Phonon collapse and van der Waals melting of the 3D charge density wave of VSe$_2$

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Among transition metal dichalcogenides (TMDs), VSe$_2$ is considered to develop a purely 3-dimensional (3D) charge-density wave (CDW) at $T_{CDW}=110$ K. Here, by means of high resolution inelastic x-ray scattering (IXS), we show that the CDW transition is driven by the collapse of an acoustic mode at the critical wavevector $q_{CDW}=(2.25\; 0\; 0.7)$ r.l.u. and critical temperature $T_{CDW}=110$ K. The softening of this mode starts to be pronounced for temperatures below $2\times T_{CDW}$ and expands over a rather wide region of the Brillouin zone, suggesting a large contribution of the electron-phonon interaction to the CDW formation. This interpretation is supported by our first principles calculations that determine a large momentum-dependence of the electron-phonon interaction, peaking at the CDW wavevector, in the presence of nesting. Fully anharmonic $ab\; initio$ calculations confirm the softening of one acoustic branch at $q_{CDW}$ as responsible for the CDW formation and show that van der Waals interactions are crucial to melt the CDW. Our work also highlights the important role of out-of-plane interactions to describe 3D CDWs in TMDs.

A comprehensive and detailed understanding of electronic ordering and charge-density-wave (CDW) formation is attracting great efforts in condensed matter physics. In particular, its dynamical nature is the focus of strong debate in correlated oxides and high $T_c$ superconducting cuprates, where fluctuations of the charge order parameter, dispersive CDW excitations, and phonon anomalies are observed. Microscopically, the subtle balance between electron-phonon interaction (EPI) and nested portions of the Fermi surface (singularities in the electronic dielectric function, $\chi_q$, at $q_{CDW}=2k_F$) determines the origin and stabilization of the charge periodicities. While the Fermi surface nesting scenario survives for 1D and quasi-1D systems (Peierls transition), its role in higher dimensions remains largely questioned.

Among the solids showing electronic charge ordering, layered transition metal dichalcogenides (TMDs) represent the first crystalline structures where 3D CDWs were discovered. 1T-VSe$_2$ (space group $P\overline{3}m1$) belongs to the series of layered TMDs that develops a 3D-CDW as a function of temperature, $T_{CDW}=110$ K. However, unlike the isostructural 1T-TiSe$_2$, which adopts a commensurate $2\times2\times2$ CDW ordering with $q_{CDW}=(0.5\; 0\; 0.5)$, 1T-VSe$_2$ develops a more complex incommensurate 3D pattern in its CDW phase with a $q_{CDW}=(0.25\; 0\; -0.3)$ CDW wavevector. 1T-VSe$_2$ is rather unique among the 1T-polytypes because it develops anomalies in its transport properties and magnetic susceptibility that more closely resemble those of 2H-polytypes: e.g., $T_{CDW}[2H-NbSe_2]=33$ K, $T_{CDW}[2H-TaSe_2]=122$ K and presents the lowest onset temperature among them, i.e., $T_{CDW}[1T-TiSe_2]=200$ K, $T_{CDW}[1T-TaSe_2]=550$ K. The sizable difference between $T_{CDW}[1T-VSe_2]$ and its 1T counterparts can be attributed to the occurrence of large fluctuation effects that lower the mean-field transition temperature or to the out-of-plane coupling between neighboring VSe$_2$ layers assisted by the weak short-range van der Waals interactions. Moreover, the theoretical input based on $ab\; initio$ calculations is also limited for all these TMDs undergoing CDW transitions due to the breakdown of the standard harmonic approximation for phonons, which cannot explain the stability of the high-temperature undistorted phases. This hinders the study of both the origin and the melting of the electronically modulated state, complicating the comprehensive understanding of the CDW formation.

From the electronic point of view, angle resolved photoemission (ARPES) experiments in VSe$_2$ reported asymmetric dogbone electron pockets centred at $M(L)$ that follow the threefold symmetry of the Brillouin zone (BZ) interior, with nesting vectors closely matching those observed by x-ray scattering. The formation of the CDW results from the 3D warping of the Fermi surface in the ML plane (fig. 1a shows the high-symmetry points of the Brillouin zone of the hexagonal lattice of VSe$_2$).
Figure 1. (a) The $k$-vector types of space group $P\overline{3}m1$ (164)\textsuperscript{17}. (b) Temperature dependence of the elastic line at (2.25 0 0.7) r.l.u. showing the onset of the CDW at 110 K. Inset, scaling analysis of the elastic peak. (c) Energy-momentum dependence of the low energy acoustic phonons at 300 K for selected momentum transfers, identifying the $\omega_1$ and $\omega_2$ phonons. (d) Close-up view of the phonon fitting at 300 K for selected momentum transfers, identifying the $\omega_1$ and $\omega_2$ phonons. (e) Experimental (points) and calculated (solid lines) dispersion of the low energy acoustic phonons at 300 K. The grey line stands for the silent mode, not observed experimentally. (f) Momentum dependence of the linewidth for $\omega_1$ and $\omega_2$ obtained from the fitting of the experimental spectra to damped harmonic oscillators. The calculated linewidth including the contribution of the electron-phonon interaction and anharmonicity is shown as dashed lines.

Moreover, photoemission data also find a partial suppression of the density of states near $E_F$ on the nested portion below 180 K, indicating that a pseudogap opens at the Fermi surface\textsuperscript{20}. However, a detailed investigation of the electronic structure is complicated by the 3D nature of the CDW order, and the momentum dependence of the EPI and the response of the lattice to the opening of the gap at $E_F$ remains unsolved. In fact, inelastic x-ray scattering (IXS) and theoretical calculations discarded the Fermi surface nesting scenario proposed for 2$H$-NbSe\textsubscript{2}\textsuperscript{21,22} and 1$T$-TiSe\textsubscript{2}\textsuperscript{23,24} and emphasized the critical role of the momentum dependence of the electron-phonon interaction. In addition, it has been recently demonstrated that large anharmonic effects are required to suppress the CDW phases in TMDs and understand their phase diagrams\textsuperscript{16,25–27}.

Here, we report the temperature dependence of the soft phonon mode in VSe\textsubscript{2} by high resolution IXS. We show that a low energy acoustic branch at $q_{CDW}$ undergoes a softening of $\approx$3 meV from $2\times T_{CDW}$ down to $T_{CDW} = 110$ K. The phonon gets overdamped upon cooling and the anomalies are broad in momentum space, identifying the electron-phonon interaction as the driving force of the electronically modulated structural instability. Density functional theory (DFT) calculations including non-perturbative anharmonic effects through the stochastic self-consistent harmonic approximation (SSCHA)\textsuperscript{28–30} can reproduce the temperature dependence of the soft mode and the $T_{CDW}$ onset only when the out-of-plane van der Waals interactions are considered. The results of our calculations show strongly momentum-dependent electron-phonon matrix-elements, matching the linewidth extracted experimentally, and corroborating the critical role of the EPI in the formation of the CDW.

High-quality single crystals of VSe\textsubscript{2} with dimensions $2\times2\times0.05$ mm$^3$ were grown by chemical vapor transport (CVT) using iodine as transport agent. The high-resolution IXS experiments were carried out using the HERIX spectrometer at the 30-ID beamline of the Advanced Photon Source (APS), Argonne National Laboratory. The incident beam energy was 23.72 keV and the energy and momentum resolution was 1.5 meV and 0.7 nm$^{-1}$, respectively\textsuperscript{31}. The components $(h k l)$ of the scattering vector are expressed in reciprocal lattice units (r.l.u.), $(h k l) = ha^* + kb^* + lc^*$, where $a^*$, $b^*$, $c^*$.
and c* are the reciprocal lattice vectors. The experimental lattice constants of the hexagonal unit cell at room temperature are a= 3.346 Å, c= 6.096 Å, and γ = 120°. Here, we focus on the low energy acoustic phonon branches dispersing along the (0<h<0.5 0 -0.3) direction in the Brillouin zone near the reciprocal lattice vector G_{201}, thus, in the range (2+h 0 -0.3) with 0<h<0.5. The variational SSCHA method was used to calculate temperature-dependent phonons fully accounting for non-perturbative anharmonic effects. The variational free energy minimization of the SSCHA was performed by calculating forces on 4 supercells (commensurate with q_{CDW}) making use of DFT within the Perdew-Burke-Ernzerhof (PBE) method. 

The frequency and the phonon lifetime, the experimental lattice constants of the hexagonal unit cell at room temperature are a= 3.346 Å, c= 6.096 Å, and γ = 120°. Here, we focus on the low energy acoustic phonon branches dispersing along the (0<h<0.5 0 -0.3) direction in the Brillouin zone near the reciprocal lattice vector G_{201}, thus, in the range (2+h 0 -0.3) with 0<h<0.5. The variational SSCHA method was used to calculate temperature-dependent phonons fully accounting for non-perturbative anharmonic effects. The variational free energy minimization of the SSCHA was performed by calculating forces on 4 supercells (commensurate with q_{CDW}) making use of DFT within the Perdew-Burke-Ernzerhof (PBE) method. The variational free energy minimization of the SSCHA was performed by calculating forces on 4 supercells (commensurate with q_{CDW}) making use of DFT within the Perdew-Burke-Ernzerhof (PBE) method.

Figure 2. (a) IXS energy-loss scans at (2+h 0 0.7) r.l.u for 0.15<h<0.35 and 150 K. The dotted green line follows the dispersion of the soft phonon mode, ω_1 (see text). Each spectrum is vertically shifted for clarity. (b) Energy loss scans as a function of temperature at (2.25 0 0.7) r.l.u. The black arrow follows the softening of the low energy acoustic mode upon cooling. In both (a) and (b) red lines are the result of the fitting to damped harmonic oscillator functions convoluted with the instrumental resolution. (c) Momentum dependence of the frequency of the ω_1 and ω_2 branches at 150 K. The anharmonic phonon dispersions of the acoustic modes obtained at 150 K are plotted as solid lines. The grey line represents the acoustic mode that is silent in IXS. (d) Experimental (symbols) and theoretical (dashed lines) momentum dependence of the linewidth for ω_1 and ω_2. The theoretical calculation accounts for both the electron-phonon and anharmonic contributions to the linewidth.
olution limited across the whole BZ. Nevertheless, the linewidth of the $\omega_1$ branch is no longer resolution limited between $0.2<h<0.3$ r.l.u. and develops an anomalously large broadening of $\sim 4$ meV at $h=0.25$ r.l.u. Again, the experimental broadening is well captured by our calculations (dashed lines in Fig. 1(f)), indicating that the large enhancement of the broadening is mainly due to the EPI even if the anharmonic contribution to the linewidth also peaks at $h=0.25$ r.l.u. (supplementary information).

Given the observation of the phonon broadening at room temperature and the good agreement between theory and experiment, we proceed with the analysis of the lattice dynamics at lower temperatures. At 250 K, the phonon with energy $\sim 7$ meV ($\omega_2$) shows a clear asymmetric broadening at $q_{CDW}$, i.e., the corresponding branch $\omega_2$ appears to develop a redshift as a function of temperature (Fig. 2(b)). The dispersion of $\omega_2$ at 150 K is similar to the one at 300 K. Contrarily, $\omega_1$ lowers its energy, softening from room temperature down to 110 K. The softening extends over a wide region of momentum space $0.225<h<0.3$ r.l.u. ($0.15$ Å$^{-1}$) at 150 K, see green dotted line in Fig. 2(a). The pronounced instability of this acoustic mode and its broad extension in momentum space are consistent with the results of our anharmonic phonon calculations (solid lines in Fig. 2(c)).

The momentum space spread of the softening indicates a substantial localization of the phonon fluctuations in real space due to the EPI, questioning the pure nesting mechanism suggested by ARPES\textsuperscript{18}. More importantly, the softening of this branch represents the first indication of the lattice response to the formation of the 3D-CDW in VSe$_2$. The analysis of the linewidth reveals that the lifetime of $\omega_2$ remains nearly constant across the BZ and is resolution limited (Fig. 2(d)). On the other hand, the softening of the $\omega_1$ mode at 150 K is accompanied by an enhancement of the linewidth, as shown in Fig. 2(d) (6 meV linewidth at 120 K, Fig. 3(f)) and, again, well modelled by the \textit{ab initio} calculations (dashed lines in Fig. 2(d)).

At the critical temperature, $T_{CDW}=110$ K, the spectrum is dominated by an elastic central peak at zero energy loss (FWHM= 0.05 r.l.u. and $\Delta E=1.6$ meV), thus, the soft mode is no longer resolvable (see Fig. 3(a-d)). Fig. 3(e) displays the temperature dependence of $\omega_1$ as well as the frequency of the phonon obtained \textit{ab initio} with and without including van der Waals corrections. Our anharmonic calculations, which predict that the $\omega_1$ frequency vanishes between 75 and 110 K, are in rather good agreement with the experimentally measured phonon frequencies and the CDW temperature onset, $T_{CDW}=110$ K. When the SSCHA anharmonic calculation is repeated without including the van der Waals corrections (blue triangles in Fig. 3(e)), the softest acoustic mode at $q_{CDW}$ remains unstable even at room temperature. Remarkably, the weak van der Waals forces (of the order of $\sim1 \text{mRy}/a_0$ for a typical SSCHA supercell calculation) are responsible for the stabilization of the 1T structure of VSe$_2$ and play a crucial role in melting the CDW. On the other hand, the damping ratio, $\Gamma/\omega_2$, increases upon cooling and the phonon becomes critically overdamped at $q_{CDW}$ and 110 K\textsuperscript{41}. The critical exponent derived from the fitting of the phonon frequency vs reduced temperature ($\chi(q,\omega)$) shows a clear softening and the harmonic theoretical frequencies obtained with and without van der Waals corrections. The shaded area defines the CDW region. (f) Temperature dependence of the linewidth. Inset, squared frequency of the soft mode as a function of the reduced temperature. Lines are guides to eye.

![Figure 3](image-url)
constant matrix elements (see Supplementary Information) but captures the full Fermi surface topology and also affects the real part of the non-interacting susceptibility, $\chi_0$, as well as the nesting function, $\zeta$, at the same wavevectors. (d) Ratio between the full width at half maximum given by the electron-phonon interaction and the nesting function.

much more strongly on momentum than the nesting function itself and resembles the linewidth dependence. This result supports that the EPI is the main driving force of the CDW transition in $1T-VSe_2$ despite the presence of nesting. Nevertheless, the $q$-range over which the phonon softens, $\Delta q \approx 0.075$ r.l.u., is a factor of 3 less than in $1T-TiSe_2$, where EPI and excitonic correlations are responsible for the structural instability and the CDW order, pointing to an intricate relationship between EPI and Fermi surface nesting scenarios in $VSe_2$.

In conclusion, we have observed with high resolution IXS that the CDW transition in $1T-VSe_2$ is driven by the collapse of an acoustic mode at $q_{CDW}=(0.25 \ 0 \ -0.3)$ exactly at $T_{CDW}=110$ K. The high-temperature $1T-VSe_2$ phase is stable thanks to anharmonic effects. The observed wide softening in momentum space, the calculated strongly momentum dependent electron-phonon linewidth that peaks at $q_{CDW}$, and the weaker dependence on the wavevector of the susceptibility suggest that the EPI is the main driving force of the CDW transition despite the presence of nesting. Moreover, the results show that van der Waals forces are responsible for the melting of the CDW. We attribute the dominant role of van der Waals forces here to the out-of-plane nature of the CDW, which is in contrast to, for instance, $2H$-NbSe$_2$, where the CDW implies an in-plane modulation and the bulk and monolayer transition temperatures seem to be similar$^{27,42}$. Indeed, our anharmonic phonon calculations straightforwardly explain the enhancement of the CDW in monolayer VSe$_2$, $T_{CDW}=220$ K$^{43}$, where the out-of-plane van der Waals interactions are absent. The critical role of out-of-plane coupling of layers has also been highlighted in cuprate superconductors$^{44-46}$.

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