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Strong anharmonicity induces quantum melting of charge density wave in 2H-NbSe$_2$ under pressure


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The pressure and temperature dependence of the phonon dispersion of 2H-NbSe$_2$ is measured by inelastic X-ray scattering. A strong temperature dependent soft phonon mode, reminiscent of the Charge Density Wave (CDW), is found to persist up to a pressure as high as 16 GPa, far above the critical pressure at which the CDW disappears at 0 K. By using ab initio calculations beyond the harmonic approximation, we obtain an accurate, quantitative, description of the (P,T) dependence of the phonon spectrum. Our results show that the rapid destruction of the CDW under pressure is related to the zero mode vibrations - or quantum fluctuations - of the lattice renormalized by the anharmonic part of the lattice potential. The calculations also show that the low-energy longitudinal acoustic mode that drives the CDW transition barely contributes to superconductivity, explaining the insensitivity of the superconducting critical temperature to the CDW transition.

The interplay between charge density wave order, i.e. a static modulation of the electronic density close to the Fermi level, and superconductivity has attracted much attention. This is the central issue of a long standing debate in simple transition metal dichalcogenides without strong electronic correlations, such as 2H-NbSe$_2$. At $T_{\text{CDW}}=33.5$ K, 2H-NbSe$_2$ undergoes a second order phase transition towards an incommensurate CDW phase which coexists with superconductivity below $T_c = 7.2$ K. The anisotropy and temperature dependence of the electronic band structure has been widely studied by ARPES and STM measurements. The CDW is coupled to a periodic lattice distortion through a strong electron-phonon coupling. The transition is associated with a softening of a longitudinal acoustic phonon mode as temperature is lowered to $T_{\text{CDW}}$. It was already noticed that the high order phonon fluctuations and strong electron-phonon interactions explain some of the key features of the formation of the CDW in this system. In the specific case of NbSe$_2$ at ambient pressure, the reduction of the phonon lifetime through the electron-phonon coupling is a key ingredient on the temperature dependence of the phonon dispersion.

At ambient pressure, published ab initio calculations reproduce successfully the lattice instability on a wide part of the Brillouin zone around the experimentally observed $q_{\text{CDW}}$. However, these calculations are essentially unaffected, as shown on the (T,P) phase diagram in Fig. 1. Indeed, they predict a CDW instability up to $P_c = 14$ GPa, a pressure that largely exceeds the experimentally observed one. This persistence of the CDW instability in the harmonic calculations is reminiscent of the effect of iso-valent and iso-electronic substitution of Se with lighter S. The harmonic calculation also predicts a CDW instability for NbS$_2$ that is not observed experimentally.

Taken together, these facts indicate that for an accurate description of the ground state (even at T=0K) of these systems, calculations beyond the standard harmonic approximation must be carried out. The impact of anharmonicity has recently been highlighted in different systems. To mention only a few, the thermodynamical properties of the metal-insulator transition in strongly correlated VO$_2$, the transport properties of thermoelectric PbTe or the electron-phonon interaction above the Verwey transition in magnetite Fe$_3$O$_4$ are all strongly...
influenced by anharmonicity. Even at low temperatures, where its effects are expected to be weaker, it must be taken into account to explain the pressure dependence of the crystal structure of Calcium, the inverse isotope effect in superconducting PdH, or the phonon spectra at the proximity of the liquid-solid transition of Helium at 0K. Finally, anharmonicity is crucial for understanding the ground state of a system when a quantum electronic phase transition coupled to the lattice occurs, as in e.g. ferroelectrics or CDW compounds. In most cases however, these effects are computationally too expensive to be evaluated in standard first-principle calculations, and therefore often disregarded.

Here, we report the investigation of the temperature and pressure dependence of the phonon spectra of NbSe$_2$ by using high resolution inelastic X-ray scattering (IXS) from a crystal in a diamond anvil cell, up to pressures as large as 16 GPa at T = 20 K. We observe that the strong temperature dependence of the soft phonon mode is reduced by pressure, but still present even at 16 GPa.

We show that the temperature and pressure dependence of the phonon spectra can be accurately accounted for when the effects of anharmonicity are explicitly included in the calculation. Anharmonic effects were calculated within the newly developed stochastic self-consistent harmonic approximation (SSCHA), yielding an unprecedented agreement with the experimentally determined temperature dependence of the phonon spectra at various pressures. We show that at low temperatures, for pressures between $P_{CDW}$ and $P_C$, the CDW is destroyed by quantum fluctuations, which easily overcome the double-well lattice potential and, thus, are strongly affected by the anharmonic part of the potential. Surprisingly, we observe that anharmonic effects dominate the low-energy phonon spectrum of 2H-NbSe$_2$ in a large pressure range, extending at least up to 16 GPa $>> P_{CDW}$ and down to the lowest temperatures. Finally, we demonstrate that a large electron-phonon interaction, mostly due to optical modes rather than to the soft longitudinal acoustic mode which drives the CDW instability, contributes substantially to superconductivity in 2H-NbSe$_2$, and naturally explains its insensitivity to the occurrence of a CDW.

Single crystals of 2H-NbSe$_2$ were grown using the vapor growth technique in sealed quartz tubes with iodine as a transport agent. Typical dimensions of the crystals are 100 × 100 × 50 μm$^3$ ($\vec{a} \times \vec{b} \times \vec{c}$). Pressure was generated using a diamond anvil cell, loaded with helium as a pressure transmitting medium to ensure highly hydrostatic conditions. Temperature was lowered using a custom-designed 4He cryostat, and pressure was varied in-situ at low temperature using a helium-pressurized membrane. Each cell contained two rubies to monitor the pressure in-situ using the fluorescence technique. Measurements of the phonon dispersion of 2H-NbSe$_2$ were taken between room temperature and 20 K, and for pressures ranging from 0.2 to 16 GPa.

IXS measurements were carried out on beamline ID28 at the ESRF. The x-ray beam was aligned along the c-axis of the crystal. We used the (9,9,9) reflection on the backscattering monochromator with an incident energy of 17.794 keV, and a corresponding energy resolution of 1.3 meV HWHM (lorentzian fit of the elastic peak). The x-ray beam was aligned along the c-axis of the crystal. We used the (9,9,9) reflection on the backscattering monochromator with an incident energy of 17.794 keV, and a corresponding energy resolution of 1.3 meV HWHM (lorentzian fit of the elastic peak). The x-ray beam was aligned along the c-axis of the crystal. We used the (9,9,9) reflection on the backscattering monochromator with an incident energy of 17.794 keV, and a corresponding energy resolution of 1.3 meV HWHM (lorentzian fit of the elastic peak). The x-ray beam was aligned along the c-axis of the crystal. We used the (9,9,9) reflection on the backscattering monochromator with an incident energy of 17.794 keV, and a corresponding energy resolution of 1.3 meV HWHM (lorentzian fit of the elastic peak). The x-ray beam was aligned along the c-axis of the crystal. We used the (9,9,9) reflection on the backscattering monochromator with an incident energy of 17.794 keV, and a corresponding energy resolution of 1.3 meV HWHM (lorentzian fit of the elastic peak). The x-ray beam was aligned along the c-axis of the crystal. We used the (9,9,9) reflection on the backscattering monochromator with an incident energy of 17.794 keV, and a corresponding energy resolution of 1.3 meV HWHM (lorentzian fit of the elastic peak).
ized gradient approximation making use of the QUANTUM ESPRESSO code. An ultrasoft pseudopotential (norm-conserving) for Nb (Se), a 35 Ry energy cut-off, and a $24 \times 24 \times 8$ mesh for the electronic integrations were used. An Hermitian-Gaussian smearing of 0.01 Ry was used. Harmonic dynamical matrices were calculated within linear response in a grid of $6 \times 6 \times 4$ $q$ points. The small smearing parameter and the dense electronic mesh used are needed to converge the phonon frequency of the longitudinal acoustic mode at the CDW wave vector (cf. SI). The stochastic self-consistent harmonic approximation (SSCHA) calculations were performed using a $3 \times 3 \times 1$ supercell, yielding anharmonic dynamical matrices in the commensurate $3 \times 3 \times 1$ grid. The difference between the SSCHA dynamical matrices and the harmonic dynamical matrices in the $3 \times 3 \times 1$ grid was Fourier interpolated to the points of the finer $6 \times 6 \times 4$ grid. Adding the harmonic dynamical matrices in the $6 \times 6 \times 4$ grid to the result of the interpolation, the SSCHA dynamical matrices in the finer $6 \times 6 \times 4$ mesh were obtained. The experimental lattice parameters with relaxed internal coordinates were used because in these conditions the results weakly depend on the exchange-correlation potential chosen.

The electron-phonon calculations were performed by using maximally localized Wannier functions and interpolation of the electron-phonon matrix elements as in Ref. We used 14 Wannier functions ($d$-states of Nb and Se $p_z$ states) and a $6 \times 6 \times 4$ electron-momentum grid. We used the Fourier interpolated SSCHA dynamical matrices in the electron-phonon coupling calculations. The average electron-phonon coupling was interpolated using electron and phonon momentum grids of $24 \times 24 \times 8$ randomly displaced from the origin.

The temperature dependence of the low energy phonon dispersions recorded at pressures of 3.5 and 16 GPa are shown in Fig. 2 (some of the corresponding raw data is shown in the supplementary materials). At $T = 20$ K and $P = 3.5$ GPa, the system is very close to the quantum critical regime reported in ref. No particular enhancement of the elastic line intensity close to the CDW wavevector $q_{CDW} \approx (1.67, 0, 0)$ is observed. On the other hand, a colossal temperature dependent softening of the longitudinal acoustic phonon mode is seen: from $\sim 9$ to $\sim 1.5$ meV between room temperature and 20 K. While this mode is expected to condense around $\sim 12$ K, this temperature could not be reached at this pressure with the current experimental set-up. As we increase pressure to 16 GPa, the amplitude of the phonon softening is significantly reduced, but remains sizeable as the mode’s energy almost decreases by a factor of 2 from 300 to 20 K. So far, most of the theoretical and experimental work on NbSe$_2$ has focused on the interplay between the electronic susceptibility and the electron-phonon interaction as possible mechanisms for the CDW formation. The large temperature dependence indicates that strong anharmonic effects survive over a pressure range that is way larger than the experimentally reported CDW stability range ($0 < P < P_{CDW}$) and might therefore play an important role that was up to now largely disregarded.

In Fig. 3, we plot the square of the soft phonon frequency measured at $T = 20$ K at $q_{CDW}$ as a function of pressure. The linear dependence indicates that the mode hardens as $\sqrt{P - P_{CDW}}$. We also plot the square of the phonon frequency calculated within the harmonic approximation, which is negative - i.e. indicating that the system is unstable against CDW formation - up to 14 GPa $> P_{CDW}$. This is reminiscent of the situation encountered at ambient pressure in NbS$_2$, where we have
observed a large phonon softening upon cooling, insufficient however to induce the CDW formation despite the predictions of the harmonic ab-initio calculation\textsuperscript{22}.

To quantify the effect of anharmonicity and check whether it is responsible for the destabilization of the CDW between $P_{CDW}$ and 14 GPa, we have carried out a series of calculations for the pressures and temperatures experimentally investigated, within the SSCHA approach\textsuperscript{27,34} (see SI) which allows us to access directly the anharmonic free energy of the system, with full inclusion of the anharmonic potential terms.

The results are superimposed to our experimental dispersions in Fig.2. Not only is the instability suppressed as experimentally observed, but the agreement between the measured and calculated dispersions over the entire pressure range is remarkable compared to harmonic ab-initio calculation. A small overestimation of phonon calculation is nevertheless observed in the range around $q_{CDW}$.

A key result here is that, even at low temperature, anharmonic terms play a key role in the destruction of the harmonically stable long-range CDW order. This is surprising at first glance since anharmonic effects usually manifest themselves at finite temperature, through the effect of many-body interactions between thermally excited phonons. These account for the lattice thermal expansion and for the decay of the phonons lifetime at high temperatures, but are usually strongly suppressed at low temperatures. On the other hand, given that atoms vibrate even at zero temperature due to the zero-point fluctuations, their motion can in principle be affected by the anharmonic potential. This appears to be the case in this system where, below 14 GPa, the harmonic part of the potential that drives the lattice instability is overwhelmed by the anharmonic part. The balance between these two parts of the potential tells whether there is a lattice instability (driven by the CDW) or not. This bears stark analogy with the destruction of long range magnetic order from spin-spin quantum fluctuations in low dimensional quantum magnets\textsuperscript{40}.

Finally we note that these many-body effects are relevant not only at $q = q_{CDW}$, but extend up to the M point, the boundary of the Brillouin zone at $q = a^*/2$, where two low-energy modes, the longitudinal acoustic mode that drives the CDW transition and an optical mode, are substantially hardened with respect to the result of the harmonic calculation.

The importance of the electron-phonon interaction in the CDW formation has been emphasized\textsuperscript{12,38}, but its role in superconductivity remains debated, as is, more generally, the interplay between these two orders. Indeed, the absence of reliable ab initio phonon calculations in the high symmetry phase, has prevented a calculation of the superconducting critical temperature. Having achieved a detailed understanding of the low energy part of the
TABLE I. Calculated $\lambda$, logarithmic frequency average $\omega_{\log}$, and $T_c$ values for 2H-NbSe$_2$ at 3.5, 7 and 16 GPa. The McMillan equation with $\alpha^* = 0.16$ is used to calculate $T_c$. Experimental data are taken from Ref.20.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>$\lambda$</th>
<th>$\omega_{\log}$ (meV)</th>
<th>$T_c$ calc. (K)</th>
<th>$T_c$ exp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>1.28</td>
<td>12.6</td>
<td>11.3</td>
<td>7.8</td>
</tr>
<tr>
<td>7</td>
<td>1.16</td>
<td>13.7</td>
<td>10.5</td>
<td>8.2</td>
</tr>
<tr>
<td>16</td>
<td>0.91</td>
<td>16.4</td>
<td>7.8</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Experimental phonon spectra and having shown how anharmonicity can suppress the long range ordered CDW phase, we can now address the superconducting properties of NbSe$_2$ by calculating the Eliashberg function and the integrated electron-phonon coupling (see SI) as a function of pressure. As of now, this calculation can only be done in the high pressure phase, where the number of atoms per unit cell is low enough. We show in Fig. 4 the results of the calculation at 7 GPa (data for other pressures are shown in the SI). We find that the average electron-phonon coupling is as large as $\lambda = 1.16$ (see Tab. I for other pressures), demonstrating that NbSe$_2$ is a strong coupling superconductor.

Previous works$^{1,12,16,17,41}$ identified the large electron-phonon coupling of the soft acoustic mode at $q_{\text{CDW}}$ as the mechanism responsible for the CDW formation. For this reason, it is natural to expect that this soft mode also plays a key role in superconductivity. However, its contribution to the average electron-phonon coupling is less than 17% (as it can be inferred from the integrated $\lambda(\omega)$ in Fig. 4), meaning that it has only a marginal role in superconductivity. Indeed, the strong coupling of this mode is very localized around $q_{\text{CDW}}$, and its contribution to $\lambda$ averages out when integrating over the Brillouin zone. The modes sustaining superconductivity are given by the two main contributions to the Eliashberg function: a broad peak centred around $\approx 11.5$ meV and a second one in the $22 - 26$ meV region. These two features contribute to $\approx 70\%$ of the total electron-phonon coupling. Further insights are obtained by decomposing the phonon density of states (DOS) in atomic vibrations along different directions. As the DOS and $\alpha^2 F(\omega)$ are very similar, the decomposition will also apply to the Eliashberg function. The low energy feature at 11.5 meV is mainly due to Nb and Se vibrations parallel to the Nb plane, corresponding to the flat phonon band along YM suffering from a large anharmonic correction, while the features in the $22 - 26$ meV range are mostly attributed to out-of-plane and in-plane Se displacements with a non negligible Nb component. In both modes sustaining superconductivity there is a substantial Se component, upturning the conventional wisdom that in superconducting dichalcogenides the chalcogene is accessory while the transition metal plays a key role$^4$. Our work demonstrates that the superconducting properties strongly depend on both the transition metal and the chalcogene, offering a natural explanation for the different relation between CDW and superconductivity encountered in different dichalcogenides$^{42-44}$. Moreover, as optical phonon modes contribute strongly to superconductivity in 2H-NbSe$_2$, while the CDW is determined by the softening of the longitudinal acoustic mode, the superconducting $T_c$ is insensitive to the presence of the CDW, explaining the phase diagram in Fig. 1.

Our work points toward the key role of anharmonicity in destroying the CDW order not only through the usual thermal phonon-fluctuations, but also through quantum phonon-fluctuations, and on a very wide pressure range above the quantum phase transition. Our results, in this respect, are fundamental and relevant for a very large set of materials exhibiting a CDW instability - or more generally a second order electronic quantum phase transition coupled to the lattice - such as transition metal dichalcogenides, cuprates, Bechgaard salts and transition metal bronzes.

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