60–63].

On the other hand, there is no sharp phase mode in the experimental data [44,45]. How can one reconcile the experimental data with our results? The first observation is that we use the dissipationless Hartree-Fock approximation. Including the electron-lattice scattering should lead to a finite lifetime of the phase mode. As their coupling is nonlinear, estimating its lifetime requires simulation with the inclusion of fluctuations effects. We performed a minimal calculation, including the lowest order electron-electron and electron-lattice fluctuations, to test this scenario. At short times accessible to our simulations (covering few oscillations only) the decay of the phase mode remained weak; see SM [52]. In Raman experiments, there is a broad excitonic continuum [45] with a gap of ≈ 20 meV, which could be a natural candidate for the overdamped phase mode. The second option is that the electron-lattice coupling is strong enough that the phase mode enters the single-particle continuum. Once again, the inclusion of scattering would strongly reduce its lifetime. This scenario is less probable, as it is inconsistent with the experimental observation of electronic softening across the critical temperature and estimations of the lattice distortion. The last and most exotic option is that the phase mode acquires a larger mass due to long-range quadrupole-quadrupole interaction. Because the quadrupole interaction falls with the fifth power of the distance, we expect that such an effect is small, but should be nevertheless investigated in future.

In conclusion, we calculated collective and Raman responses in Ta_2NiSe_5 . In contrast to the standard excitonic insulator response, we have identified the amplitude mode living well above the single-particle gap and matched the Raman spectroscopy data, opening the possibility of Higgs spectroscopy in this material. We found a massive phase mode with a mass that rapidly grows with the strength of the electron-lattice interaction. We expect such behavior to be generic in material realizations where, in general, the excitonic condensation breaks a discrete symmetry only. Our results can therefore be readily applied to other material candidates, e.g., $1T\text{-TiSe}_2$ [11–13] and $\text{Ta}_2\text{Pd}_3\text{Te}_5$ [15–18]. In the

experiments, the phase mode is not observed (or at least is not a clear resonance) and we propose different scenarios for the discrepancy, which remains an important problem for future research and should be resolved for the excitonic picture to be viable.

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