Weak Dimensionality Dependence of the Charge Density Wave Transition in NbSe$_2$

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Contradictory experiments have been reported about the dimensionality effect on the charge density wave transition in 2H NbSe$_2$. While scanning tunnelling experiments on single layers grown by molecular beam epitaxy measure a charge density wave transition temperature in the monolayer similar to the bulk, around 33 K, Raman experiments on exfoliated samples observe a large enhancement of the transition temperature up to 145 K. By calculating from first principles the charge density wave temperature, we determine that the intrinsic charge density wave is barely affected by dimensionality as suggested by the scanning tunnelling experiments. The transition temperature is estimated by calculating the temperature dependence of the phonon spectra within a non-perturbative approach to deal with anharmonicity and determining at which temperature the phonon energy of the mode driving the instability vanishes. The obtained transition temperature in the bulk is around 59 K, in rather good agreement with experiments, and it is just slightly increased in the single-layer limit to 73 K, showing the weak dependence of the transition on dimensionality. Our results demonstrate that the charge density wave melts due to the ionic contribution to the entropy, not the electronic one, and underline that environmental factors, such as sample preparation or the substrate, have a large impact on the transition temperatures.

A charge density wave (CDW) is a structural distortion of the crystal lattice that induces a modulation of the electronic density [1]. CDWs in transition metal dichalcogenides (TMDs) [2] are particularly relevant because they seem to compete with superconductivity [3–9] and form a phase diagram similar to the high-temperature superconductors [10, 11]. The origin of the CDW instability and its interaction with superconductivity in TMDs continues to be a topic on intense debate [12–15], as it might enlighten the hidden physics in strongly correlated materials where different phases compete.

TMDs tend to adopt layered crystal structures. Each layer is formed by transition metal atoms sandwiched by covalently bonded chalcogen (see Fig. 1). Due to the weak van der Waals interaction that holds together the layers in the bulk, TMDs can be exfoliated down to the monolayer [16]. Monolayer TMDs can currently also be synthesized by chemical means [17]. This has opened the possibility to study the effect of dimensionality on CDW transitions. The results obtained thus far, however, do not show a clear trend and it is generally not clear whether experimental results are affected by environmental factors. In monolayer TaS$_2$ the CDW present in the bulk disappears [18], while in the isoelectronic and isostructural TaSe$_2$ it remains unchanged [19]. Even if NbS$_2$ has no CDW transition in the bulk [20], a CDW transition has been observed in the monolayer grown on top of bilayer graphene [21]. This result seems substrate dependent, as a monolayer grown on Au(111) does not show any CDW feature down to 30 K [22]. Similarly, in monolayer TiSe$_2$ the CDW temperature ($T_{CDW}$) is enhanced with respect to the bulk, but the value of $T_{CDW}$ is strongly substrate dependent [23, 24].

The effect of thickness on the $T_{CDW}$ in NbSe$_2$ is even more controversial. The most stable polytype of NbSe$_2$ is the 2H shown in Fig. 1, which undergoes a CDW transition at 33 K to an incommensurate structure very close to a $3\times3$ ordering [3, 25]. Inelastic x-ray experiments evidence that the CDW transition is second order. In fact, a longitudinal acoustic (LA) phonon mode collapses exactly at 33 K at $q_{CDW} \sim 2/3\Gamma M$ [26], a momentum consistent with the periodicity of the CDW phase. In other TMDs as well, the phonon frequency of the mode that drives the CDW is strongly reduced by cooling and eventually vanishes at $T_{CDW}$ [27, 28]. The CDW transition temperature in the NbSe$_2$ monolayer has been determined by Raman measurements in exfoliated samples on sapphire substrates [29, 30], as well as by scanning tunnelling microscopy (STM) in single-layers grown by molecular beam epitaxy (MBE) on bilayer graphene, which confirmed that the CDW order remains $3\times3$ [31]. The problem is that while the Raman experiments on exfoliated samples estimate a huge enhancement of $T_{CDW}$ up to 145 K [29, 30], STM experiments determine that dimensionality does not affect $T_{CDW}$ as the CDW occurs
FIG. 1. Crystal structure of bulk NbSe$_2$ in the 2H polytype. The unit cell is depicted, which is formed by two non-equivalent layers. The crystal structure of the monolayer is marked in the figure, which only contains one single layer. The lattice parameters used are given in the Supplementary Material [32]. In the right panel the Brillouin zone is shown, which is restricted to the ΓMK plane in the monolayer.

between 25 K and 45 K [31]. It remains unclear whether the contradicting results arise due to the different sample preparation techniques, substrate effects, or any other reason.

In this work we present first-principles calculations of $T_{\text{CDW}}$ both in bulk and monolayer NbSe$_2$. We determine that the intrinsic CDW transition temperature is barely affected by dimensionality. The theoretically calculated phonon spectrum and $T_{\text{CDW}}$ in the bulk are in good agreement with inelastic x-ray experiments. Since the value obtained for the monolayer in a completely comparable calculation is very similar, it is confirmed that bulk and suspended monolayer NbSe$_2$ are expected to have a similar CDW transition temperature as suggested by the STM experiments.

Calculating temperature-dependent phonon frequencies in systems that undergo a second-order structural phase transition upon cooling, like a CDW transition, is not a trivial task. The harmonic approximation cannot describe temperature dependent phonons, and, more dramatically, in these situations it predicts that the high-temperature undistorted phase is unstable, i.e., that it is not a minimum of the Born-Oppenheimer potential $V$. This jeopardizes any perturbative approach to include anharmonic effects. We overcome this problem by making use of the stochastic self-consistent harmonic approximation (SSCHA) [33–35]. The SSCHA is a quantum variational method that minimizes the free energy of the system $F$ without approximating $V$ with respect to centroid positions $\mathbf{R}$, which determine the most probable ionic positions, and effective force constants $\Phi$, which are related to the amplitude of the ionic fluctuations around $\mathbf{R}$. The SSCHA accurately includes the entropic contribution of ionic fluctuations to the free energy down to 0 K. All anharmonic phonon frequencies in this work are obtained in the static limit of the SSCHA theory [34] in which the phonon frequencies are obtained diagonalizing the Hessian of the SSCHA free energy $F$, 

$$F = \frac{1}{\sqrt{M_a M_b}} \sum_{\mathbf{R}_a, \mathbf{R}_b} \frac{\partial^2 F}{\partial \mathbf{R}_a \partial \mathbf{R}_b},$$

where $a$ and $b$ label both an atom and a Cartesian index and $M_a$ is the mass of atom $a$. The application of the SSCHA requires the calculation of atomic forces on supercells. We used $6 \times 6 \times 1$ supercells both for the bulk and the monolayer, which are commensurate with $q_{\text{CDW}} = 2/3\Gamma M$, and the forces were calculated on these supercells using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) parametrization of the exchange-correlation functional [36] (see Supplementary Material[32] for further details on the calculations). The validity of the $6 \times 6 \times 1$ supercell was confirmed in the monolayer case by determining $T_{\text{CDW}}$ as well with a larger $9 \times 9 \times 1$ supercell, which yielded a converged value. The calculation of phonons following this approach has already been successfully applied to TMDs [13, 37, 38], where phonon frequencies in agreement with experiments have been obtained, and to other calchogenides [39, 40].

In Fig. 2 we first show the harmonic phonon spectra calculated for the bulk and the monolayer. As it has been already pointed out in the literature [26, 41, 42], in both cases the harmonic phonons show many unstable modes. Following the displacement pattern of any of them, $V$
should be lowered. Even if in both cases the longitudinal acoustic mode is unstable close to $q_{\text{CDW}} = 2/3\Gamma M$, there are some differences in the harmonic phonon spectra. The most unstable mode along $\Gamma M$ in the monolayer is shifted to smaller momentum with respect to the bulk, around $0.56\Gamma M$, in agreement with previous calculations [41]. Remarkably, there is no instability at the $M$ point in the monolayer, but a deep instability emerges along $MK$. Even if it has been argued that the CDW order can be inferred from the $q$ point where the deepest instability occurs in the harmonic calculation [41, 42], this can only be understood as a first hint and it may yield to a wrong interpretation. The order of the CDW can only be determined theoretically by calculating the phonon spectra as a function of temperature and seeing at which $q$ a phonon becomes unstable on cooling, which requires a full anharmonic non-perturbative calculation. Furthermore, the harmonic phonon spectra, and consequently the momenta for which the largest instability is observed, is strongly dependent on the calculation parameters in NbSe$_2$, e.g. the smearing used for the integrals over the Brillouin zone, and, thus, lacks significance (see Supplementary Material [32]).

A CDW phase, as any order in condensed matter, melts due to entropy or, in other words, fluctuations. The SS-CHA calculations we have performed only include entropy effects on the ionic fluctuations, not on the electrons. The electronic system in the DFT calculations needed for the SSCHA is always treated at 0 K. The anharmonic renormalization of the phonon spectra obtained in this way is still huge for the low-energy modes that are unstable in the harmonic approximation (see Fig. 3). The temperature dependence of these modes is very remarkable, evidencing that ionic fluctuations, which strongly feel the anharmonic part of the potential, melt the CDW. In the bulk case, the obtained phonon spectra at 250 K is in very good agreement with inelastic x-ray experiments [26]. At 50 K our calculations are in rather good agreement with experiments as well, but underestimate the frequency of the LA mode at $q_{\text{CDW}} = 2/3\Gamma M$, which it is still imaginary. The LA mode stabilizes between 50 K and 100 K in our calculations. Similarly, this mode also stabilizes in a similar temperature range in the monolayer. The deep instability along $MK$ in the monolayer is washed out by anharmonicity at all temperatures.

In order to verify that the melting of the CDW phase in NbSe$_2$ is indeed due to ionic entropy and not due to temperature effects on the electrons, we calculate the harmonic phonon frequency of the longitudinal acoustic mode at $q_{\text{CDW}} = 2/3\Gamma M$ properly accounting for temperature effects on the electrons without any ionic fluctuation. This is done by using the explicit temperature dependent Fermi-Dirac distribution function in the DFT calculation of the harmonic phonon frequency. As shown in Fig. 4 the CDW does melt, but at around 900 K both for bulk and monolayer NbSe$_2$. This temperature is 30 times the experimentally observed $T_{\text{CDW}}$. The CDW does not melt due to temperature effects on electrons; as mentioned above, it melts due to ionic thermal fluctuations.

Once we have determined the origin of the CDW melting, we focus our attention on the determination of the CDW order and temperature. The anharmonic phonon spectra in Fig. 3 are obtained by directly Fourier interpolating the SSCHA free energy Hessian obtained in the $6\times6\times1$ supercell. In this Fourier interpolated spectra, the CDW instability occurs close to $q_{\text{CDW}} = 2/3\Gamma M$ both in the bulk and in the monolayer, driving a $3\times3$ CDW ordering in agreement with experiments. A calculation in a larger $9\times9\times1$ supercell for the monolayer shows that the Fourier interpolated spectra is not fully

FIG. 3. Anharmonic phonon spectra calculated from the SS-CHA free energy Hessian as a function of temperature for (a) bulk and (b) monolayer NbSe$_2$. In the bulk case the results are compared with the experimental points obtained with inelastic x-ray scattering [26]. In all figures the grey area denotes imaginary phonon frequencies. Temperature effects are only included in the ionic system, i.e., the ionic entropy is considered, not the electronic entropy.
converged yet with the supercell size (see Supplementary Material [32]) and, thus, inferring the CDW order from a Fourier interpolated spectra is risky. The phonon frequency of the LA mode at $q_{CDW} = 2/3\Gamma M$ is, on the contrary, well converged with the supercell size (see Supplementary Material [32]). Considering that the $3\times3$ ordering of the CDW is an experimental fact both in the bulk and the monolayer, we can estimate $T_{CDW}$, and readily compare it between the bulk and the monolayer, by studying the temperature dependence of the anharmonic phonon frequency of the LA mode at $q_{CDW} = 2/3\Gamma M$.

As shown in Fig. 4, the square of the calculated phonon frequency of the LA mode at $q_{CDW} = 2/3\Gamma M$ shows a temperature dependence in agreement with the experimental trend when entropic terms are only considered for the ions [26]. The frequencies are slightly underestimated and, consequently, the value of the theoretical $T_{CDW}$ is around $\sim 59$ K, close to the experimental value of $33$ K, but slightly overestimated. Interestingly, in the monolayer, the frequency of the LA mode at $q_{CDW}$, as well as its temperature dependence, is practically on top of the bulk result. The CDW temperature in the monolayer is consequently very close to the bulk result, $\sim 73$ K. Considering that the SSCHA calculations in the bulk and in the monolayer are performed with the same supercell, with consistent DFT parameters, the comparison between the results is perfectly justified. We can thus conclude that the CDW temperature in NbSe$_2$ is weakly dependent on the dimensionality, supporting the results obtained with STM experiments [31].

In conclusion, we show making use of first principles calculations within the stochastic self-consistent harmonic approximation that the CDW in both bulk and monolayer NbSe$_2$ melts due to ionic thermal fluctuations, not thermal effects on the electrons, and that the CDW transition temperature is weakly dependent on the dimensionality. Our results support the STM measurements on single layers grown by MBE [31], but question the Raman results on exfoliated samples that estimate a large enhancement of $T_{CDW}$ in the monolayer [29, 30]. It is to be seen whether the enhanced $T_{CDW}$ observed in Raman experiments is a consequence of the sample deterioration, e.g., oxidation, during the exfoliation process or it is affected by the substrate. Indeed, similar theoretical calculations as those presented here have recently shown that strain or charge doping from the substrate can affect the CDW transition in other TMDs [37, 38].

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### FIG. 4

(a) Anharmonic phonon frequency squared obtained from the SSCHA free energy Hessian at $q_{CDW} = 2/3\Gamma M$ as a function of temperature. These SSCHA calculations include entropy effects only on the ions, but not on the electrons, which are treated at 0 K in all calculations. The results are compared with the values obtained including fluctuations only on the electronic system, but not on the ions. The latter cannot capture all the experimental trend [26], which is also plotted, and remark that the melting of the CDW is exclusively due to ionic entropy. (b) The same data but only showing the results coming from the SSCHA free energy Hessian at low temperatures. $T_{CDW}$ is estimated at 59 K for the bulk and at 73 K for the monolayer. The experimental CDW occurs at 33 K [26]. The grey area denotes imaginary phonon frequencies in both figures.

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