Anharmonicity Reveals the Tunability of the Charge Density Wave Orders in Monolayer VSe₂

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ABSTRACT: VSe₂ is a layered compound that has attracted great attention due to its proximity to a ferromagnetic state that is quenched by its charge density wave (CDW) phase. In the monolayer limit, unrelated experiments have reported different CDW orders with different transition temperatures, making this monolayer very controversial. Here we perform first-principles nonperturbative anharmonic phonon calculations in monolayer VSe₂ in order to estimate the CDW order and the corresponding transition temperature. They reveal that monolayer VSe₂ develops two independent charge density wave orders that compete as a function of strain. Variations of only 1.5% in the lattice parameter are enough to stabilize one order or the other. Moreover, we analyze the impact of external Lennard-Jones interactions, showing that these can act together with anharmonicity to suppress the CDW orders. Our results solve previous experimental contradictions, highlighting the high tunability and substrate dependency of the CDW orders of monolayer VSe₂.

KEYWORDS: anharmonic effects, charge density wave, competing orders, 2D materials, van der Waals interactions, strain

Two-dimensional (2D) materials are an ideal platform to artificially engineer heterostructures with new functionalities due to the weak van der Waals bonding between layers. Monolayers hosting symmetry-broken phases, such as superconductivity, magnetism, ferroelectricity, and charge density waves (CDWs), or multiferroicity, represent the most interesting building blocks to design novel phases of matter. One of the main challenges in the task of engineering novel functional materials with broken-symmetry monolayers is to overcome the restrictions imposed by the reduced dimensionality, which may prevent the formation of these phases, and the competition between ordered phases due to the subtle interplay of different interactions. For instance, CDW phases have been reported to destroy or promote 2D ferromagnetism. VSe₂ is a paradigmatic example of this as, despite some early claims, it is now clear both experimentally and theoretically that the CDW order quenches the emergence of itinerant ferromagnetism. In its bulk form, VSe₂ develops a commensurate 4 × 3 CDW phase below 110 K. The CDW phase opens pseudogaps at the Fermi level impeding the emergence of ferromagnetism. Inelastic X-ray scattering experiments and nonperturbative anharmonic phonon calculations have proven that the CDW transition is driven by the collapse of a low-energy acoustic mode and that the electron–phonon coupling is the origin of the instability, as suggested as well by other quantitative models. These anharmonic calculations have shown that van der Waals interactions are essential to melt the CDW and obtain a charge density wave temperature (T_{CDW}) in agreement with experiments. This suggests that the CDW in the monolayer may also be characterized by similar phonon softening effects but with limited influence of van der Waals interactions.

The main problem in the monolayer of VSe₂ is that the CDW is not fully understood yet, as unrelated experiments have reported distinct CDW orders with different transition temperatures. A nonmonotonic evolution of T_{CDW} as a function of the number of layers has been reported in refs 32–34 but retaining an in-plane 4 × 4 modulation. A metastable phase with modulation 4 × \sqrt{3} has also been identified for the few-layer case. In the purely 2D limit different CDW orders with nonequivalent modulations have been found. A 4 × 4 order was observed in VSe₂ films grown on bilayer graphene on top of SiC and on highly oriented pyrolytic graphite (HOPG) with a T_{CDW} of ∼ 140 ± 5 K and a lattice parameter of a = 3.31 ± 0.05 Å. On the contrary, a \sqrt{3} × \sqrt{7} modulation has been observed in VSe₂ samples grown on several substrates by molecular beam epitaxy by different groups, with a consistent T_{CDW} = 220 K. Some

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other orders have also been reported: a combination of \(2 \times \sqrt{3}\) and \(\sqrt{3} \times \sqrt{7}\) with a \(T_{\text{CDW}} \sim 135\, K\)\textsuperscript{25,26} and a \(4 \times 1\) modulation with \(T_{\text{CDW}} \sim 350\, K\)\textsuperscript{26,36} These experimental contradictions point to the presence of different competing CDW orders, which can lead to different low-temperature phases depending on the substrate.\textsuperscript{26,36}

By calculating the harmonic phonons of the VSe\(_2\) monolayer within density functional theory (DFT), theoretical studies have also described the competition of different CDW orders and how strain can influence the ground state.\textsuperscript{37} Harmonic phonon calculations, however, cannot explain that above \(T_{\text{CDW}}\) the 1T phase is the ground state. In the presence of competing orders, only calculations considering anharmonicity can disentangle what is the CDW order and the transition temperatures, as it has already been shown in different transition metal dichalcogenides (TMDs).\textsuperscript{30,38–41} Therefore, in order to unveil the intrinsic CDW orders of monolayer VSe\(_2\) and how they are affected by external fields, a DFT study including anharmonicity is required.

In this work, we present a theoretical analysis of the CDW orders arising in monolayer VSe\(_2\) using nonperturbative anharmonic phonon calculations based on the stochastic self-consistent harmonic approximation (SSCHA).\textsuperscript{12–45} This formalism has been crucial to understand and characterize the CDWs in several TMDs\textsuperscript{30,38–41} as it overcomes the limitations of the harmonic analysis, allowing to determine the dependence of the CDW order as a function of temperature. We demonstrate the emergence and competition of two intrinsic CDW orders in monolayer VSe\(_2\) as for a lattice parameter of \(a = 3.35\, \text{Å}\) a \(\sqrt{3} \times \sqrt{7}\) order dominates with \(T_{\text{CDW}} = 217\, \text{K}\), while for slightly smaller \(a = 3.30\, \text{Å}\) the \(4 \times 4\) order prevails with \(T_{\text{CDW}} = 223\, \text{K}\). Moreover, the non-perturbative anharmonic procedure allows us to demonstrate that the CDW can be suppressed by the inclusion of Lennard-Jones energy terms, which might appear naturally or may be artificially induced by the interplay between the monolayer and a particular substrate.

We start our analysis performing harmonic phonon calculations on monolayer VSe\(_2\). The normal state (NS) unit cell is shown in Figure 1a. The value of the experimentally reported lattice parameter \(a = 3.31 \pm 0.05\, \text{Å}\) is in rather good agreement with the theoretical one of \(3.35\, \text{Å}\) obtained at the Perdew–Burke–Ernzerhof\textsuperscript{46} level without considering the zero-point motion.\textsuperscript{23,27} Therefore, in this study we perform calculations for two lattice parameters \(a = 3.35\, \text{Å}\) and \(a = 3.30\, \text{Å}\) which provide a good representation of the experimental range. Density functional perturbation theory (DFPT)\textsuperscript{47} is used to compute the harmonic phonon band structure for both lattice parameters (see the Supporting Information for a detailed description of the calculations). Both harmonic phonon bands (see Figure 1b) show two dominant instabilities at \(q_1 = 3/5\Gamma\) and \(q_2 = 1/2\Gamma M\). These are associated with the two intrinsic CDW orders of monolayer VSe\(_2\), with modulations shown in Figure 1c,d, that lower its Born–Oppenheimer energy. The instability at \(q_1\) is associated with a \(\sqrt{3} \times \sqrt{7}\) supercell, while the one at \(q_2\) leads to a \(4 \times 4\) modulation. Both softened phonon modes have an out-of-plane component in the displacement vectors, as it is also the case of the CDW instability in the bulk form of this compound. In spite of providing the two intrinsic CDW orders, harmonic calculations do not suffice to predict which of these CDW orders is the dominant one or the associated transition temperature for each lattice parameter. In fact, the small change in the lattice parameter does not impact the weight of the instabilities. Our nonperturbative anharmonic calculations based on a free energy formalism within the SSCHA can give the answer to these questions (see the Supporting Information for a detailed description of the SSCHA method and the technical aspects of these calculations).

Figure 2 shows the temperature evolution of the phonon band structure obtained with the SSCHA method for two lattice parameters \(a = 3.35\, \text{Å}\) (in red in the top panels of Figure 2) and \(a = 3.30\, \text{Å}\) (in blue in the lower panels of Figure 2). At high enough temperature (\(T = 250\, \text{K}\)) the IT NS phase (Figure 1a) is dynamically stable for both lattice parameters as shown in Figures 2a,d, showing that anharmonicity melts the CDW phase as it happens in other TMDs.\textsuperscript{40,48–41} By decreasing the temperature, the phonon modes associated
with the CDW instabilities at $q_1$ and $q_2$ soften. In particular, for $a = 3.35 \text{ Å}$ at 200 K (Figure 2b) we can observe that the mode at $q_1 = 3/5\sqrt{K}$ becomes unstable, even if the one at $q_2$ remains stable. This result indicates that for this lattice parameter the $\sqrt{3} \times \sqrt{7}$ CDW order dominates. However, for $a = 3.30 \text{ Å}$ at 200 K (Figure 2e) the phonon mode at $q_2 = 1/2\Gamma M$ is unstable, but not at $q_1$. Therefore, for the smaller lattice parameter, the $4 \times 4$ CDW order is the dominant one. At low enough temperatures (Figures 2c,f) both $q$-vectors show unstable modes. However, note that this situation is not indicating that at low temperatures both CDW orders coexist, although it is a clear signature that the anharmonic free energy landscape becomes more complex. Once one of the CDW orders becomes stable when the temperature is decreased, the system collapses to it, and the analysis in terms of the anharmonic phonons of the NS phase is no longer useful to describe the evolution of each of the CDW phases at low temperatures. Nevertheless, the anharmonic phonons at low temperature shown in Figure 2c,f confirm that both $q_1$ and $q_2$ are the intrinsic CDW orders of VSe$_2$ that can be accessed through a transition from the NS phase.

To analyze in more detail the competition between the two CDW orders as a function of the lattice parameter, Figure 3a shows the temperature evolution of the frequency of the phonon mode that softens at $q_1$ and $q_2$. For the larger lattice parameter, $a = 3.35 \text{ Å}$, the frequency at $q_1$ becomes negative (imaginary) at higher temperature than at $q_2$, and hence the $\sqrt{3} \times \sqrt{7}$ CDW order is the dominant (left panel in Figure 3a in red). The opposite behavior is observed for the smaller lattice parameter $a = 3.30 \text{ Å}$. The frequency at $q_2$ becomes negative at higher temperature than that at $q_1$, and hence the $4 \times 4$ CDW order is dominant (right panel in Figure 3a in blue). From Figure 3a we can obtain the transition temperature for each lattice parameter: for $a = 3.35 \text{ Å}$ the $\sqrt{3} \times \sqrt{7}$ order emerges at $T_{CDW} = 217 \text{ K}$, while for $a = 3.30 \text{ Å}$ the $4 \times 4$ order arises at $T_{CDW} = 223 \text{ K}$. Importantly, our anharmonic calculations including the zero point energy predict an associated in-plane pressure of 0.7 GPa for $a = 3.35 \text{ Å}$ and 1.3 GPa for $a = 3.30 \text{ Å}$.

Considering that its in-plane pressure is lower, these results point out that the intrinsic CDW order in monolayer VSe$_2$ is $\sqrt{3} \times \sqrt{7}$ with a $T_{CDW} = 217 \text{ K}$, which is in perfect agreement with the experiments on refs 20 and 23 and that the $4 \times 4$ order, which is the in-plane projection of the bulk $4 \times 4 \times 3$ CDW order, appears only under strain. Our results provide an explanation for the different CDW orders observed for small variations ($\sim 1.5\%$) of the lattice parameter. However, our results show that the $\sqrt{3} \times \sqrt{7}$ and $4 \times 4$ modulations are the intrinsic CDW orders and point out that those different modulations are a consequence of the interplay between the highly dynamically unstable NS of VSe$_2$ monolayer and the particular substrate.

Having established the competition between the two intrinsic CDW orders of monolayer VSe$_2$ as a function of the lattice parameter, we study now the origin of these CDW orders. In order to do so, we use DFPT to compute both the nesting function $\gamma(q)$ (Figure 3b), which is given by

$$
\gamma(q) = \frac{1}{N} \sum_{\mathbf{k}} \sum_{\mathbf{n}} \delta(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{nk}} - \epsilon_{\mathbf{p}})
$$

(1)

and the phonon line width associated with the electron–phonon interaction (see Figure 3c).

$$
\gamma^2(q) = \frac{2 \pi \hbar \omega(q)}{N} \sum_{\mathbf{k}} \sum_{\mathbf{n}} \langle b_{\mathbf{nk}+\mathbf{q},\mathbf{nk}}(\mathbf{p}) \rangle^2 \delta(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{nk}} - \epsilon_{\mathbf{p}})
$$

(2)

In eqs 1 and 2 $\epsilon_{\mathbf{nk}}$ is the energy of band $n$ with wavenumber $\mathbf{k}$, $\epsilon_{\mathbf{p}}$ the Fermi energy, and $N$ is the number of $\mathbf{k}$ points in the sum over the first Brillouin zone (1BZ). The nesting function

![Figure 2. Nonperturbative anharmonic calculations of the NS of monolayer VSe$_2$. (a–c) For lattice parameter $a = 3.35 \text{ Å}$ and temperatures of 250, 200, 100 K respectively. (d–f) For lattice parameter $a = 3.30 \text{ Å}$ and temperatures 250, 200, 150 K. The phonon melting occurs first at the $q_1(q_2)$ point for $a = 3.35 \text{ Å}$ ($a = 3.30 \text{ Å}$) as shown in panels (b) and (e).]
purely electronic instability. The equation for connect and, thus, reveal if the instability emerges from a softened modes at Figure 3.

3.35 Å (a = 3.30 Å) are shown in red (blue) in the left (right) panels. We can see in Figure 3b that, for both lattice parameters the phonon line width allows us to establish which is the main driving force of the CDW orders in monolayer VSe₂. In a different way, Figure 3c shows that the phonon line width coming from the electron–phonon interaction abruptly peaks at both q₁ and q₂ for both lattice parameters, meaning that in all cases the enhancement comes from the mode and momentum dependence of the electron–phonon matrix elements. Therefore, the two intrinsic CDW orders developed by monolayer VSe₂ are driven by the electron–phonon coupling, in agreement with the theoretical predictions for 2D systems. Besides, the electron–phonon interaction also plays a key role in the CDW transition in 3D systems, as in bulk 17'-VSe₂, in which case the presence of nesting is symbolic.

Figure 3. (a) Temperature evolution of the frequencies of the softened modes at q₁ and q₂ as obtained in the SSCHA calculations. (b) Nesting function γ(q). It does not clearly peak at q₁ and q₂. (c) Phonon line width ν(1)(q) given by the electron–phonon interaction. Sizable peaks appear at the CDW q-vectors. All of the results for a = 3.35 Å (a = 3.30 Å) are shown in red (blue) in the left (right) panels. peaks for q indicates that nested regions of the Fermi surface connect and, thus, reveal if the instability emerges from a purely electronic instability. The equation for γ(1)(q) is very similar to the nesting function, but the value is weighted by the mode μ and momentum q dependent electron–phonon matrix elements gₘμ(q) and, thus, reveals if the instability emerges from electron–phonon interactions. The electron–phonon line width is independent of the phonon frequency w(q) as the electron–phonon matrix elements scale as w(q)⁻¹/₂. It is worth noting that both quantities need to be computed in order to establish the origin of the CDW orders. For 2D systems like monolayer VSe₂, despite the existence of nesting conditions at the q points associated with the CDW orders, a purely electronic picture does not suffice to produce a CDW order and electron–phonon interactions play a key role to drive the transition. Therefore, the direct comparison between the nesting function and the electron–phonon line width allows us to establish which is the main driving force of the CDW orders in monolayer VSe₂.

We can see in Figure 3b that, for both lattice parameters the nesting function does not show any strong peak at the CDW vectors despite the existence of small shoulders near q₁ and q₂. The reason for this is that this functional allows us to properly describe both bulk and monolayer limits of VSe₂, oppositely to the widely used GGA-PBE functional (see the Supporting Information for a more detailed description of the election of the exchange correlation functional to study the CDW orders of VSe₂). In the latter case, a huge overestimation of TCDDW occurs in bulk due to the lack of van der Waals interactions that cause a melting of the CDW phase. Motivated by these results in the bulk, we explore here the effect that external van der Waals interactions may cause in the CDW orders of monolayer VSe₂. These van der Waals interactions might naturally appear by proximity effect between the analyzed monolayer and other layers, such as the substrate or in van der Waals heterostructures. We will introduce these external interactions in a phenomenological way. This approach allows us to derive general conclusions for the pure effect of van der Waals interactions on CDW orders, i.e., factoring out effects that could appear in particular substrates, such as charge transfer.

First, to illustrate the effect of external van der Waals forces on the CDW, we make use of a simple one-dimensional double-well fourth order potential

\[ V(r) = A(r - r₀)² + B(r - r₀)⁴ \]

where A and B are the coefficients of the different powers, r is the position of the atoms, and r₀ is the equilibrium atomic position in the high temperature phase. The CDW occurs when the free energy calculated with this potential is lower at r ≠ r₀ than at r = r₀ = 0. Obviously the lower and wider the minimum of the well the more probable it is to find a broken-symmetry CDW order. We can now add to the potential \( V(r) \) a \( E_{ij}(r) \) Lennard-Jones energetic contribution to mimic the role played by external van der Waals interactions

\[ E_{ij}(r) = \frac{C}{rᵢ} + \frac{D}{(rᵢ - r₀)⁶} \]

where \( C \) and \( D \) are the coefficients that control the strength of the Lennard-Jones interactions, \( rᵢ \) is a cutoff radius that prevents a divergence at \( r = r₀ \), and \( D = C/rᵢ \) is simply a constant that fixes the potential to be equal to 0 at \( r₀ \). The effect of the Lennard-Jones interactions on \( V(r) \) can be seen in Figure 4a for different values of \( C \). We can observe that an increase in the strength of the Lennard-Jones interactions makes the potential shallower. Therefore, Lennard-Jones interactions tend to quench the low-temperature CDW phase and promote the high-temperature symmetric phase.
implemented in the QUANTUM ESPRESSO package.

The strength of the Lennard-Jones interactions that quenches both CDW orders tends to weaken or even suppress the CDW orders in monolayer VSe₂, in this work we analyze the CDW orders of monolayer VSe₂ using non-perturbative anharmonic phonon calculations that allow us to determine the CDW orders of this system and their corresponding transition temperatures. We analyze the effect of strain and external van der Waals interactions, since these two parameters are intrinsic to any experiment. We demonstrate the competition between two intrinsic CDW orders as a function of the lattice parameter. Variations of 1.5% in the lattice parameter are enough to drive the system from the \( \sqrt{3} \times \sqrt{7} \) to the \( 4 \times 4 \) order. Transition temperatures on the order of 220 K have been found for both CDW orders, in very good agreement with experiments. We show that external Lennard-Jones interactions tend to weaken or even suppress the CDW orders. These results together help to understand the great variability of CDW orders and associated material properties found in the experiments of monolayer VSe₂. Moreover, they pave the way to tune CDW orders occurring in van der Waals materials, thus promoting competing orders that might arise in these systems.

**ASSOCIATED CONTENT**

**Supporting Information**

Detailed explanation of the computational methods, the election of the exchange correlation functional and the effect of external Lennard-Jones interactions at the harmonic level. The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c04584.

Detailed explanation of the computational methods, the election of the exchange correlation functional and the effect of external Lennard-Jones interactions at the harmonic level (PDF)

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Notes
The authors declare no competing financial interest.

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