Orthorhombic-to-monoclinic transition in Ta$_2$NiSe$_5$ due to a zone-center optical phonon instability

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(Dated: February 20, 2020)

I study dynamical instabilities in Ta$_2$NiSe$_5$ using density functional theory based calculations. The calculated phonon dispersions show two unstable optical branches. All the acousting branches are stable, which shows that an elastic instability is not the primary cause of the experimentally observed orthorhombic-to-monoclinic structural transition in this material. The largest instability of the optical branches occurs at the zone center, consistent with the experimental observation that the size of the unit cell does not multiply across the phase transition. The unstable modes have the irreps $B_{1g}$ and $B_{2g}$. Full structural relaxations minimizing both the forces and stresses find that the monoclinic $C2/c$ structure corresponding to the $B_{2g}$ instability has the lowest energy. Electronic structure calculations show that this low-symmetry structure has a sizable band gap. This suggest that a $B_{2g}$ zone-center optical phonon instability is the primary cause of the phase transition. An observation of a softening of a $B_{2g}$ zone-center phonon mode as the transition is approached from above would confirm the mechanism proposed here. If none of the $B_{2g}$ modes present in the material soften, this would imply that the transition is caused by electronic or elastic instability.

INTRODUCTION

There have been continual experimental efforts at finding excitonic insulators, which are electron-hole condensate analogues of superconductors, since they were theoretically proposed to exist in the 1960s in small-band-gap semiconductors or semimetals [1, 2]. Ta$_2$NiSe$_5$ shows a second-order phase transition with a resistivity anomaly near $T_c = 328$ K [3, 4], and Wakasaka et al. have proposed that this material is an excitonic insulator based on their observation of an extremely flat valence band edge below $T_c$ [5]. Additional experimental features purporting to support an excitonic insulator phase in Ta$_2$NiSe$_5$ have been reported [6–19]. However, collective phenomena like Meissner effect and dissipationless flow that are observed in superconductors and superfluids have not yet been observed in Ta$_2$NiSe$_5$.

There seem to be no symmetry arguments forbidding the formation of a complex order parameter of the type $\Delta e^{i\theta}$ in excitonic insulators. However, there are experimental indications that such a complex order parameter cannot explain the low-temperature phase of Ta$_2$NiSe$_5$. The high- and low-temperature phases of Ta$_2$NiSe$_5$ occur in the $Cmcm$ orthorhombic and $C2/c$ monoclinic structures, respectively [3, 4]. The low-temperature phase arises when the $m_x$ ($x \rightarrow -x$) and $m_z$ ($z \rightarrow -z$) mirror symmetries of the high-temperature phase are broken, and a deviation from $90^\circ$ of the angle $\beta$ between the $a$ and $c$ axes that breaks these mirror symmetries was observed in the 1980s [3, 4]. This occurs when an elastic strain $\varepsilon_{B_{2g}} = \varepsilon_{xz}$ with the irreducible representation (irrep) $B_{2g}$ spontaneously develops in the high-temperature orthorhombic structure as its $c_{55}$ elastic modulus softens and becomes unstable while the $T_c$ is crossed. Nakano et al. have observed such a softening of the transverse acoustic mode corresponding to the $c_{55}$ elastic modulus in their inelastic x-ray scattering measurements [21]. In addition, they have also determined intra-unit-cell antiferroelectric atomic displacements that break the mirror symmetries. If the $\varepsilon_{B_{2g}}$ strain is not the primary order parameter, the softening of the $c_{55}$ elastic modulus can only occur when there is a linear coupling between the order parameter and the strain [22]. However, a complex order parameter cannot couple linearly to strain and, hence, cannot be the cause of the spontaneous development of the $\varepsilon_{B_{2g}}$ strain in Ta$_2$NiSe$_5$. This has previously been pointed out by Zenker et al. [23]. Nevertheless, several theoretical studies have proposed a complex order parameter for the low-temperature phase [24–32].

Nakano et al. find that the antiferroelectric displacement pattern observed in the low-temperature phase could be decomposed to two $B_{2g}$ phonon modes of the high-temperature phase that respectively involve movements of Ta and Se ions [21]. Although they observed a strong softening of the transverse acoustic mode with the irrep $B_{2g}$ corresponding to the $c_{55}$ elastic modulus as the $T_c$ is approached from 400 K, they did not observe a similar softening in the only $B_{2g}$ optical phonon mode that they could resolve between 30 and 100 cm$^{-1}$. However, the optical modes do exhibit a large linewidth broadening. This suggests the presence of a large electron-phonon coupling and supports the argument that an electronic instability drives the phase transition in Ta$_2$NiSe$_5$.

The fact that any $B_{2g}$ instability of the $Cmcm$ phase breaks the $m_x$ and $m_z$ mirror symmetries has important implications on the electronic structure of Ta$_2$NiSe$_5$. The highest-lying valence and lowest-lying conduction bands belong to different irreps in the high-temperature $Cmcm$ phase [24]. Therefore, they cannot hybridize to open a gap. When the $m_x$ and $m_z$ mirror symmetries...
are broken, the two bands can hybridize and lead to a gap opening. Mazza et al. [33] and Watson et al. [34] have both highlighted the importance of the loss of the two mirror symmetries in describing the low-symmetry \( C2/c \) phase. Mazza et al. constructed a minimal model based on Ta and Ni \( d_{xz} \) orbitals and studied the effects of on-site \( U \) and nearest-neighbor \( V \) Coulomb interactions using variational Hartree-Fock calculations. They find a purely electronic instability for realistic yet narrow range of \( U \) and \( V \) that is outside the values of \( U \) and \( V \) that they calculated using first-principles constrained RPA calculations. Watson et al. have demonstrated that the loss of the two mirror symmetries leads to band hybridization and gap opening using polarization dependent angle-resolved photoemission spectroscopy. They also performed density functional theory (DFT) calculations that showed that the \( B_{2g} \) atomic displacements found by Nakano et al. reasonably reproduce the electronic spectrum measured by them, and this leads them to proposed that a structural instability, which could be either due to an unstable elastic or zone-center optical phonon mode, causes the phase transition in \( \text{Ta}_2\text{NiSe}_5 \).

The proposed electronic and structural instabilities should lead to distinct temperature-dependent signatures in the measurement of the zone-center phonon modes. If the dynamical instability is due to an unstable optical phonon mode, one would observe a softening of a \( B_{2g} \) phonon mode as the \( T_c \) is approached from above, while no such softening should be observed if the instability is electronic or due to an unstable elastic mode corresponding to a uniform shear distortion of the lattice. A \( B_{2g} \) optical phonon instability has neither been observed in previous experiments nor been reported in existing theoretical studies, and this motivates further investigations of the dynamical properties of \( \text{Ta}_2\text{NiSe}_5 \).

In this paper, I present the results of first-principles calculation of the phonon dispersions of \( \text{Ta}_2\text{NiSe}_5 \) performed using an exchange-correlation functional that incorporates the van der Waals interactions. The dispersions exhibit two unstable optical branches along the \( \Gamma-Z-T-Y-\Gamma \) path, with the largest instability occurring at \( \Gamma \). All the acoustic branches are stable, which suggests that an elastic mode instability is not the primary order parameter. The unstable modes have the irreps \( B_{1g} \) and \( B_{2g} \) at the zone center, with the \( B_{1g} \) mode having a larger magnitude of imaginary frequency. However, atomic displacements along the \( B_{2g} \) mode results in larger spontaneous strains than the displacements along the \( B_{1g} \) mode. After full structural relaxations that minimize both the forces and stresses, the \( C2/c \) monoclinic structure due to the \( B_{2g} \) phonon instability has a lower total energy than the monoclinic structure that is stabilized due to the \( B_{1g} \) instability. The theoretically obtained structural parameters of the monoclinic phase agree well with the experimentally determined ones. Electronic structure calculations on the monoclinic structure show a band gap that is comparable to the values reported from experimental studies. This suggests that the unstable \( B_{2g} \) zone-center optical phonon causes the phase transition found in \( \text{Ta}_2\text{NiSe}_5 \), which should lead to an observation of a softening of the \( B_{2g} \) phonon mode as the \( T_c \) is approached from above.

**COMPUTATIONAL METHODS**

The structural relaxations and phonon calculations were performed using the pseudopotential-based planewave method as implemented in the Quantum ESPRESSO software package [35]. I used the pseudopotentials generated by Dal Corso [36] and cutoffs of 60 and 600 Ry for the basis-set and charge-density expansions, respectively. A \( 12 \times 12 \times 4 \) grid was used in the Brillouin zone integration with a Marzari-Vanderbilt smearing of 0.01 Ry. The dynamical matrices were calculated on an \( 8 \times 8 \times 4 \) grid and Fourier interpolation was used to obtain the phonon dispersions. Most of the calculations presented here were performed using the optB88-vdW exchange-correlation functional that accurately treats the van der Waals interaction [37]. Some structural relaxations were also performed using the LDA, PBE [38], and PBEsol [39] functionals. Spin-orbit interaction was neglected in these calculations. I made extensive use of the AMPLIMODES [40], SPGLIB [41], and PHONOPY [12] packages during the analysis of my results.

The electronic structure calculations were done using the ELK software package [43], which implements the general full-potential linearized augmented planewave method. I used the Tran-Blaha modified Becke-Johnson (mBJ) potential in these calculations to obtain improved band gaps [44]. A \( 12 \times 12 \times 4 \) grid was used in the Brillouin zone integration with a Fermi-Dirac smearing of 0.002 Ry. The cutoffs for the planewaves in the basis-set and charge-density expansions were determined by the parameters \( RK_{\text{max}} = 8 \) and \( G_{\text{max}} = 16 \), respectively. Spin-orbit interaction was included in these calculations.

**RESULTS AND DISCUSSION**

\( \text{Ta}_2\text{NiSe}_5 \) has a layered structure [3][4], which is shown in Fig. 1. Each layer is three atoms thick and is composed of Se sheets at the top and bottom sandwiching a Ta/Ni sheet. The Se atoms octahedrally and tetrahedrally coordinate the Ta and Ni atoms, respectively. These polyhedra are stacked such that the Ta and Ni atoms form chains along the \( a \) axis. Along the \( c \) axis, each Ni chain is separated by two Ta chains. This suppresses hopping along the \( c \) axis. Thus, the electronic structure exhibits a quasi-one-dimensional feature with dispersions that are smaller along the \( b \) and \( c \) axes than along the \( a \) axis that is parallel to the chain direction [10][24].
FIG. 1. Crystal structure of orthorhombic Ta$_2$NiSe$_5$ viewed along two axes.

TABLE I. Calculated lattice parameters of orthorhombic Ta$_2$NiSe$_5$ obtained using different exchange-correlation functionals. The volume is given per formula unit.

| functional      | $a$ (Å) | $b$ (Å) | $c$ (Å) | volume (Å$^3$/f.u.) |
|-----------------|---------|---------|---------|---------------------|
| LDA             | 3.4021  | 12.6548 | 15.3822 | 331.12              |
| PBE             | 3.5040  | 14.2895 | 15.7444 | 394.17              |
| PBEsol          | 3.4325  | 13.0700 | 15.4981 | 347.65              |
| optB88-vdW      | 3.5075  | 13.0352 | 15.7537 | 360.14              |
| Experiment      | 3.5029  | 12.8699 | 15.6768 | 353.37              |

$^a$ Ref. [15].

The calculated lattice parameters of orthorhombic Ta$_2$NiSe$_5$ obtained from full structural relaxation calculations using various exchange-correlation functionals along with the experimental ones [45] are shown in Table I. The LDA underestimates the volume by 6.3%, while the PBE overestimates it by 11.6%. The PBEsol yields a volume that is closer to the experimental value. It underestimates the volume by 1.6%, but it also gives a larger out-of-plane lattice constant $b$. The optB88-vdW functional overestimates the volume by 1.9%, which is a slightly worse performance compared to the PBEsol. However, the optB88-vdW lattice parameters are uniformly closer to the experimental values compared to the PBEsol lattice parameters. It is interesting to note that the PBE gives values for the in-plane lattice constants $a$ and $b$ that are closest to the experiment despite overestimating the out-of-plane lattice constant $b$ by 11.0%. The optB88-vdW improves the description of the van der Waals interaction and gives a value of $b$ that is much closer to the experiment. The calculated internal atomic parameters obtained using this functional and the experimentally determined ones [45] are given in Table II, and the respective values are in good agreement with each other. Since optB88-vdW is structurally the most accurate functional among the four that I tested, further investigations of the dynamical properties of Ta$_2$NiSe$_5$ are performed using it.

The Brillouin zone of orthorhombic Ta$_2$NiSe$_5$ (Bottom) Calculated phonon dispersions of fully-relaxed orthorhombic Ta$_2$NiSe$_5$ obtained using the optB88-vdW functional.

FIG. 1. Crystal structure of orthorhombic Ta$_2$NiSe$_5$ viewed along two axes.

FIG. 2. (Top) The Brillouin zone of orthorhombic Ta$_2$NiSe$_5$. (Bottom) Calculated phonon dispersions of fully-relaxed orthorhombic Ta$_2$NiSe$_5$ obtained using the optB88-vdW functional.

TABLE II. Calculated internal atomic parameters of orthorhombic Ta$_2$NiSe$_5$, obtained using the opt88B-vdW functional.

| atom     | site | theory | experiment |
|----------|------|--------|------------|
| Ta       | 8f   | 0.5    | 0.1114     |
| Ni       | 4c   | 0.0    | 0.25       |
| Se(1)    | 8f   | 0.5    | 0.25       |
| Se(2)    | 8f   | 0.0    | 0.486      |
| Se(3)    | 4c   | 0.0    | 0.354170   |

$^a$ Ref. [15].
unstable mode at $\Gamma$ has the irrep $B_2$.

The $B_{1g}$ and $B_{2g}$ optical phonon instabilities lead to $P2_1/m$ and $C2/c$ structures, respectively. This result showing the $B_{1g}$ mode to have a larger instability than the $B_{2g}$ mode is at odds with the experiments that find the low-temperature structure to be $C2/c$. I displaced the atomic positions of the orthorhombic $Cmcm$ structure according to the eigenvectors of the $B_{1g}$ and $B_{2g}$ modes and performed structural relaxation calculations within the optB88-vdW functional to see which low-symmetry structure is more energetically stable. When only the atomic positions are relaxed by minimizing the forces, the $P2_1/m$ structure is more stable than the $C2/c$ structure. However, the relaxation of only the atomic positions results in the development of stresses, which are larger in the $C2/c$ structure. When full structural relaxation is performed by minimizing both the forces and stresses, I find that the $C2/c$ structure is more stable than the $P2_1/m$ structure. The calculated energy difference between the two structures is small, with a value of 26.0 $\text{meV}$ per formula unit. The energies of these monoclinic structures are $\sim$1 $\text{meV}$ per formula unit lower than that of the orthorhombic structure.

The atomic displacements obtained from the eigenvector of the unstable $B_{2g}$ optical phonon mode are shown in Fig. 3 and the fully-relaxed structural parameters of the $C2/c$ structure are given in Table III. These are in agreement with the distortions in the low-temperature $C2/c$ structure reported by Nakano et al. using synchtron x-ray diffraction experiments. They suggested that atomic displacements in the $C2/c$ structure result from the condensation of two $B_{2g}$ optical phonon modes. In contrast, I find that only one $B_{2g}$ optical phonon instability is responsible for the transition to the low-temperature structure. This $B_{2g}$ mode causes the Se ions at two $8f$ Wyckoff sites to displace out-of-phase with the Ta ions at the $8f$ site along the chain direction $a$ axis and leads to the loss of both the $m_x$ and $m_z$ mirror symmetries, whereas the Ni and Se ions at the $4c$ Wyckoff sites do not move. This displacement pattern results in the formation of an electric dipole moment in the TaSe$_6$ octahedra. However, the phase of the atomic displacements is opposite in the TaSe$_6$ octahedral chains that lie on either side of the NiSe$_4$ tetrahedra. As pointed out by Nakano et al., this results in an intra-unit-cell antiferroelectric distortion that preserves the global inversion symmetry in the low-temperature phase of Ta$_2$NiSe$_5$. In addition to the Ta and Se ions moving against each other, the $B_{2g}$ mode causes the two different sets of Se ions at $8f$ positions to move by different amounts. This causes a slight shear distortion of the TaSe$_6$ octahedra, and the phase of the shear distortion is opposite for the nearest-neighbor octahedra along the $c$ axis.

The electronic density of states and band structure of monoclinic $C2/c$ Ta$_2$NiSe$_5$ calculated using the mBJ potential are shown in Fig. 4. While the optB88-vdW functional is constructed to accurately yield the structural parameters of layered materials, the mBJ potential has been developed to give improved band gaps. The mBJ band structure reported here reasonably agrees with the one calculated by Watson et al., although there are some qualitative and quantitative differences. I obtain a gap at $\Gamma$ of 137 $\text{meV}$. The value of the smallest direct and indirect gaps are 80 and 74 $\text{meV}$, respectively, both of which occur near $\Gamma$ along the $\Gamma$–X path. In the density of states, the first peaks below and above the gap are at the relative values of $-117$ and $192$ $\text{meV}$, respectively, with a gap of 309 $\text{meV}$ between the peaks. For comparison, a gap of 160 $\text{meV}$ is observed for optical excitations in spectroscopy experiments and 300 $\text{meV}$ is found in scanning tunneling spectroscopy experiment. Neither the calculated valence nor conduction band is flat near $\Gamma$ along the $\Gamma$–X path, and their respective band edges lie slightly away from $\Gamma$. A curvature in the valence band edge near $\Gamma$ has been observed by Watson et al. in their ARPES experiment, and this contradicts the expectation of a flat band in an excitonic condensate phase.

### Table III. Calculated internal atomic parameters of monoclinic Ta$_2$NiSe$_5$ obtained using the opt88B-vdW functional.

| atom site | $x$  | $y$  | $z$  | $x$  | $y$  | $z$  |
|-----------|-----|-----|-----|-----|-----|-----|
| Ta        | 0.2 | 0.01| 0.18| 0.14| 0.22| 0.34|
| Ni        | 0.1 | 0.15| 0.32| 0.15| 0.17| 0.33|
| Se(1)     | 0.2 | 0.35| 0.54| 0.35| 0.63| 0.82|
| Se(2)     | 0.7 | 0.68| 0.87| 0.68| 0.87| 0.87|
| Se(3)     | 0.4 | 0.48| 0.62| 0.54| 0.71| 0.86|

*Ref. [21].
the only B2g mode. To the transverse acoustic mode corresponding to the three possible chain-direction out-of-phase distortions below Tc that arises due to the softening of the c\textsubscript{55} elastic modulus. The corresponding elastic strain \(\varepsilon_{xz}\) and the unstable phonon mode have the same \(B_{2g}\) irrep, and this allows a linear coupling between the two. When there is such a term in the free energy, Landau theory analysis shows that the elastic modulus also diverges as the \(T_c\) is approached \[22\], resulting in the coexistence of both the \(B_{2g}\) distortions. Nakano \textit{et al.} have observed a softening of the transverse acoustic mode corresponding to the \(c_{55}\) elastic modulus near transition \[21\], but they did not see a softening of the only \(B_{2g}\) optical phonon mode that they could resolve between 30 and 100 cm\(^{-1}\). There are three \(B_{2g}\) optical phonon modes corresponding to the three possible chain-direction out-of-phase displacements of the three 8\textsubscript{f} Wyckoff sites present in the structure. If the zone-center optical phonon mode is the primary instability, one should observe a softening of the \(B_{2g}\) optical mode shown in Fig. 3 before the acoustic mode starts softening when the \(T_c\) is approached from high temperatures.

DFT calculations approximately incorporate the many-body exchange and correlation interactions arising out of the Coulomb repulsion between electrons, but they do not describe the many-body phenomena of electron-hole pairing and pair condensation that is associated with an excitonic insulator. Therefore, the dynamical instability described here is different from the excitonic instability proposed by Wakisaka \textit{et al.} based on their observation of a flat band in the low-temperature phase \[3\]. A purely electronic excitonic mechanism for the phase transition in Ta\textsubscript{2}NiSe\textsubscript{5} has been supported by a body of theoretical studies \[24–32\], but such an electronic instability or, indeed, an optical phonon one has not been unambiguously observed in any experimental study. As discussed above, a mechanism that leads to a complex order parameter cannot be the cause of the phase transition because the transition involves the loss of symmetry operations belonging to the \(B_{2g}\) irrep. Hence, among the theoretical studies that support a purely electronic mechanism, the one by Mazza \textit{et al.} \[33\] is remarkable because they not only use the hopping and interaction parameters derived from first principles but also allow the breaking of the m\textsubscript{1} and m\textsubscript{2} mirror symmetries that have been previously reported by a synchrotron x-ray diffraction experiment \[21\]. They find that an electronic order parameter that breaks the mirror symmetries has a finite value for a narrow range of Coulomb interaction parameters \(U\) and \(V\). Although the range is realistic, the calculated values of \(U\) and \(V\) that they obtained from their first-principles constrained RPA calculations lie outside this range. Therefore, a reasonable interpretation of their result is that an electronic mechanism does not underlie the phase transition observed in Ta\textsubscript{2}NiSe\textsubscript{5}, which further gives credence to a mechanism based on a dynamical instability.

Ultimately, the nature of the instability that drives the phase transition in Ta\textsubscript{2}NiSe\textsubscript{5} can only be validated by experiments. In this regard, electronic and phonon instabilities will display different responses in inelastic scattering experiments. The presence of a \(B_{2g}\) zone-center optical phonon instability will be reflected by a softening of this mode as the \(T_c\) is approached from above. This optical mode should soften before the electronic and elastic modes belonging to the \(B_{2g}\) irrep also start becoming unstable near the \(T_c\). On the other hand, if the transition is due to either electronic or elastic instability, none of the zone-center \(B_{2g}\) optical phonon modes should soften as the temperature is lowered.

FIG. 4. (Top) Electronic density of states per formula unit and (bottom) band structure of fully relaxed monoclinic Ta\textsubscript{2}NiSe\textsubscript{5} calculated using the mBJ potential.
SUMMARY AND CONCLUSIONS

This paper presents the calculated phonon dispersions of Ta$_2$NiSe$_5$ in the high-temperature orthorhombic $Cmcm$ phase. They exhibit two optical phonon branches that are unstable along the $\Gamma$–$Z$–$T$–$Y$–$\Gamma$ path. The largest instability is at the zone center, consistent with the absence of an increase in the size of the unit cell across the transition as deduced from x-ray diffraction studies. All the acoustic branches are stable, which indicates that the zone-center optical instability is the primary instability driving the transition. The two unstable modes at the zone center have the $B_{1g}$ and $B_{2g}$ irreps. Full structural relaxations minimizing both the forces and stress show that the monoclinic $C2/c$ structure corresponding to the $B_{2g}$ instability is lowest in energy, and this structure exhibits a sizable band gap. Although my DFT calculations cannot compute purely electronic instabilities, the fact that the ground state phase obtained in the present study correctly describes the experimentally determined structural and electronic properties of the low-temperature phase suggests that a zone-center optical phonon instability is responsible for the phase transition in Ta$_2$NiSe$_5$. An observation of a $B_{2g}$ zone-center optical phonon softening before the enhancement of $B_{2g}$ electronic and elastic instabilities near $T_c$ would confirm the mechanism proposed here. However, if none of the $B_{2g}$ optical phonons present in the material soften as the $T_c$ is approached from above, this would imply that the transition is due to either electronic or elastic instability.

ACKNOWLEDGEMENTS

I am grateful to B. J. Kim and Indranil Paul for insightful discussions. This work was supported by GENCI-CINES (grant 2019-A0070911099), the Swiss National Supercomputing Center (grant s820), and the European Research Council (grant ERC-319286 QMAC).

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