Failed excitonic quantum phase transition in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$

Pavel A. Volkov,$^{1,}$* Mai Ye,$^{1,}$† Himanshu Lohani,$^2$ Irena Feldman,$^2$ Amit Kanigel,$^2$ and Girsh Blumberg$^{1,3,}$†

$^1$Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854, USA
$^2$Department of Physics, Technion - Israel Institute of Technology, Haifa 32000, Israel
$^3$National Institute of Chemical Physics and Biophysics, 12618 Tallinn, Estonia

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We study the electronic phase diagram of the excitonic insulator candidates Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$\[x=0, \ldots, 1]\ using Raman spectroscopy. Critical excitonic fluctuations are observed, that diminish with \(x\) and ultimately shift to high energies, characteristic of a quantum phase transition. Nonetheless, a symmetry-breaking transition at finite temperatures is detected for all \(x\), exposing a cooperating lattice instability that takes over for large \(x\). Our study reveals a failed excitonic quantum phase transition, masked by a preemptive structural order.

Introduction: One of the fascinating manifestations of interactions between electrons in solids is the emergence of electronic orders. The fluctuations close to the respective quantum critical points are also believed to be the drivers of a wealth of yet unexplained behaviors, including strange metallicity and high-\(T^\text{c}\) superconductivity\[1–4\]. In many cases (such as, e.g., nematic\[5, 6\] or density-wave\[7, 8\] orders) electronic order breaks the symmetries of the crystalline lattice and the corresponding transitions can be, symmetry-wise, identical to structural ones. This raises the question of the role of the interplay between electronic and lattice degrees of freedom in the ordering. Even in cases where the lattice only weakly responds to the transition\[9, 10\], the critical temperatures\[11, 12\] and quantum critical properties\[13\] can be strongly modified. Moreover, in a number of cases the origin of the order is still under debate\[14–16\], as the lattice may develop an instability of its own.

The electronic-lattice dichotomy has recently come to the fore in studies of Ta$_2$NiSe$_5$\[17–19\] - one of the few candidate materials for the excitonic insulator (EI) phase\[16, 20–24\]. EI results from a proliferation of excitons driven by Coulomb attraction between electrons and holes in a semiconductor or a semimetal\[25–29\]. Ta$_2$NiSe$_5$ exhibits a phase transition at \(T_c = 328\text{ K}\); while the pronounced changes in band structure\[18\], transport\[19\] and optical\[30\] properties are consistent with the ones expected for an EI, they allow an alternative interpretation in terms of a purely structural phase transition\[31–33\]. Indeed, EI state in Ta$_2$NiSe$_5$ is expected to break mirror symmetries of the lattice due to the distinct symmetries of the electron and hole states forming the exciton\[34\], similar to a structural transition\[31\]. Intriguingly, substitution of Se with S has been shown to suppress \(T_c\) in transport experiments to zero\[19\], suggesting a possible quantum phase transition (QPT) at \(x = x_c\) in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. Increasing \(x\) enhances the band gap in the electronic structure\[35\], which is known to suppress the EI\[27, 28\], consistent with an EI QPT. On the other hand, the lattice degrees of freedom also evolve with \(x\) making it imperative to separately assess the roles of electronic and lattice degrees of freedom throughout the phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. A promising technique to address this challenge is to probe the critical dynamics with polarization-resolved Raman scattering\[36–38\], that also allows to detect symmetry breaking independently\[39–41\].

In this Letter, we use polarization-resolved Raman scattering to study the dynamics of electronic excitations throughout the phase diagram of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. We reveal the presence of low-energy excitonic modes that soften on cooling towards \(T_c(x)\) and deduce an excitonic transition temperature \(T_{cx}(x) < T_c(x)\). On increasing sulfur content \(x\), \(T_{cx}(x)\) is suppressed to negative values and for \(x = 1\) low-energy excitons are no longer observed, as expected for an excitonic insulator quantum phase transition. However, the actual \(T_c(x)\) remains finite for all \(x\), implying the presence of a cooperating lattice instability, obscuring the suppression of the excitonic order. The study thus reveals a “failed” excitonic quantum phase transition in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ masked by a preemptive structural order, that takes over as the electronic instability is suppressed.

Experimental: We performed Raman scattering experiments on four Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ samples with varying Se/S content grown using the chemical vapor transport (CVT) method\[42\]. The measurements were performed in a quasi-back-scattering geometry on samples cleaved to expose the ac crystallographic plane with the 647 nm line from a Kr$^+$ ion laser excitation, details presented in Ref.\[42\]. The selection rules in the high-temperature orthorhombic (point group \(D_{2h}\)) phase imply that ac polarization geometry probes excitations with \(B_{2g}\) symmetry (same as that of the order parameter), while \(aa\) geometry probes the fully symmetric \(A_g\) ones\[36–38, 42\]. Below \(T_c\), the \(B_{2g}\) symmetry is reduced to \(C_{2h}\) and the two irreducible representations merge, such that excitations from \(ac\) geometry above \(T_c\) may appear in \(aa\) geometry and vice versa. Their appearance allows to determine \(T_c\) from the Raman spectra.

Data overview: Summarized temperature dependence of the Raman susceptibility \(\chi^{\prime\prime} (\omega, T)\) is presented in Fig. 1. The samples with \(x = 0, 0.25, 0.67\) show qualitatively similar spectra. At low energies, phonon peaks...
FIG. 1. Overview of the polarization-resolved Raman response $\chi''(\omega,T)$ in Ta$_2$NiSe$_5$ ($T_c=160K$). (a-d) Response in $aa$ polarization geometry corresponding to fully symmetric ($A_g$) excitations above (red) and below (blue) $T_c$ for $x = 0.25$. Shading highlights the bare electronic contribution to the response. (e-f) Same for $ac$ geometry, probing the excitations with the symmetry of the order parameter ($B_{2g}$) for $T > T_c$, (red). Unlike $aa$ geometry, phonons show an extremely anisotropic Fano lineshape (hatching), indicating their strong interaction with the electronic continuum (red shading). For $T < T_c$ (blue) excitations observed in $aa$ geometry above $T_c$ appear (arrow) due to symmetry breaking. (i-l) Temperature dependence of $\chi''(\omega,T)$; an enhancement at low energies near $T_c$ (arrow) is observed for $x = 0, 0.25, 0.67$. For $x = 1$ no low-energy response is present. (m-p) Details of $\chi''(\omega,T)$ for regions marked by dashed lines in (i-k). (m-o) Fano lineshape of low-energy phonons due to interaction with electronic continuum. (p) High-energy peak due to an uncondensed exciton in Ta$_2$NiSe$_5$.

are observed on top of a smooth background, which we attribute to electronic excitations. On cooling, a pronounced redistribution of electronic intensity in a wide range of energies is observed, leading to a formation of a gap-like suppression followed by a high-energy peak Fig.1(a)-(c). This peak at 380 meV for Ta$_2$NiSe$_5$ has been attributed to the coherence factors at the gap edge of an EI [36]. In $ac$ geometry, a pronounced enhancement at low energies is evident close to $T_c$, consistent with critical mode softening near a second-order phase transition, Fig.1(i)-(k). In the same temperature region, the lineshapes of the low-energy phonons show strongly asymmetric Fano form (Fig.1(m)-(o)) - a known signature of interaction with an electronic exciton continuum [36, 42, 43]. This indicates the presence of low-energy symmetry-breaking electronic excitations, that soften close to $T_c$. At low temperatures, the asymmetry disappears (Fig.1(e)-(g)), a behavior consistent with a gap opening in an EI. On increasing sulfur content $x$, the temperature where the strongest low-energy enhancement is observed progressively lowers (Fig.1(i)-(k)), and the $A_g$-symmetry peak at about 380 meV becomes less pronounced and moves slightly to lower energy.

The signatures for Ta$_2$NiS$_5$ ($x = 1$) are rather different: in the $ac$ geometry, no signatures of low-energy electronic excitations are visible at all temperatures, indicating the presence of a direct gap. This implies that between $x = 0.67$ and $x = 1$ the electronic structure undergoes a Lifschitz transition from a semimetallic to an insulating one. The intensity in the $aa$ geometry at low
Electronic contribution to the phase transition: To elucidate the origin of the transition as a function of \( x \), we investigate the soft-mode behavior observed for \( x \leq 0.67 \) (Fig. 1(i-k)). In particular, we analyze the asymmetric lineshapes of the low-energy part of \( \chi''(\omega,T) \) around \( T_c \) (Fig. 1(m-o)) using an extended Fano model [42]. The model assumes three phononic oscillators interacting with a continuum of excitonic origin. The latter is expected to arise from the excitonic fluctuations in a semimetal, overdamped due to the allowed decay into particle-hole pairs. The dynamics of the system is governed by the time-dependent Landau equations [44–47]:

\[
\{ \partial_t + \Omega_e(T) \} \varphi + \sum_{i=1}^{3} v_i \eta_i = 0, \\
\{ \partial_t^2 + \gamma_i(T) \partial_t + \omega^2_{pi}(T) \} \eta_i + v_i \varphi = 0,
\]

where \( \eta_i=1,2,3 \) and \( \varphi \) are the collective coordinates (order parameters) of the optical phonons and excitons, respectively. \( \Omega_e(T) \) is the characteristic energy of the excitonic fluctuations, \( \omega_{pi}(T) \) and \( \gamma_i(T) \) are the phonon frequencies and scattering rates, and a bilinear exciton-phonon-coupling \( v_i \) is assumed. The linear response of the system Eq. (1) determines the Raman susceptibility. The resulting purely excitonic linear response function has then the form of a broad continuum \( \chi_{cont}(\omega,T) \propto -\Omega_e(T) \omega^2 \), in contrast to the Lorentzian phonon peaks. The interaction between the phonons and the excitonic continuum leads to an asymmetric broadening of the peaks [42], allowing to capture the observed lineshapes in great detail [36, 42].

We now discuss the parameters deduced from the Fano model fits. The phonon frequencies \( \omega_{pi}(T) \) do not soften near \( T_c \) [42], ruling out a zone-center phonon instability [31]. On the other hand, \( \Omega_e(T) \) (Fig. 2(b), solid lines) consistently softens above \( T_c \) for all semimetallic samples. The linear temperature dependence \( \Omega_e(T) \sim T - T_{ex} \) implies that a purely electronic transition would have taken place at \( T_{ex} < T_c \) for \( x = 0, 0.25 \) (Fig. 3, blue symbols). The strongly negative \( T_{ex} \) for \( x = 0.67 \) indicates that the exciton softening alone would not have lead to a transition at this sulfur concentration.

The suppression of the excitonic instability with \( x \) is even more evident in TaqNiS$_2$, Fig. 1(d.h.i), where the low-energy electronic response is altogether absent due to a direct band gap [35]. Instead, we observe a sharp \( B_{2g} \)-symmetry mode at 0.3 eV, Fig. 1(p), consistent with an in-gap exciton. It is followed by a weaker feature at 0.325 eV and an intensity ‘tail’ at higher energies up to around 0.4 eV [48] A ‘leakage’ of these features is also observed in \( aa \) geometry due to symmetry breaking, Fig. 1(d). On heating, all the features broaden and eventually smear out above 100 K. The increase of the linewidth of the excitonic features can be attributed to the interaction with acoustic and optical phonons [49].

Symmetry-breaking transition: We address first the presence of a phase transition by studying the appearance of new modes in the broken-symmetry phase, as outlined above. In Fig. 2(a) we show the temperature dependence of such a ‘leakage’ phonon intensity marked by arrow in Fig.1(c)-(h). One can see the appearance of the ‘leak’ed intensity below \( T_c \) in the pure Se case, as well as the decrease of \( T_c \) with S doping. At low \( x \) the obtained values of \( T_c \) agree with the ones deduced from transport and specific heat measurements [19, 42], Fig. 3. However, in contrast to the transport data reported in Ref.19, we find that the symmetry-breaking transition persists for all compositions, although the ‘leakage’ intensity is strongly suppressed with higher \( x \). The latter suggests that the phase transition signatures in thermodynamic and transport measurements may become too weak to be observed at large \( x \), especially since the system becomes more insulating with \( x \). The structural signatures, e.g. the deviation of the monoclinic angle \( \beta \) from 90°, should be also strongly suppressed, being already weak at \( x = 0 \) [17].

FIG. 2. The parameters deduced from the Raman response data, Fig. 1. (a) Integrated ‘leakage’ intensity into \( ac \) scattering geometries of the lowest-energy \( A_9 \) phonon mode labeled in panels Fig. 1(e-h), normalized by the intensity in the dominant \( aa \) geometry. The mode’s appearance in the \( ac \) scattering geometry below \( T_c \) implies the onset of symmetry breaking. (b) Bright points: Excitonic energy \( \Omega_e(T) \), Eq. (1); Bleak points: the renormalized energy \( \Omega^{ren}(T) \) including the exciton-phonon interaction obtained from the Fano fits to the lineshapes in Fig. 1. Lines represent linear fits to the points.
Lattice effects and the phase diagram: The presented observations show that the excitonic instability on its own cannot explain the occurrence of a transition for samples with large $x$, calling for a more careful consideration of the lattice effects. First, the coupling of excitons with the otherwise inert optical phonons can increase the transition temperature. Indeed, a zero-energy solution of Eqs. (1) exists when $\Omega_c^{comb}(T) = \Omega_c(T) - \sum_i \varepsilon_i^2/\omega_i^2(T)$ becomes zero. The deduced $\Omega_c^{comb}(T)$ shown in Fig. 2(b), dashed lines, indeed softens to zero at a temperature $T_{comb}(x)$ higher than $T_{xx}(x)$, green points in Fig. 3. $T_{comb}(x=0.67)$ is however still negative, while the actual $T_c$ is 170 K. For Ta$_2$NiS$_5$, where the soft excitons are absent, the optical phonon modes exhibit around 15% softening on cooling. However, their energies never soften below 6.5 meV, Fig. 1(i), ruling them out as the driving force of the transition for Ta$_2$NiS$_5$ [42].

The only remaining option is an instability of the acoustic modes in Ta$_2$NiS$_5$, i.e. ferroelasticity [50], driven by softening of the $B_{2g}$ shear modulus $C_{ac}(T)$. The acoustic modes are not observed in Raman due to their extremely low energies and weak coupling to light [42, 51]. The intrinsic softening of shear modulus also affects the excitonic-driven transition via linear coupling $\lambda$ to the strain tensor component $\varepsilon_{ac}$ that leads to enhancement of transition temperature defined by $\Omega_c^{comb}(\gamma^{PE}_{comb}) - \lambda^2/2C_{ac}(T_{comb}) = 0$, cf. Refs. [11, 12]. We capture $T_c(x)$ quantitatively assuming an $x$-independent Curie-Weiss softening of shear modulus $C_{ac}^{-1}(T) = C_{ac(0)}^{-1} + \frac{\rho}{T-120K}$, the black line in Fig. 3. Ignoring ferroelastic softening (i.e., taking $C_{ac}^{-1}(T) = C_{ac(0)}^{-1}$, the purple dashed line in Fig. 3) leads to a large deviation from actual $T_c(x)$ already at $x = 0.67$ and a complete suppression of ordering at $x_c \approx 0.8$.

This picture bears important consequences for the physics of Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$. At low $x$, the transition is driven to a good approximation, only by the excitonic softening. On increasing $x$, the lattice softening becomes more important, and for $x = 1$ the transition is purely ferroelastic. In the absence of ferroelasticity, a lattice-shifted electronic QPT would have occurred at $x_c \approx 0.8$. While the presence of the lattice symmetry breaking at $T_c$ suppresses the signatures of the QPT at low $T$, at temperatures higher than 120 K, the associated critical fluctuations are expected to appear [13].

Conclusions: In this work, we used polarized Raman scattering to reveal a "failed" excitonic insulator quantum phase transition at $x_c \approx 0.8$ in Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$, hidden by the onset of symmetry breaking due to a lattice instability. While at low sulfur content $x$ we observed a soft excitonic mode driving the transition, at large $x$ the mode ultimately transforms into a high-energy exciton, and only a cooperating ferroelastic instability is found to yield an explanation of the observed symmetry breaking transition. While the lattice instability masks the presence of the excitonic quantum phase transition, the associated critical fluctuations may still explain the correlation effects in Ta$_2$NiSe$_5$ at high temperatures. Furthermore, a controlled suppression of the structural instability by, strain [54] or pressure [19], can turn Ta$_2$Ni(Se$_{1-x}$S$_x$)$_5$ into a platform to study the excitonic QPT at low temperatures as well as quantum critical ferroelasticity [56].
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* pv184@physics.rutgers.edu
† mye@physics.rutgers.edu
‡ girsh@physics.rutgers.edu

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