

Multi-phonon diffuse scattering in solids from first-principles: Application to 2D MoS₂, bulk MoS₂, and black Phosphorous

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Time-resolved diffuse scattering experiments have gained increasing attention due to their potential to reveal non-equilibrium dynamics of crystal lattice vibrations with full momentum resolution. Although progress has been made in interpreting experimental data on the basis of one-phonon scattering, understanding the role of individual phonons can be sometimes hindered by multi-phonon excitations. In Ref. [arXiv:2103.10108] we have introduced a rigorous approach for the calculation of the all-phonon inelastic scattering intensity of solids from first-principles. In the present work, we describe our implementation in detail and show that multi-phonon interactions are captured efficiently by exploiting translational and time-reversal symmetries of the crystal. We demonstrate its predictive power by calculating the diffraction patterns of monolayer molybdenum disulfide (MoS₂), bulk MoS₂, and black phosphorus (bP), and we obtain excellent agreement with our measurements of thermal electron diffuse scattering. Remarkably, our results show that multi-phonon excitations dominate in bP across multiple Brillouin zones, while in MoS₂ play a less pronounced role. We expand our analysis for each system and we examine the effect of individual atomic and interatomic vibrational motion on the diffuse scattering signals. Our findings indicate that distinct features are explained by the collective displacement of MoS and specific pairs of P atoms. We further demonstrate that the special displacement method reproduces the thermally distorted configuration which generates precisely the all-phonon diffraction pattern. The present methodology opens the way for high-throughput calculations of the scattering intensity in crystals and the accurate interpretation of static and time-resolved diffuse scattering experiments.

I. INTRODUCTION

Nonequilibrium phenomena as diverse as phase transitions, polaron formation, electrical and thermal management in semiconductor devices, all derive from microscopic interactions between electrons and phonons, spins and phonons, as well as phonons with phonons [1–4]. Our understanding of such phenomena hinges on the development of joint experimental and theoretical tools which can access these interactions at the mode-resolved level with sufficient temporal resolution. Towards this goal, exciting methodological developments were recently achieved on the experimental side with structural probes, either using Femtosecond X-ray Diffuse Scattering or Femtosecond Electron Diffuse Scattering (FEDS) [5–14]. For the first time, these methods yield access to nonequilibrium phonon populations in momentum space, beyond the zone-center modes traditionally accessible with optical spectroscopies.

In these experiments, the observable depends on the

temporal evolution of the scattering intensity $I(\mathbf{Q}, t)$, where \mathbf{Q} is an arbitrary scattering wavevector determined by the difference in momentum of the incident and scattered radiation. The key information obtained is the changes in the diffracted intensities, as they reflect how different phonons get populated as a function of time t . In FEDS, these changes are visualized by computing the difference diffraction pattern $\Delta I(\mathbf{Q}, t)$ [13, 15]. In Figs. 1(a) and (b) we present a schematic illustration of FEDS and an exemplary $\Delta I(\mathbf{Q}, t)$ of bulk molybdenum disulfide (MoS₂). The left subplot in Fig. 1(b) simply shows the diffraction intensity as collected on the detector. Each \mathbf{Q} on this pattern can be expressed as a summation of a Bragg peak vector \mathbf{G} (centers of the Brillouin zones), and reduced phonon wavevectors \mathbf{q} . The right subplot shows $\Delta I(\mathbf{Q}, 100 \text{ ps})$ and displays a hot but thermalized distribution of phonons in the MoS₂ sample. The blue/red features represent a decrease/increase in the signal due to Bragg/diffuse scattering. The larger the intensity of the red features indicates regions of reciprocal space with higher phonon scattering probability. Recent works have shown that $\Delta I(\mathbf{Q}, t)$ can change profoundly and qualitatively as time evolves, reflecting non-thermal lattice dynamics [7, 9, 13]. Phonon populations typically evolve towards a hot, but thermal distribution

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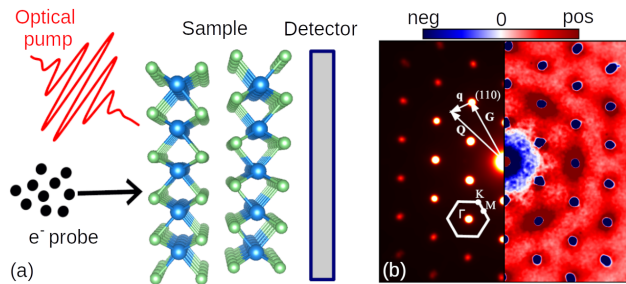


FIG. 1. (a) Schematic illustration of FEDS experiment on bulk MoS₂. More details about the setup can be found in Sed. III A and Ref. [16]. (b) Exemplary diffraction pattern of bulk MoS₂. Left subplot shows the raw diffraction pattern as collected on the detector. \mathbf{G} indicates the Bragg peak vector (110), \mathbf{q} the reduced phonon wavevector and $\mathbf{Q} = \mathbf{G} + \mathbf{q}$ the scattering vector. A hexagonal Brillouin zone with the high-symmetry points Γ , K , and M are also shown. Right subplot shows the difference diffraction pattern $\Delta I(\mathbf{Q}, 100 \text{ ps}) = I(\mathbf{Q}, 100 \text{ ps}) - I(\mathbf{Q}, t < t_0)$, where $I(\mathbf{Q}, t < t_0)$ is the average diffraction pattern prior to photoexcitation.

[e.g. right subplot of Fig. 1(b)] with a highly material-specific timescale.

Although FEDS measurements possess a wealth of information, data interpretation is rather complex due to the energy-integrated nature of the experiment and the multiple scattering phenomena involved. Therefore, before analysing the highly non-equilibrium phonon distributions, it is necessary to fully understand thermal diffuse scattering, i.e., inelastic scattering induced by phonons, using first-principles calculations. Recent first-principles calculations of diffuse diffraction [10, 12–14, 17–19] rely on the quantum theory of one-phonon scattering [20, 21]. Despite their great success in explaining some of the main features in the diffraction pattern, one-phonon interactions are considered inadequate to explain diffuse scattering at large $|\mathbf{Q}|$ and/or high temperatures [21, 22]. In fact, in these cases, the intensity contributed by multi-phonon can become comparable with, and even larger than, that of one-phonon excitations. A multi-phonon process occurs when the momentum transfer to the beam in a single scattering event is specified by more than one phonons. Other mechanisms that contribute to diffraction signals, usually forming a diffuse background, are multiple-phonon interactions (i.e. more than one electron scattering events [21]), inelastic scattering on plasmons and defects, or surface imperfections making the role of multi-phonon scattering inconclusive [23]. This situation highlights the need for computational tools that directly probe multi-phonon contributions and, in essence, go a step forward to extract phonon population dynamics across the entire Brillouin zone [12].

In Ref. [22] we have introduced a methodology for the calculation of the all-phonon scattering in solids, which enables us to single out the contribution of phonon in-

teractions, and thus isolate their scattering signatures. In the present work, we further validate our implementation by first calculating one- and multi-phonon diffraction patterns of monolayer MoS₂. Using the same system, we also demonstrate that the special displacement method (SDM) [24, 25] can provide an alternative route for the assessment of multi-phonon contributions. We then apply our technique for the calculation of bulk MoS₂ and black phosphorus (bP) diffraction patterns and obtain excellent agreement with experiment. Importantly, our results reveal that multi-phonon interactions are more manifested in bP than in MoS₂. For all systems, we also analyse the response of elastic and inelastic scattering to individual atomic and interatomic thermal motion. Our findings reveal that collective displacements of specific pairs of atoms are responsible for the distinct features observed in the scattering signals. Although this work focuses on a comparison between theory and FEDS measurements, we emphasize that the developments presented here are fully applicable to X-ray, or neutron, diffuse scattering.

The organization of this manuscript is as follows: in Secs. II A and II B we describe the theory of quantum mechanical scattering in solids and derive the main equations used to evaluate the respective phonon contributions. In Sec. II C and Appendix A we demonstrate that SDM can serve as an equivalent, but different, approach for calculating the all-phonon scattering intensity. In Sec. II D we describe the Einstein model for diffuse scattering. Sections III A and III B report all experimental and computational details of the measurements and calculations performed in this work. In Sec. IV we present our results for three semiconductors. More specifically in Sec. IV A we report scattering intensity calculations of 2D MoS₂ using the exact theory, special displacements, and the Einstein model. In Secs. IV B and IV C we report the phonon scattering intensities of bulk MoS₂ and bP, respectively, and compare our calculations of the difference diffraction patterns with experiment. The results are accompanied by an analysis of the multi-phonon contribution across multiple Brillouin zones, as well as of the diffuse scattering signatures of individual atomic and interatomic thermal motion. Our conclusions and outlook are presented in Sec. V.

II. THEORY

In this section we present the theoretical framework underpinning the evaluation of multi-phonon scattering intensity. Starting from the Laval-Born-James [26–28] theory, we derive the zero-phonon, one-phonon, and all-phonon scattering intensities in the harmonic approximation. We also demonstrate that exact diffraction patterns can be evaluated using SDM in the limit of dense Brillouin sampling. We stress that all subsequent expressions apply for electron, X-ray, and neutron diffuse scattering under the assumption of the kinematic approx-

imation [21]. In the following we adopt a similar notation as in Ref. [29].

A. Scattering intensity

Based on the adiabatic formulation of the quantum mechanical scattering theory, originally developed by Laval [26], Born [27], and James [28] (LBJ), the intensity of the wave scattered by the atoms in a crystal is given by [30]:

$$I_{\alpha n, \beta m}(\mathbf{Q}) = \left| \langle X_{\alpha n} | \sum_{p\kappa} f_{\kappa}(\mathbf{Q}) e^{i\mathbf{Q} \cdot [\mathbf{R}_p + \boldsymbol{\tau}_{\kappa} + \Delta\boldsymbol{\tau}_{p\kappa}]} | X_{\beta m} \rangle \right|^2. \quad (1)$$

Here the many-body electron-nuclear system is described in terms of the Born-Huang expansion [31], with $|X_{\alpha n}\rangle$ and $|X_{\beta m}\rangle$ representing the initial n and final m Born-Oppenheimer vibrational states which are associated with electronic states denoted by the Greek indices α and β . The summations run over all atoms κ in the unit cell and over all p indices of the direct lattice vectors \mathbf{R}_p . The lattice vectors define a Born-von Kármán supercell which contains N_p unit cells. The atomic scattering amplitude is denoted by $f_{\kappa}(\mathbf{Q})$ and is evaluated at the scattering vector \mathbf{Q} . The displacement vector of the atom κ from its equilibrium position vector $\boldsymbol{\tau}_{\kappa}$ is represented by $\Delta\boldsymbol{\tau}_{p\kappa}$. We note that for generality and brevity reasons, the scattering intensity $I(\mathbf{Q})$ is expressed in scattering units depending on the probe-sample interaction [30].

If we set the initial and final electrons in their Born-Oppenheimer ground state, i.e. $\alpha = \beta = 0$, perform the summation over all final vibrational states of the scatterer in Eq. (1), and use the closure relationship $\sum_m |X_{0m}\rangle \langle X_{0m}| = \mathbb{I}$, then we obtain:

$$I_{0n}(\mathbf{Q}) = \langle X_{0n} | I^{\{\tau\}}(\mathbf{Q}) | X_{0n} \rangle, \quad (2)$$

where

$$I^{\{\tau\}}(\mathbf{Q}) = \left| \sum_{p\kappa} f_{\kappa}(\mathbf{Q}) e^{i\mathbf{Q} \cdot [\mathbf{R}_p + \boldsymbol{\tau}_{\kappa} + \Delta\boldsymbol{\tau}_{p\kappa}]} \right|^2 \quad (3)$$

represents the scattering intensity arising from an instantaneous atomic configuration defined by the set of atomic displacements $\{\Delta\boldsymbol{\tau}_{p\kappa}\}$. We note that setting the electronic states at their ground level is justified for a system at thermal equilibrium before, and after, diffraction [27].

The LBJ scattering intensity at finite temperature T is obtained from Eq. (2) by taking the ensemble average over all possible configurations of the nuclei. That is:

$$I(\mathbf{Q}, T) = \frac{1}{Z} \sum_n \exp(-E_{0n}/k_B T) I_{0n}(\mathbf{Q}), \quad (4)$$

where E_{0n} stands for the energy of the nuclear state $|X_{0n}\rangle$, $Z = \sum_n \exp(-E_{0n}/k_B T)$ is the canonical partition function, and k_B is the Boltzmann constant. The

above relation can also be recognized as the Williams-Lax [32, 33] thermal average of the scattering intensity. This can be understood by writing the scattering intensity as a Fermi Golden rule [similar to Eq. (3) of Ref. [25]], consider no electronic excitations, and integrate over the energy transfer to the crystal [20].

B. Exact evaluation: Zero-phonon, one-phonon and all-phonon scattering intensities

Now, starting from Eq. (4) and employing the harmonic approximation, we derive the formulas of the zero-phonon (elastic scattering), one-phonon and multi-phonon (inelastic scattering) contributions. To this aim we adopt the normal mode coordinate formalism and first write the atomic displacement vector as:

$$\Delta\boldsymbol{\tau}_{p\kappa} = \left(\frac{M_0}{N_p M_{\kappa}} \right)^{1/2} \sum_{\mathbf{q}\nu} e^{i\mathbf{q} \cdot \mathbf{R}_p} \mathbf{e}_{\kappa, \nu}(\mathbf{q}) z_{\mathbf{q}\nu}, \quad (5)$$

where $z_{\mathbf{q}\nu}$ are the complex-valued normal coordinates associated with the mode of reduced wavevector \mathbf{q} and branch index ν , M_{κ} is the mass of the κ th atom, and M_0 is the atomic mass unit. The phonon polarization vector of the normal mode is denoted as $\mathbf{e}_{\kappa, \nu}(\mathbf{q})$ with Cartesian components $e_{\kappa\alpha, \nu}(\mathbf{q})$.

In the framework of the harmonic approximation, the nuclear wavefunction $|X_{0n}\rangle$ is expressed as a Hartree product of uncoupled quantum harmonic oscillators and the nuclear energy E_{0n} as a summation over the associated energy quanta. Writing the harmonic oscillators in terms of Hermite polynomials and employing the Mehler's sum rule [34] leads to the following integral form for the LBJ scattering intensity [25, 35]:

$$I(\mathbf{Q}, T) = \left\langle I^{\{\tau\}}(\mathbf{Q}) \right\rangle_T \quad (6)$$

$$= \prod_{\mathbf{q}\nu} \int \frac{dz_{\mathbf{q}\nu}}{\pi u_{\mathbf{q}\nu}^2} e^{-|z_{\mathbf{q}\nu}|^2 / u_{\mathbf{q}\nu}^2} I^{\{\tau\}}(\mathbf{Q}).$$

Here $\langle \cdot \rangle_T$ represents the ensemble thermal average which is taken as a multidimensional Gaussian integral over the normal coordinates in the same way with a Williams-Lax observable in the harmonic approximation [36]. The widths of the Gaussians are determined by the mode-resolved mean-square displacement of the atoms at temperature T :

$$u_{\mathbf{q}\nu}^2 = \frac{\hbar}{2M_0\omega_{\mathbf{q}\nu}} [2n_{\mathbf{q}\nu}(T) + 1], \quad (7)$$

where $n_{\mathbf{q}\nu}(T)$ represents the Bose-Einstein occupation of the phonon with frequency $\omega_{\mathbf{q}\nu}$. We note that Eq. (7) is indefinite for the zero-frequency translational modes (acoustic modes at Γ). These modes do not impose any change on the properties of the lattice and thus the associated mean-square displacement can be set to zero.

The exact expression for the calculation of the temperature-dependent scattering intensity is obtained with the aid of the Bloch identity [20]:

$$\langle e^{i\mathbf{Q}\cdot\Delta\boldsymbol{\tau}_{p\kappa}} \rangle_T = e^{-\frac{1}{2}\langle (\mathbf{Q}\cdot\Delta\boldsymbol{\tau}_{p\kappa})^2 \rangle_T}. \quad (8)$$

Hence, combining Eqs. (3) and (6) yields:

$$I(\mathbf{Q}, T) = \sum_{pp'} \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\mathbf{R}_p - \mathbf{R}_{p'} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'}]} \times e^{-\frac{1}{2}\langle \{\mathbf{Q}\cdot(\Delta\boldsymbol{\tau}_{p\kappa} - \Delta\boldsymbol{\tau}_{p'\kappa'})\}^2 \rangle_T}. \quad (9)$$

By replacing now $\Delta\boldsymbol{\tau}_{p\kappa}$ with the normal-coordinate transformation of Eq. (5), considering translational invariance of the lattice, and using the identity $\langle z_{\mathbf{q}\nu} z_{\mathbf{q}'\nu'}^* \rangle_T = u_{\mathbf{q}\nu}^2 \delta_{\mathbf{q}\mathbf{q}', \nu\nu'}$, we obtain the following com-

$$P_{p,\kappa\kappa'}(\mathbf{Q}, T) = \frac{2M_0 N_p^{-1}}{\sqrt{M_{\kappa} M_{\kappa'}}} \sum_{\mathbf{q} \in \mathcal{B}, \nu} u_{\mathbf{q}\nu}^2 \text{Re} \left[\mathbf{Q} \cdot \mathbf{e}_{\kappa, \nu}(\mathbf{q}) \mathbf{Q} \cdot \mathbf{e}_{\kappa', \nu}^*(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_p} \right] + \frac{M_0 N_p^{-1}}{\sqrt{M_{\kappa} M_{\kappa'}}} \sum_{\mathbf{q} \in \mathcal{A}, \nu} u_{\mathbf{q}\nu}^2 \mathbf{Q} \cdot \mathbf{e}_{\kappa, \nu}(\mathbf{q}) \mathbf{Q} \cdot \mathbf{e}_{\kappa', \nu}(\mathbf{q}) \cos(\mathbf{q} \cdot \mathbf{R}_p). \quad (12)$$

Here the summations are restricted to: (i) the group \mathcal{B} containing phonons with wavevectors that lie in the Brillouin zone and are not time-reversal partners, and (ii) the group \mathcal{A} containing phonons that remain invariant under time-reversal [25]. $\text{Re}[\cdot]$ represents the function that returns the real part of the argument inside the square brackets. Combining the partitioning of phonons in groups \mathcal{A} and \mathcal{B} with the use of translational symmetry of the crystal enables the efficient calculation of the all-phonon diffuse scattering intensity. This aspect is central in this manuscript and allows for the rapid assesment of multi-phonon excitations. The summations over different pairs of atoms in Eq. (10) can be conveniently partitioned into different parts to examine individual ($\kappa = \kappa'$) and distinct ($\kappa \neq \kappa'$) scattering contributions [38].

Physically, the Debye-Waller factor, $e^{-W_{\kappa}}$, determines the attenuation of the scattering intensity at temperature T owing to the vibrational motion of atom κ . The phononic factor, $e^{P_{p,\kappa\kappa'}}$, includes all-phonon contributions to diffuse scattering associated with the individual or combined thermal motion of atoms κ and κ' in unit cell p . For example, the zero-phonon, I_0 , and one-phonon, I_1 , contributions are obtained by retaining the zeroth and first-order terms in the Taylor expansion of $e^{P_{p,\kappa\kappa'}}$ [20]. Hence, if we use the standard sum rule $\sum_p \exp(i\mathbf{Q}\cdot\mathbf{R}_p) = N_p \delta_{\mathbf{Q}, \mathbf{G}}$, where \mathbf{G} is a reciprocal lattice vector and observe that $I_0(\mathbf{G}, T) = I_0(-\mathbf{G}, T)$, we

can write the zero-phonon, or Bragg scattering, term as:

$$I_{\text{all}}(\mathbf{Q}, T) = N_p \sum_p \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\mathbf{R}_p + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'}]} \times e^{-W_{\kappa}(\mathbf{Q}, T)} e^{-W_{\kappa'}(\mathbf{Q}, T)} e^{P_{p,\kappa\kappa'}(\mathbf{Q}, T)}. \quad (10)$$

In this formula the exponent of the Debye-Waller factor is defined as:

$$-W_{\kappa}(\mathbf{Q}, T) = -\frac{M_0}{N_p M_{\kappa}} \sum_{\mathbf{q} \in \mathcal{B}, \nu} |\mathbf{Q} \cdot \mathbf{e}_{\kappa, \nu}(\mathbf{q})|^2 u_{\mathbf{q}\nu}^2 \quad (11) - \frac{M_0}{2N_p M_{\kappa}} \sum_{\mathbf{q} \in \mathcal{A}, \nu} |\mathbf{Q} \cdot \mathbf{e}_{\kappa, \nu}(\mathbf{q})|^2 u_{\mathbf{q}\nu}^2,$$

and the exponent of the phononic factor as:

can write the zero-phonon, or Bragg scattering, term as:

$$I_0(\mathbf{Q}, T) = N_p^2 \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) \cos[\mathbf{Q} \cdot (\boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'})] \times e^{-W_{\kappa}(\mathbf{Q}, T)} e^{-W_{\kappa'}(\mathbf{Q}, T)} \delta_{\mathbf{Q}, \mathbf{G}}. \quad (13)$$

This expression is directly related to the Laue's interference condition and has very sharp maxima whenever $\mathbf{Q} = \mathbf{G}$, or reduces to zero otherwise.

Similarly to the zero-phonon term, one can obtain a compact formula for the one-phonon contribution to the scattering intensity by following a straightforward, but more lengthy, derivation. The final result is:

$$I_1(\mathbf{Q}, T) = N_p \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) \frac{e^{-W_{\kappa}(\mathbf{Q}, T)} e^{-W_{\kappa'}(\mathbf{Q}, T)}}{\sqrt{M_{\kappa} M_{\kappa'}}} \times \sum_{\nu} \text{Re} \left[\mathbf{Q} \cdot \mathbf{e}_{\kappa, \nu}(\mathbf{Q}) \mathbf{Q} \cdot \mathbf{e}_{\kappa', \nu}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_{\kappa}]} \right] u_{\mathbf{Q}\nu}^2. \quad (14)$$

C. All-phonon scattering intensity using the special displacement method

Recently, it has been shown that any Williams-Lax thermal average in the form of Eq. (6) can be evaluated using the special displacement method (SDM) developed by Zacharias and Giustino (ZG) [24, 25]. SDM amounts to applying ZG displacements on the nuclei away from

their equilibrium positions given by [25]:

$$\Delta\tau_{p\kappa}^{\text{ZG}} = \sqrt{\frac{M_0}{N_p M_\kappa}} \left[\sum_{\mathbf{q} \in \mathcal{B}, \nu} S_{\mathbf{q}\nu} u_{\mathbf{q}\nu} 2 \operatorname{Re} \left[e^{i\mathbf{q} \cdot \mathbf{R}_p} \mathbf{e}_{\kappa, \nu}(\mathbf{q}) \right] + \sum_{\mathbf{q} \in \mathcal{A}, \nu} S_{\mathbf{q}\nu} u_{\mathbf{q}\nu} \cos(\mathbf{q} \cdot \mathbf{R}_p) \mathbf{e}_{\kappa, \nu}(\mathbf{q}) \right]. \quad (15)$$

In the above relation the amplitudes of the normal coordinates entering Eq. (5) are set to $|z_{\mathbf{q}\nu}| = u_{\mathbf{q}\nu}$, and their signs to $S_{\mathbf{q}\nu}$. For practical calculations, the choice of signs is made such that the following function is minimized:

$$E(\{S_{\mathbf{q}\nu}\}, T) = \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \left| \sum_{\substack{\mathbf{q} \in \mathcal{B} \\ \nu < \nu'}} \operatorname{Re} [e_{\kappa\alpha, \nu}(\mathbf{q}) e_{\kappa'\alpha', \nu'}^*(\mathbf{q})] u_{\mathbf{q}\nu} u_{\mathbf{q}\nu'} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'} + \sum_{\substack{\mathbf{q} \in \mathcal{A} \\ \nu < \nu'}} e_{\kappa\alpha, \nu}(\mathbf{q}) e_{\kappa'\alpha', \nu'}^*(\mathbf{q}) u_{\mathbf{q}\nu} u_{\mathbf{q}\nu'} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'} \right| \quad (16)$$

We note that the above function reduces exactly to zero in the limit of dense Brillouin zone sampling, since all summands inside the modulus remain nearly the same and have opposite sign for adjacent \mathbf{q} -points [25]. More details about the allocation of the signs $S_{\mathbf{q}\nu}$, as well as the ordering of phonons for the construction of ZG displacements are given in Sec. III B. Minimization of Eq. (16) guarantees that: (i) the error in the calculation of the temperature-dependent observable is eliminated, and (ii) the quantum mechanical anisotropic displacement tensor of the atoms, defined as [39]

$$U_{\kappa, \alpha\alpha'}(T) = \frac{2M_0}{N_p M_\kappa} \sum_{\mathbf{q} \in \mathcal{B}, \nu} \operatorname{Re} [e_{\kappa\alpha, \nu}(\mathbf{q}) e_{\kappa\alpha', \nu}^*(\mathbf{q})] u_{\mathbf{q}\nu}^2 + \frac{M_0}{N_p M_\kappa} \sum_{\mathbf{q} \in \mathcal{A}, \nu} e_{\kappa\alpha, \nu}(\mathbf{q}) e_{\kappa\alpha', \nu}(\mathbf{q}) u_{\mathbf{q}\nu}^2, \quad (17)$$

is recovered. This quantity also determines the thermal ellipsoids of the crystal and its diagonal elements are closely related to the exponent of the Debye-Waller factor given by Eq. (11).

The calculation of the scattering intensity at finite temperatures using SDM requires to simply set $\Delta\tau_{p\kappa} = \Delta\tau_{p\kappa}^{\text{ZG}}$ in Eq. (3), and thus calculate Eq. (4) for a single distorted configuration. That is:

$$I_{\text{ZG}}(\mathbf{Q}, T) = \left| \sum_{p\kappa} f_\kappa(\mathbf{Q}) e^{i\mathbf{Q} \cdot [\mathbf{R}_p + \boldsymbol{\tau}_\kappa + \Delta\tau_{p\kappa}^{\text{ZG}}]} \right|^2. \quad (18)$$

The proof that the Williams-Lax thermal average of a generic observable can be evaluated using the ZG displacements is provided in Ref. [25]. In Appendix A, we demonstrate, using a different approach, that Eq. (18) is equivalent to Eq. (10), as long as Eq. (16) is minimized. This finding reinforces the concept that nuclei

positions defined by ZG displacements can describe accurately thermal disorder in solids and, here, can be viewed as the *collection of scatterers that best reproduce the diffuse scattering intensity*.

D. Scattering intensity using the Einstein model

For an Einstein solid, the scattering intensity can be evaluated by assuming that all atoms vibrate independently and with the same frequency [40]. These approximations allow one to replace: (i) the mode-resolved mean-square displacement of the atoms $u_{\mathbf{q}\nu}^2$ by a constant $u_{\text{E}}^2 = \hbar / (2M_0\omega_{\text{E}}) [2n_{\text{E}}(T) + 1]$, where ω_{E} is the average phonon frequency of the crystal and n_{E} the associated Bose-Einstein occupation, and (ii) the phonon polarization vectors $\mathbf{e}_{\kappa, \nu}(\mathbf{q})$ with a normalized isotropic eigenvector [41]. Applying (i) and (ii) to Eq. (10), the scattering intensity within the Einstein model reads:

$$I_{\text{E}}(\mathbf{Q}, T) = N_p^2 \sum_{\kappa\kappa'} f_\kappa(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) \cos[\mathbf{Q} \cdot (\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'})] \times e^{-C_{\kappa\kappa}(\mathbf{Q}, T)} e^{-C_{\kappa'\kappa'}(\mathbf{Q}, T)} \delta_{\mathbf{Q}, \mathbf{G}} \quad (19) + N_p \sum_{\kappa\kappa'} f_\kappa(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) \cos[\mathbf{Q} \cdot (\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'})] \times e^{-C_{\kappa\kappa}(\mathbf{Q}, T)} e^{-C_{\kappa'\kappa'}(\mathbf{Q}, T)} \left[e^{2C_{\kappa\kappa'}(\mathbf{Q}, T)} - 1 \right],$$

where $C_{\kappa\kappa'}(\mathbf{Q}, T) = M_0 u_{\text{E}}^2 \mathbf{Q}^2 / \sqrt{4M_\kappa M_{\kappa'}}$. The first and second summations represent the elastic and inelastic terms, respectively. The above oversimplified expression provides a quick estimate of the contribution of the first and higher order excitations based on the power series expansion of $e^{2C_{\kappa\kappa'}(\mathbf{Q}, T)}$. For example, keeping terms up to the first order in $C_{\kappa\kappa'}(\mathbf{Q}, T)$ yields the Einstein model's analogue of Eq. (14).

III. METHODS

A. Experiment

The FEDS measurements are performed in transmission using the compact diffractometer described in detail elsewhere [16]. Briefly, the output of a REGEN amplifier (Astrella, Coherent, 4 kHz, pulse duration 50 fs) is split into a pump arm and a probe arm. A commercial optical parametric amplifier is used to generate pump pulses with tunable wavelength. The electron probe is generated from two-photon absorption of around 500 nm photons obtained from a home-built NOPA and subsequent photoemission from a gold photo-cathode. The photo-emitted electron bunches are accelerated towards the anode to reach 60-90 keV as they exit the gun. Each electron bunch is estimated to contain $\simeq 10^3$ electrons, with an estimated duration at the sample of $\simeq 200$ fs. Diffraction patterns are recorded with a phosphor screen fiber-coupled to a CMOS detector (TVIPS).

For sample preparation, bulk black phosphorus and MoS₂ crystals were purchased from *HQ Graphene*. Free-standing thin films were obtained in both cases by mechanical exfoliation and subsequent transfer to TEM grids using the floating technique [42]. Due to their air-sensitivity, the bP flakes were transferred to vacuum immediately after preparation to prevent degradation of the bulk film.

All data were processed using the open-source python module *scikit-ued* [43]. In particular, a six-fold (two-fold) symmetrization operation was performed on the raw MoS₂ (bP) diffraction patterns for visualization purposes only.

B. Computational details

Ab initio calculations were performed using planewaves basis sets and the PBE generalized gradient approximation [44] to density-functional theory (DFT), as implemented in the **Quantum ESPRESSO** software package [45, 46]. We used the primitive cells of monolayer MoS₂ (space group P6m2), bulk MoS₂ (space group P6₃/mmc), and bp (space group Cmce) that contain 3, 6, and 4 atoms, respectively. We employed Hartwigsen-Goedecker-Hutter [47] norm-conserving pseudopotentials for bulk and monolayer MoS₂, and Troullier-Martins [48] norm-conserving pseudopotentials for bP. The planewaves kinetic energy cutoff was set to 120 Ry for bulk and monolayer MoS₂, and 90 Ry for bP. Self-consistent-field calculations were performed using Brillouin zone **k**-grids of 10×10×1 (monolayer MoS₂), 10×10×3 (bulk MoS₂), and 12×10×10 (bP) points. To limit interactions between periodic replicas of the monolayer, we used an interlayer vacuum of 15 Å. The optimized lattice parameters were $a = 3.168$ Å for monolayer MoS₂; $a = 3.191$ Å and $c = 12.431$ Å for bulk MoS₂; $a = 3.307$ Å, $b = 4.554$ Å, and $c = 11.256$ Å for bP. We determined the interatomic force constants by means of density-functional perturbation theory calculations [49] using Brillouin-zone **q**-grids of 8×8×1 (monolayer MoS₂), 8×8×2 (bulk MoS₂), and 5×5×5 (bP) points.

The zero (I_0), one (I_1), and all (I_{all}) phonon scattering intensities were calculated using Eqs. (13), (14) and (10), respectively. For the calculation of the exponent of the Debye-Waller [Eq. (11)] and phononic [Eq. (12)] factors, the full set of phonon eigenmodes and eigenfrequencies was obtained by using standard Fourier interpolation of dynamical matrices on **q**-grids of 50×50×1 (monolayer) and 50×50×50 (bulk systems) points, unless specified otherwise. Equivalent modulo **G** scattering vector grids (**Q**-grids) were employed to sample the diffraction pattern per Brillouin zone of each system. We must emphasize that it is erroneous to compute the all-phonon scattering intensity using nonequivalent **Q**- and **q**-grids, since this violates the momentum selection rule and gives rise to artefacts in the diffraction pattern. For MoS₂ systems we show diffraction patterns calculated in the

Q_x - Q_y planes at $Q_z = 0$, where Q_x , Q_y , and Q_z are the Cartesian components of **Q**. bP diffractions patterns are obtained as the average of the scattering intensities at $Q_z = 0$ and $Q_z = 2\pi/c = 0.56$ Å⁻¹ planes. The atomic scattering amplitudes $f_\kappa(\mathbf{Q})$ for each atom were obtained analytically as a sum of Gaussian functions [50] using the parameters in Ref. [51]. For the calculation of the full diffraction maps of MoS₂ and bP crystals, we applied a six-fold and four-fold rotation symmetry around the Γ -point, respectively.

The sets of special displacements [Eq. (15)] of each structure were generated via the **ZG** executable (**ZG.x**) under the **EPW** software package [52]. The general procedure for applying SDM is described in Ref. [25]. In short, here we (i) used the same **q**-grid as for the Debye-Waller and phononic factors, (ii) ordered the phonon eigenmodes and frequencies along a simple space-filling curve that passes through all **q**-points, (iii) ensured similarity by enforcing a smooth Berry connection between the phonon eigemodes at adjacent **q**-points, and (iv) assigned 2^{n-1} unique combinations of n signs $\{S_{\mathbf{q}\nu}, \dots, S_{\mathbf{q}\nu'}\}$ to every 2^{n-1} **q**-points, where n is equal to the number of phonon branches. These choices together with the dense grids employed guarantee fast minimization of Eq. (16). The **ZG** scattering intensity was calculated with Eq. (18) using the same **Q**-grid as for the all-phonon scattering intensity. We emphasize that implementing Eq. (18) is much more straightforward than Eq. (10). Hence, SDM serves as a guide for validating the calculations of the all-phonon diffuse scattering intensity.

The **FORTRAN** code used for the calculation of all-phonon contributions to the scattering intensity together with instructions for reproducing the results of this manuscript is available at the **EPW/ZG** tree ([https://gitlab.com/...](https://gitlab.com/)). The **ZG** scattering intensity was computed with **ZG.x**. It is worth noting that the fine grids employed for the purposes of this work do not have high computational requirements since they do not involve extra DFT steps. In fact, these codes act as post-processing steps and allow for the rapid evaluation of the (**ZG** or **LBJ**) scattering intensity of any material, provided that the interatomic force constants have been already computed. No restrictions are imposed on the methodology followed for the evaluation of interatomic force constants; this can be by means, for example, of density-functional perturbation theory [49], the frozen-phonon method [53], the self-consistent harmonic approximation [54], or ab-initio molecular dynamics [55].

IV. RESULTS

A. Monolayer MoS₂

Figures 2(a), (b), and (c) show the all-phonon scattering intensity at $T = 300$ K in the reciprocal space of monolayer MoS₂ and its decomposition into zero-plus-one-phonon, and multi-phonon contributions, re-

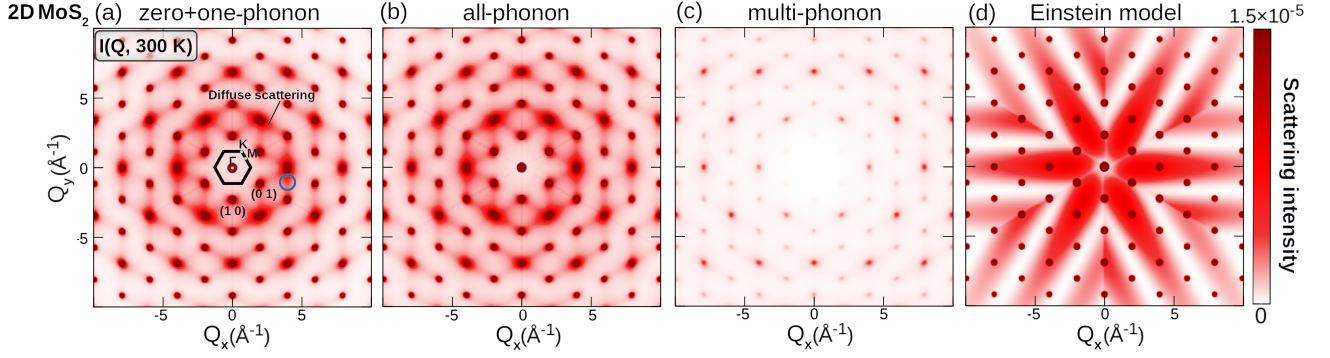


FIG. 2. (a) Zero-plus-one-phonon, (b) all-phonon, (c) multi-phonon, and (d) Einstein model scattering intensity of monolayer MoS₂ calculated for $T = 300$ K. In plot (a) we show the fundamental Brillouin zone together with the high-symmetry points Γ , K and M. We also show the (1 0) and (0 1) Bragg peaks, as well as an example of diffuse scattering signal. Blue circle indicates a rapid decrease in the diffuse scattering intensity. The sampling of the Brillouin zone was performed using a 50×50 \mathbf{q} -grid. For all plots the scattering intensity is divided by the Bragg peak at the centre of the Brillouin zone, i.e with $I_0(\mathbf{Q} = \mathbf{0}, T)$.

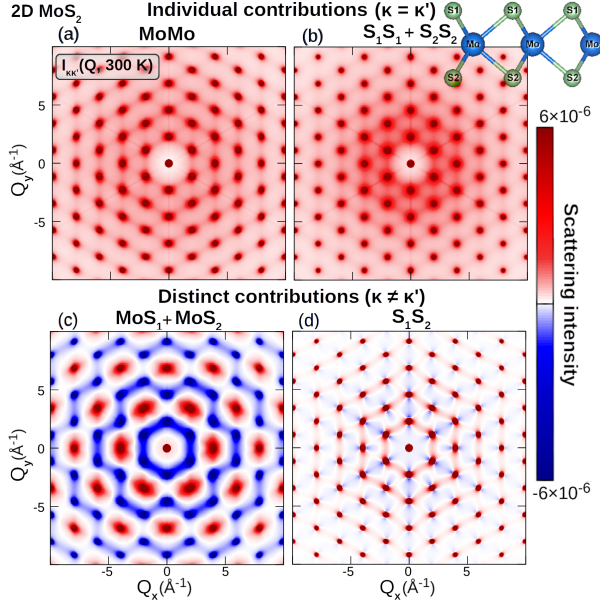


FIG. 3. Individual and distinct atomic contributions to the all-phonon scattering intensity of monolayer MoS₂ calculated for $T = 300$ K. (a) and (b) is for the Mo and S individual scattering terms. (c) and (d) is for the MoS and S₁S₂ distinct scattering terms. The Brillouin zone sampling was performed using a 50×50 \mathbf{q} -grid. Data is divided by the total Bragg intensity at the centre of the Brillouin zone, i.e with $I_0(\mathbf{Q} = \mathbf{0}, T)$.

spectively. All-phonon and zero-plus-one-phonon excitations were accounted for via Eq. (10) and combining Eqs. (11) and (12), respectively; full computational details are provided in Sec. III B. Both sets of data have been normalized such that the scattering intensity at the zone-center is equal to 1. The multi-phonon scattering intensity was obtained from $I_{\text{multi}} = I_{\text{all}} - I_0 - I_1$. Our results show that the diffuse diffraction pattern of monolayer MoS₂ is determined to a large extent by one-phonon

scattering, while multi-phonon interactions play a secondary role without introducing new features. To quantitatively assess the effect of multi-phonon processes on the diffraction pattern we report in Fig. 5(a) the percentage $\mathcal{P} = I_{\text{multi}} / (I_1 + I_{\text{multi}}) \times 100$ as a function of $|\mathbf{Q}|$, i.e. the distance of the scattering vector from the zone-center. The response of the scattering intensity to multi-phonon excitations increases as we move radially outwards from the center, exceeding 50% for $|\mathbf{Q}| \geq 12 \text{ \AA}^{-1}$. However, when $\mathbf{Q} \sim \mathbf{G}$ (centers of Brillouin zones), we find that single-phonon contributions dominate and \mathcal{P} reduces significantly.

In Fig. 2(d), we present the total scattering intensity in the Einstein model calculated using Eq. (19) and setting $\omega_E = 287.4 \text{ cm}^{-1}$. With no surprise, the Einstein model fails completely to explain diffuse scattering in 2D MoS₂ resembling diffraction patterns calculated for isotropic systems [56]. However, this approximation can provide a rough prediction of the multi-phonon contributions to diffuse scattering by evaluating the total energy transfer to the crystal, $\Delta\mathcal{E}$, as defined in Ref. [22]. For the range presented in Fig. 2, the Einstein model yields $\Delta\mathcal{E}_E = 10\%$ in very close agreement with the exact value $\Delta\mathcal{E} = 11\%$ obtained within the LBJ theory. It is worth nothing that a corresponding calculation of the percentage \mathcal{P} will miss the reduced contribution of multi-phonon interactions at the Bragg peaks [22].

To understand the main features in the diffraction pattern of monolayer MoS₂ we examine the individual atomic ($\kappa = \kappa'$) and interatomic ($\kappa \neq \kappa'$) terms entering Eq. (14). Figures 3(a) and (b) show our calculations for the Mo and S individual contributions to the all-phonon scattering intensity. In both cases, the Bragg scattering amplitude decreases gradually with the distance from the zone-center. In view of Eq. (13), this gradual decrease is attributed solely to the attenuation coming from the Debye-Waller and atomic form factors, since the modulation factor $\cos[\mathbf{Q} \cdot (\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'})]$ simplifies to 1 for the individual terms. The same holds for the strong diffuse scat-

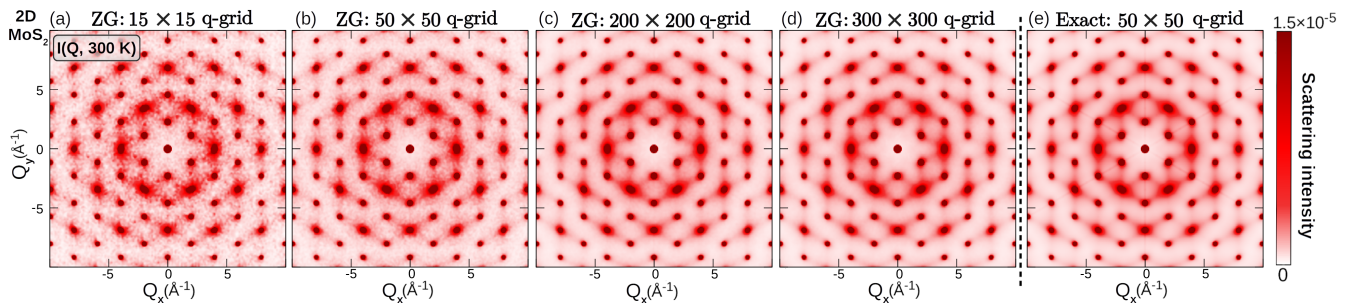


FIG. 4. (a)-(d) Convergence of the ZG scattering intensity of monolayer MoS₂ at $T = 300$ K with respect to the Brillouin sampling. (e) Exact all-phonon scattering intensity calculated using Eq. (10). All data is divided by the Bragg peak at the centre of the Brillouin zone, i.e with $I_0(\mathbf{Q} = \mathbf{0}, T)$.

tering concentrated in the vicinity of the Bragg peaks. Within the first Brillouin zone, the diffraction maps exhibit a relatively weak intensity as a result of the small transferred momenta.

Figures 3(c) and (d) show the response of the all-phonon scattering intensity to each inequivalent distinct pairing: MoS and S₁S₂. It is evident that MoS collective displacements tend to decrease, or increase, the Bragg scattering intensity depending on the factor $\cos[\mathbf{Q} \cdot (\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'})]$ and the symmetry of the structure. In particular, our analysis shows that for a Bragg scattering vector $\mathbf{Q} = (h k)$, the MoS pairs enhance (suppress) the total intensity when $|h - k| = 3n$ ($\neq 3n$), where h, k and n are integers. MoS paired thermal fluctuations also contribute to the diffuse scattering constructively, or destructively, explaining the rapid decrease in the scattering probability between adjacent Bragg peaks, as indicated in Fig. 2(a). For S₁S₂ distinct terms, the cosine modulation factor simplifies to 1 owing to the positions of the two inequivalent S atoms, thereby enhancing Bragg scattering. The correlated vibrational motion between sulfide atoms tends to reduce diffuse scattering in a way that a star-like domain is formed in the diffraction pattern of monolayer MoS₂.

Evaluation of the all-phonon scattering intensity using the ZG displacement

As described in Secs. IIC and IIIB, SDM constitutes an alternative way for the evaluation of the scattering intensity and can be used as a tool to further verify our implementation of Eq. (10). Here we provide a detailed convergence test, using the example of monolayer MoS₂, and demonstrate that the two approaches give identical results in the limit of dense Brillouin sampling.

In order to analyze the convergence behavior of the SDM, in Figs. 4(a)-(d) we plot the dependence of the ZG scattering intensity on the \mathbf{q} -grid used to generate special displacements. For comparison purposes, in Fig. 4(e) we also present the data obtained using the exact expression in Eq. (10). The ZG scattering intensity calculated for a 15×15 \mathbf{q} -grid, commensurate with the supercell size of re-

alistic ZG DFT-calculations, compares well with the exact result and reveals all main features in the diffraction map. Deviations from the Bragg and inelastic scattering, which appear as a statistical background noise, are explained by the error in the evaluation of the ZG observable. As shown in Figs. 4(b)-(d), this error is alleviated by using finer \mathbf{q} -grids and vanishes in the limit of dense Brillouin sampling, i.e. for a 300×300 \mathbf{q} -grid. The agreement between the two methods is further substantiated in Fig. A.1, where the multi-phonon contribution to the all-phonon scattering intensity is identical when calculated with ZG displacements, or with Eq. (10). A similar conclusion can be drawn by comparing \mathcal{P} in Figs. 5(a) and (b). This successful comparison provides the first rigorous numerical proof that SDM can seamlessly capture higher-order terms in the Taylor expansion of the observable.

Following the above analysis, it becomes apparent that ZG displacements lead precisely to the thermally distorted structure that reproduces the all-phonon diffuse scattering. Although thermal diffuse scattering is fundamentally related to the phonon properties of the crystal, this concept reinforces the use of ZG displacements for the evaluation of temperature-dependent electronic and optical properties of solids, as attested in Refs. [24, 25, 57–70]. It is also evident that ZG calculations can capture accurately all terms in the Taylor expansion of the observable of interest, and thus can serve as a tool for the assessment of multi-phonon effects, including electron-multi-phonon coupling. On top of that, SDM can be upgraded straightforwardly for the calculation of ultrafast electron-phonon mediated properties [13]. In particular, nonequilibrium phonon occupations computed by the Boltzmann transport equation [4] can enter directly Eq. (7), and hence allow for the generation of time-resolved ZG displacements via Eq. (15).

B. Bulk MoS₂

Figures 6(a)-(c) show the zero-plus-one phonon, all-phonon, and ZG diffraction patterns of bulk MoS₂ at $T = 300$ K. All sets of data have been normalized such

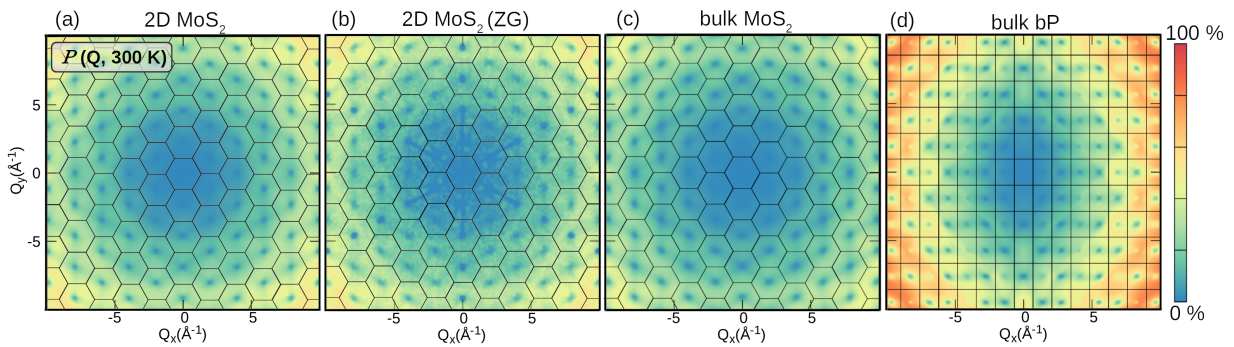


FIG. 5. Percentage contribution of multi-phonon interactions to diffuse scattering of (a),(b) monolayer MoS₂, (c) bulk MoS₂, and (d) bulk black Phosphorous (bP) calculated as $\mathcal{P} = I_{\text{multi}}/(I_1 + I_{\text{multi}}) \times 100$ at $T = 300$ K. (a), (c), and (d) represent calculations within the LBJ theory and (b) using ZG displacements. Diffraction maps are separated into Brillouin zones to highlight the extent of multi-phonon interactions.

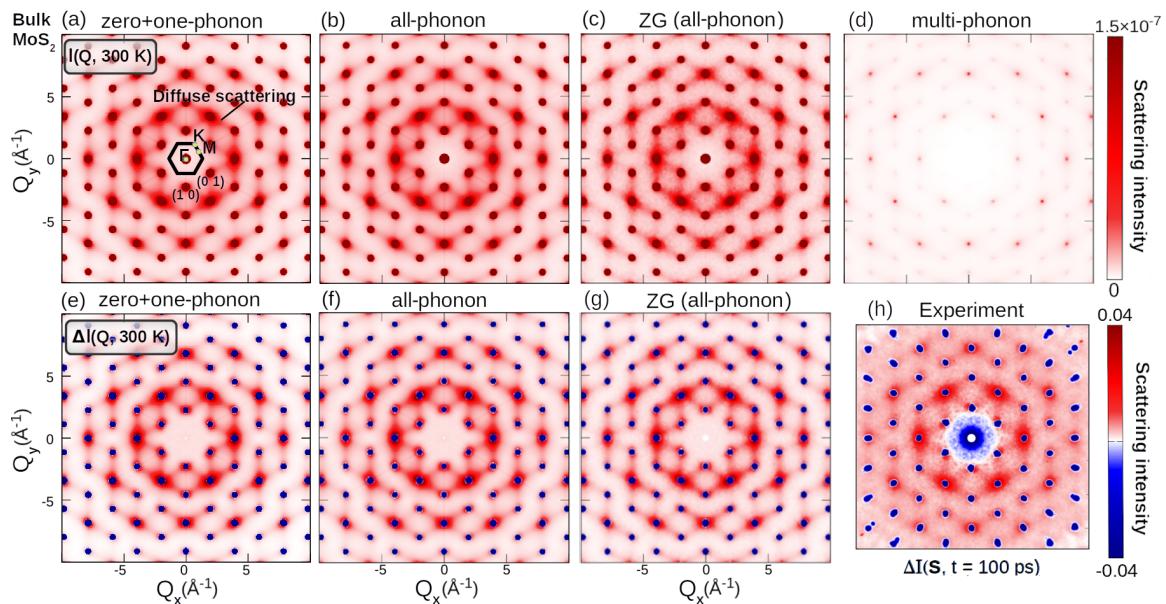


FIG. 6. (a) Zero-plus-one-phonon, (b) all-phonon, (c) ZG (all-phonon), and (d) multi-phonon scattering intensity of bulk MoS₂ calculated for $T = 300$ K. The calculated intensities are divided by the Bragg intensity at the centre of the Brillouin zone, i.e. with $I_0(\mathbf{Q} = \mathbf{0}, T)$. In plot (a) we show the fundamental Brillouin zone together with the high-symmetry points Γ , K , and M . We also show the $(1\ 0)$ and $(0\ 1)$ Bragg peaks, as well as an example of diffuse scattering signal. In plot (a) we indicate the $(1\ 0)$ and $(0\ 1)$ Bragg peaks, as well as regions of diffuse and Bragg scattering. (e) Zero-plus-one-phonon, (f) all-phonon and (g) ZG (all-phonon) diffraction maps of bulk MoS₂ calculated as $\Delta I(\mathbf{Q}, 300\text{ K}) = I(\mathbf{Q}, 300\text{ K}) - I(\mathbf{Q}, 100\text{ K})$. (h) Experimental diffraction signals of bulk MoS₂ measured at 100 ps. Signals are divided by the maximum count due to elastic scattering. For comparison purposes, the simulated data is multiplied by 500000 to match the experiment. The sampling of the Brillouin zone was performed using a $50 \times 50 \times 50$ \mathbf{q} -grid.

that the scattering intensity at the zone-center is equal to 1. The diffraction pattern of bulk MoS₂ is qualitatively identical to the diffraction pattern of its monolayer counterpart shown in Fig. 2. Quantitatively, the major difference is that the intensity of Bragg scattering in bulk MoS₂ is about two orders of magnitude higher. These findings suggest that collective displacements between any two atoms that lie in separate MoS₂ layers do not participate actively in diffuse scattering. Indeed, our analysis (not shown) confirms that these distinct pairs contribute predominantly to Bragg scattering and very

little to diffuse scattering. Similarly to the monolayer MoS₂, the main characteristics in the diffraction pattern arise from the MoS correlated displacements, while the star-like domain is due to the S_1S_2 pair.

In Fig. 6(d) we present the multi-phonon structure factor map of bulk MoS₂, obtained as the difference between the all-phonon and zero-plus-one-phonon diffraction patterns, i.e. $I_{\text{multi}} = I_{\text{all}} - I_0 - I_1$. Our results reveal that scattering beyond one phonon does not smear out the fundamental information enhancing slightly the scattering signal. This observation is further supported by

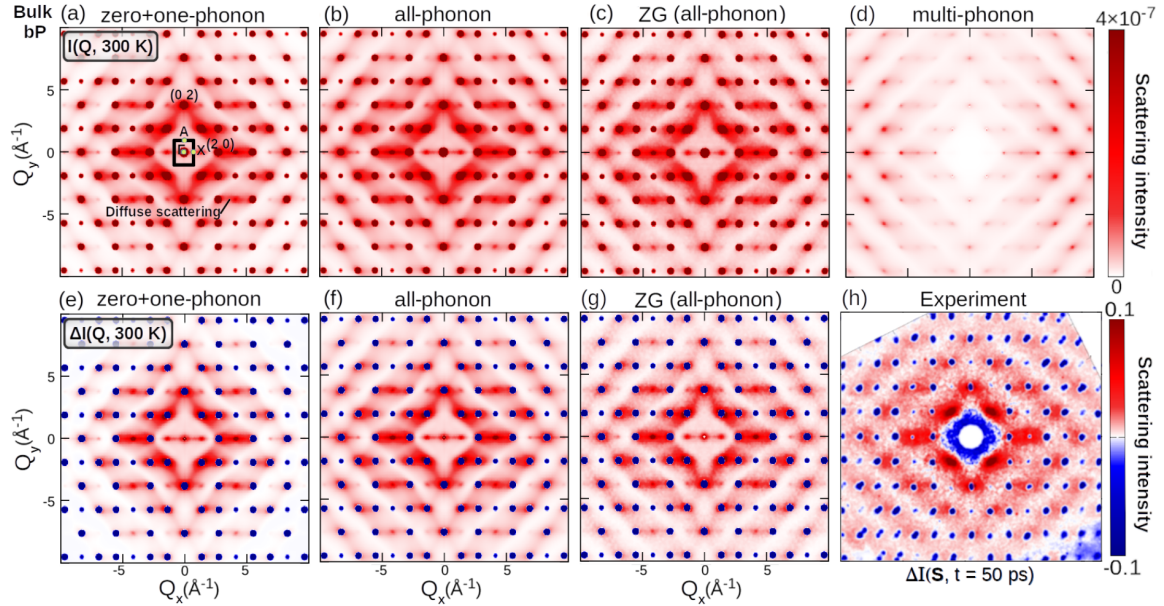


FIG. 7. (a) Zero-plus-one-phonon, (b) all-phonon, (c) ZG (all-phonon), and (d) multi-phonon scattering intensity of bulk black Phosphorous (bP) calculated for $T = 300$ K. The calculated intensities are divided by the elastic scattering at the central Bragg peak, $I_0(\mathbf{Q} = \mathbf{0}, T)$. In plot (a) we show the fundamental Brillouin zone together with the high-symmetry points Γ , A and X. We also show the (2 0) and (0 2) Bragg peaks, as well as an example of diffuse scattering signal. (e) Zero-plus-one-phonon, (f) all-phonon, and (g) ZG (all-phonon) difference diffraction maps of bulk black Phosphorous calculated as $\Delta I(\mathbf{Q}, 300 \text{ K}) = I(\mathbf{Q}, 300 \text{ K}) - I(\mathbf{Q}, 100 \text{ K})$. (h) Experimental difference diffraction signals measured at 50 ps. Signals are divided by the maximum count due to elastic scattering. Simulations are multiplied by 400000 to match the experimental maximum intensity [22]. The sampling of the Brillouin zone was performed using a $50 \times 50 \times 50$ \mathbf{q} -grid.

Fig. 5(c), which shows that the multi-phonon contribution to inelastic scattering, \mathcal{P} , never dominates over one-phonon processes for any $|\mathbf{Q}| \leq 14 \text{ \AA}^{-1}$.

In Figs. 6(e)-(h) we compare the zero-plus-one-phonon, all-phonon, and ZG difference diffraction patterns of bulk MoS₂ with the experimental signals measured at a pump-probe delay of 100 ps, $\Delta I(\mathbf{Q}, t = 100 \text{ ps})$. At this time delay, we assume that phonon thermalization is reached [13]. Blue and red colouring represent a decrease and an increase in the relative scattering intensity, respectively. Bragg peaks appear as blue dots since the exponent of the Debye-Waller factor, $-W_\kappa(\mathbf{Q}, T)$, is reduced with increasing temperature. The agreement between theory and experiment is excellent, except that we underestimate the background diffuse scattering. This discrepancy is diminished when multi-phonon interactions via Eq. (10), or ZG displacements, are accounted for. Despite multi-phonon scattering, the background observed experimentally can be due to many others factors, such as multiple phonon scattering events and inelastic scattering on plasmons [15, 21, 71].

C. Bulk black phosphorus

Figures 7(a) and (b) show the diffraction patterns of bulk bP at $T = 300$ K calculated using the zero-plus-one-phonon and all-phonon expressions, respectively. For

completeness, we also report the ZG scattering intensity at the same temperature in Fig. 7(c). In Fig. 7(d), we show the multi-phonon scattering pattern of bulk bP. Unlike 2D and bulk MoS₂, multi-phonon processes in bP strongly enhance diffraction away from the zone-center revealing, essentially, new diamond-like patterns. In Fig. 5(d), we also disclose the percentage contribution of multi-phonon excitations to diffuse scattering intensity, \mathcal{P} . We find that higher-order processes play the primary role to diffuse scattering for $|\mathbf{Q}| \geq 8 \text{ \AA}^{-1}$ reaching a maximum of 83% at $|\mathbf{Q}| = 13 \text{ \AA}^{-1}$. It is also evident from Fig. 5 that \mathcal{P} is much more prominent in bP than in MoS₂ crystals. Using our toy model developed in Ref. [22] and observe that the mean frequencies of the three crystals are similar, we can then attribute this different behaviour to the lighter mass of phosphorus.

For completeness, in Figs. 6(e)-(h) we reproduce the results of Ref. [22] and compare the zero-plus-one-phonon, all-phonon, and ZG difference diffraction patterns of bulk bP with the experimental thermalized signals measured at a pump-probe delay of 50 ps, $\Delta I(\mathbf{Q}, t = 50 \text{ ps})$ [13]. Blue/red areas represent decrease/increase in the relative scattering signal. Bragg peaks appear as blue dots as a result of the Debye-Waller effect. The zero intensity Bragg peaks, present in both calculations and measurements, are connected with the symmetry of the structure and can be explained by analysing the interatomic correlations (see below). The agreement between the all-

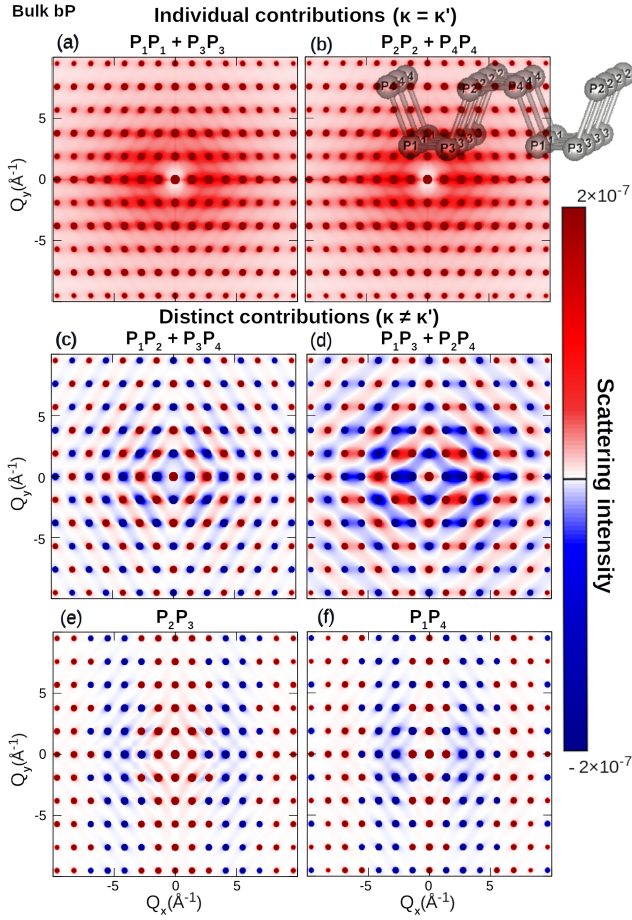


FIG. 8. Individual and distinct atomic contributions to the all-phonon scattering intensity of bulk black Phosphorous calculated for $T = 300$ K. (a) and (b) is for the individual P_1 , P_2 , P_3 , and P_4 contributions. (c), (d), (e) and (f) is for the distinct (and inequivalent) P_iP_j contributions. We also report a ball-stick model of bP. The Brillouin zone sampling was performed using a $50 \times 50 \times 50$ \mathbf{q} -grid. and data is divided by the total Bragg intensity at the centre of the Brillouin zone, i.e with $I_0(\mathbf{Q} = \mathbf{0}, T)$.

phonon theory and experiment is striking, confirming the significance of multi-phonon excitations in bP [22]. In essence, scattering beyond one-phonon is the main mechanism of the formation of the outer diamond-like domains. These features are also present in the ZG scattering difference pattern, validating once again the physical meaning of the ZG distorted structure.

In Figs. 8(a) and (b) we report the contribution to the all-phonon scattering intensity emerging from the displacements of individual phosphorus atoms. The diffraction pattern is mostly structureless and the total signal fades out with the distance from the central Bragg peak, as a result of the Debye-Waller and atomic form factors. As expected, all Bragg peaks are reproduced since scattered waves by individual atoms will undergo constructive interference.

Figures 8(c)-(f) show the response of the all-phonon

scattering intensity to displacements between pairs of P atoms. The ball-stick model shows the geometric arrangement of atoms in bP. It is evident that electrons scattered by the collective motion between atoms that lie in the same basal plane, i.e. P_1P_3 and P_2P_4 , interfere constructively, or destructively, forming diamond-like domains which explain, essentially, the characteristic diffraction pattern observed in the experiment. Regarding other pairs of bP atoms, diffuse scattering is rather insensitive to their collective motion. This result demonstrates the potential of diffuse scattering experiments to probe microscopic phenomena that occur in specific chemical bonds in solids.

V. CONCLUSIONS

In this manuscript we have benchmarked a new first-principles theory for the calculation of diffuse scattering in solids, as introduced first in Ref. [22]. In a nutshell, we have demonstrated that our method can calculate efficiently and accurately multi-phonon scattering processes using as test cases 2D MoS_2 , bulk MoS_2 , and bP.

Starting from 2D MoS_2 we have validated our methodology by comparing successfully our results obtained within the LBJ and SDM theories. These theories enable one to calculate diffraction patterns in a different fashion and at the same time justify the accuracy of each other. For completeness, we have explored in detail the formal mathematical link between the two theories. We emphasize that SDM is a broad approach with several applications in DFT and beyond [25]; here we have simply demonstrated the physical significance of SDM in reproducing all-phonon diffraction patterns. As a side point, we have also shown that the Einstein model, although fails completely in describing diffuse scattering, can provide a crude estimate for the contribution of multi-phonon interactions.

The present work helps to understand the quality of experimental measurements and investigate primary, or secondary, features in the diffraction patterns of solids. For example, our results for bulk MoS_2 reveal that the measured diffuse background signals cannot be explained completely by multi-phonon interactions. Furthermore, our multi-phonon calculations for bP demonstrate clearly the emergence of new primary features. Importantly, our finding here suggests that extracting band-resolved phonon populations from the experimental data of bP by relying only on the one-phonon theory would be inaccurate.

Beyond studying the various phonon contributions to the diffraction patterns, we examine the scattering signatures arising from individual atomic and interatomic vibrational motions. Our analysis reveals that the collective displacement between specific pairs of atoms are responsible for the main fine structures observed experimentally. Clarifying the origin of these distinct features may help interpreting the data from a bonds perspec-

tive [2], especially in materials with multiple atom species and/or multiple atoms per unit cell.

We emphasize that our methodology creates a new framework in the interpretation of time-resolved electron, or X-ray, experiments allowing for a reverse-engineering analysis to uncover transient phonon populations. In particular, one could combine the all-phonon scattering intensity with experimental data to single out multi-phonon contributions, and then extract phonon population dynamics using the strategy described in Ref. [12]. This approach requires experimental data across multiple Brillouin zones extending to regions in reciprocal space where multi-phonon excitations are dominant.

Finally, given the efficiency of our methodology it should be possible to apply it in a high-throughput manner for studying all-phonon diffuse scattering in solids. For systems experiencing a high-degree of anharmonicity one could upgrade the phonons using the self-consistent harmonic approximation [54, 72], or combine Eq. (4) with ab-initio molecular dynamics [73]. We stress that the present methodology is as simple as efficient and can be implemented straightforwardly in any software package dealing with phonon properties of materials.

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Appendix A: Equivalence between Eq. (18) and Eq. (10)

In this Appendix we show the equivalence between Eq. (18) and Eq. (10). For the sake of clarity, we exclude from the discussion the terms arising from the phonons in group \mathcal{A} . This does not constitute a limitation, since the contribution of these terms vanishes in the thermodynamic limit [25].

We start the derivation with the aid of Eq. (8) and observe that the ZG scattering intensity can be written as:

$$I_{\text{ZG}}(\mathbf{Q}, T) = \sum_{pp'} \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\mathbf{R}_p - \mathbf{R}_{p'} + \tau_{\kappa} - \tau_{\kappa'}]} e^{-\frac{1}{2} \left\{ \mathbf{Q}\cdot(\Delta\tau_{p\kappa}^{\text{ZG}} - \Delta\tau_{p'\kappa'}^{\text{ZG}}) \right\}^2}, \quad (\text{A1})$$

Substituting Eq. (15) inside Eq. (A1) and performing some straightforward algebra yields:

$$I_{\text{ZG}}(\mathbf{Q}, T) = \sum_{pp'} \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\mathbf{R}_p - \mathbf{R}_{p'} + \tau_{\kappa} - \tau_{\kappa'}]} e^{-W_{\kappa}(\mathbf{Q}, T)} e^{-W_{\kappa'}(\mathbf{Q}, T)} e^{P_{pp', \kappa\kappa'}(\mathbf{Q}, T)} e^{\Delta_{pp', \kappa\kappa'}(\mathbf{Q}, T)}, \quad (\text{A2})$$

where

$$P_{pp', \kappa\kappa'}(\mathbf{Q}, T) = \frac{2M_0 N_p^{-1}}{\sqrt{M_{\kappa} M_{\kappa'}}} \sum_{\mathbf{q} \in \mathcal{B}, \nu} u_{\mathbf{q}\nu}^2 \sum_{\alpha\alpha'} Q_{\alpha} Q_{\alpha'} \text{Re} \left[e_{\kappa\alpha, \nu}(\mathbf{q}) e_{\kappa'\alpha', \nu'}^*(\mathbf{q}') e^{i\mathbf{q}\cdot(\mathbf{R}_p - \mathbf{R}_{p'})} \right] \quad (\text{A3})$$

and

$$\Delta_{pp', \kappa\kappa'}(\mathbf{Q}, T) = \frac{2M_0}{N_p} \sum_{\alpha\alpha'} Q_{\alpha} Q_{\alpha'} \sum_{\substack{\mathbf{q} \neq \mathbf{q}' \in \mathcal{B} \\ \nu \neq \nu'}} \left[-\frac{\text{Re} [e_{\kappa\alpha, \nu}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_p}] \text{Re} [e_{\kappa'\alpha', \nu'}(\mathbf{q}') e^{i\mathbf{q}'\cdot\mathbf{R}_{p'}}]}{M_{\kappa}} - \kappa p \leftrightarrow \kappa' p' \right. \\ \left. + \frac{\text{Re} [e_{\kappa\alpha, \nu}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_p}] \text{Re} [e_{\kappa'\alpha', \nu'}^*(\mathbf{q}') e^{i\mathbf{q}'\cdot\mathbf{R}_{p'}}]}{\sqrt{M_{\kappa} M_{\kappa'}}} + \kappa p \leftrightarrow \kappa' p' \right] u_{\mathbf{q}\nu} u_{\mathbf{q}'\nu'} S_{\mathbf{q}\nu} S_{\mathbf{q}'\nu'}. \quad (\text{A4})$$

The function $\Delta_{pp', \kappa\kappa'}(\mathbf{Q}, T)$ represents the deviation from the exponents of the Debye-Waller and phononic factors. The notation $\kappa p \leftrightarrow \kappa' p'$ indicates the previous term with the indices κ , p and κ' , p' interchanged. We now take the

Taylor expansion of $e^{\Delta_{pp',\kappa\kappa'}(\mathbf{Q},T)}$ and, for simplicity, we keep only terms up to second order in atomic displacements to obtain:

$$I_{ZG}(\mathbf{Q},T) = \sum_{pp'} \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\mathbf{R}_p - \mathbf{R}_{p'} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'}]} e^{-W_{\kappa}(\mathbf{Q},T)} e^{-W_{\kappa'}(\mathbf{Q},T)} e^{P_{pp',\kappa\kappa'}(\mathbf{Q},T)} \\ + \sum_{pp'} \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot[\mathbf{R}_p - \mathbf{R}_{p'} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'}]} e^{-W_{\kappa}(\mathbf{Q},T)} e^{-W_{\kappa'}(\mathbf{Q},T)} \Delta_{pp',\kappa\kappa'}(\mathbf{Q},T). \quad (\text{A5})$$

In view of translational symmetry of the lattice, the first line of the above relation gives exactly the all-phonon term, $I_{\text{all}}(\mathbf{Q},T)$, as given by Eq. (10). The second line is recognized as the leading error in the evaluation of the ZG scattering intensity. Now we substitute Eq. (A4) into Eq. (A5), perform the summations over p and p' using twice the relation $\sum_p e^{i(\mathbf{Q}-\mathbf{q})\cdot\mathbf{R}_p} = N_p \delta_{\mathbf{Q},\mathbf{q}+\mathbf{G}}$, and apply time-reversal symmetry, i.e. $I_{ZG}(\mathbf{Q},T) = I_{ZG}(-\mathbf{Q},T)$. Hence, the ZG scattering intensity simplifies to:

$$I_{ZG}(\mathbf{Q},T) = I_{\text{all}}(\mathbf{Q},T) + \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) \cos[\mathbf{Q}\cdot(\boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'})] e^{-W_{\kappa}(\mathbf{Q},T)} e^{-W_{\kappa'}(\mathbf{Q},T)} \Delta_{\kappa\kappa'}(\mathbf{Q},T), \quad (\text{A6})$$

where the error term $\Delta_{\kappa\kappa'}(\mathbf{Q},T)$ is given by:

$$\Delta_{\kappa\kappa'}(\mathbf{Q},T) = -2 \frac{M_0 N_p}{M_{\kappa}} \sum_{\alpha\alpha'} Q_{\alpha} Q_{\alpha'} \delta_{S,G} \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu<\nu'}} \text{Re}[e_{\kappa\alpha,\nu}(\mathbf{q}) e_{\kappa\alpha',\nu'}^*(\mathbf{q})] u_{\mathbf{q}\nu} u_{\mathbf{q}\nu'} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'} \\ - 2 \frac{M_0 N_p}{M_{\kappa'}} \sum_{\alpha\alpha'} Q_{\alpha} Q_{\alpha'} \delta_{S,G} \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu<\nu'}} \text{Re}[e_{\kappa'\alpha,\nu}(\mathbf{q}) e_{\kappa'\alpha',\nu'}^*(\mathbf{q})] u_{\mathbf{q}\nu} u_{\mathbf{q}\nu'} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'} \\ + 4 \frac{M_0 N_p}{\sqrt{M_{\kappa} M_{\kappa'}}} \sum_{\alpha\alpha'} Q_{\alpha} Q_{\alpha'} \sum_{\substack{\mathbf{q}\in\mathcal{B} \\ \nu<\nu'}} \text{Re}[e_{\kappa\alpha,\nu}(\mathbf{q}) e_{\kappa'\alpha',\nu'}^*(\mathbf{q})] u_{\mathbf{q}\nu} u_{\mathbf{q}\nu'} S_{\mathbf{q}\nu} S_{\mathbf{q}\nu'}. \quad (\text{A7})$$

The first and second lines of the above expression are associated with the error in the evaluation of diffuse scattering for $\mathbf{Q} = \mathbf{G}$. By comparing now Eq. (16) with Eq. (A7), it is evident that $\Delta_{\kappa\kappa'}(\mathbf{Q},T)$ is minimized together with $E(\{S_{\mathbf{q}\nu}\},T)$ owing to the choice of signs made for the ZG displacement. We note that the same arguments also apply for the elimination of the error arising beyond second order in atomic displacements, i.e. terms including higher powers of $\Delta_{pp',\kappa\kappa'}(\mathbf{Q},T)$. This completes the proof that Eq. (18) and Eq. (10) are equivalent in the thermodynamic limit. As a numerical demonstration, in Fig. A.1 we show that multi-phonon contributions calculated with Eq. (18) and Eq. (10) are, indeed, identical.

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| <p>[1] L. Waldecker, R. Bertoni, R. Ernstorfer, and J. Vorberger, <i>Phys. Rev. X</i> 6, 021003 (2016).</p> <p>[2] C. W. Nicholson, A. Lücke, W. G. Schmidt, M. Puppini, L. Rettig, R. Ernstorfer, and M. Wolf, <i>Science</i> 362, 821 (2018).</p> <p>[3] M. X. Na <i>et al.</i>, <i>Science</i> 366, 1231 (2019).</p> <p>[4] F. Caruso, <i>J. Phys. Chem. Lett.</i> 12, 1734 (2021).</p> <p>[5] M. Trigo, J. Chen, V. H. Vishwanath, Y. M. Sheu, T. Graber, R. Henning, and D. A. Reis, <i>Phys. Rev. B</i> 82, 235205 (2010).</p> <p>[6] M. Trigo <i>et al.</i>, <i>Nat. Phys.</i> 9, 790 (2013).</p> <p>[7] L. Waldecker, R. Bertoni, H. Hübener, T. Brumme, T. Vasileiadis, D. Zahn, A. Rubio, and R. Ernstorfer, <i>Phys. Rev. Lett.</i> 119, 036803 (2017).</p> <p>[8] S. Wall <i>et al.</i>, <i>Science</i> 362, 572 (2018).</p> <p>[9] M. J. Stern, L. P. R. de Cotret, M. R. Otto, R. P. Chatelet, J.-P. Boisvert, M. Sutton, and B. J. Siwick, <i>Phys. Rev. B</i> 97 (2018).</p> | <p>[10] T. Konstantinova <i>et al.</i>, <i>Sci. Adv.</i> 4 (2018).</p> <p>[11] S. W. Teitelbaum <i>et al.</i>, <i>Phys. Rev. Lett.</i> 121, 125901 (2018).</p> <p>[12] L. P. René de Cotret, J.-H. Pöhls, M. J. Stern, M. R. Otto, M. Sutton, and B. J. Siwick, <i>Phys. Rev. B</i> 100, 214115 (2019).</p> <p>[13] H. Seiler <i>et al.</i>, (2020), arXiv:2006.12873.</p> <p>[14] M. R. Otto <i>et al.</i>, (2020), arXiv:1912.03559.</p> <p>[15] D. Zahn, P.-N. Hildebrandt, T. Vasileiadis, Y. W. Windsor, Y. Qi, H. Seiler, and R. Ernstorfer, <i>Nano Lett.</i> 20, 3728 (2020).</p> <p>[16] L. Waldecker, R. Bertoni, and R. Ernstorfer, <i>J. Appl. Phys.</i> 117, 044903 (2015).</p> <p>[17] A. Krishnamoorthy <i>et al.</i>, <i>Nano Lett.</i> 19, 4981 (2019).</p> <p>[18] X. Tong and M. Bernardi, (2020), arXiv:2009.07958.</p> <p>[19] P. Maldonado <i>et al.</i>, <i>Phys. Rev. B</i> 101, 100302 (2020).</p> |
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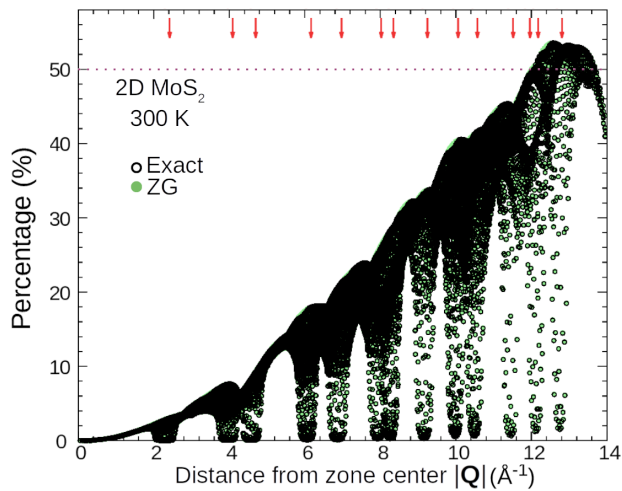


FIG. A.1. Percentage contribution of multi-phonon processes to the all-phonon scattering intensity of monolayer MoS₂, as a function of the scattering vector's distance $|\mathbf{Q}|$ from the zone-center. Black circles represent calculations using the exact formula in Eq. (10) and a Brillouin zone \mathbf{q} -grid of size 50×50 . The green discs represent calculations using ZG displacements and a Brillouin zone \mathbf{q} -grid of size 300×300 . Red arrows indicate distances for which $|\mathbf{Q}| = |\mathbf{G}|$, i.e. when Bragg scattering occurs. The horizontal dashed line intersects the vertical axis at 50%.

- [20] G. Grosso and G. Pastori Parravicini, *Solid state physics*, 2nd ed. (Elsevier, Oxford, 2014).
- [21] W. Zhong, Lin, *Elastic and Inelastic Scattering in Electron Diffraction and Imaging* (Plenum Press, 1995).
- [22] M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. C. Kelires, and R. Ernstorfer, "First-principles calculation of the all-phonon inelastic scattering in solids," (2021), arXiv:2103.10108.
- [23] I. González Vallejo, G. Gallé, B. Arnaud, S. A. Scott, M. G. Lagally, D. Boschetto, P.-E. Coulon, G. Rizza, F. Houdellier, D. Le Bolloc'h, and J. Faure, *Phys. Rev. B* **97**, 054302 (2018).
- [24] M. Zacharias and F. Giustino, *Phys. Rev. B* **94**, 075125 (2016).
- [25] M. Zacharias and F. Giustino, *Phys. Rev. Res.* **2**, 013357 (2020).
- [26] J. Laval, *Bull. Soc. Franc. Minér.* **62** (1939).
- [27] M. Born, *Rep. Prog. Phys.* **9**, 294 (1942).
- [28] R. W. James, *The Optical Principles of the Diffraction of X-rays* (G. Bell and Sons, London, 1948) Chap. V.
- [29] F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).
- [30] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of lattice dynamics in the harmonic approximation* (Academic Press, New York, 1963) p. 240.
- [31] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).
- [32] F. E. Williams, *Phys. Rev.* **82**, 281 (1951).
- [33] M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).
- [34] G. N. Watson, *J. London Math. Soc.* **s1-8**, 194 (1933).
- [35] C. E. Patrick and F. Giustino, *J. Phys.: Condens. Matter* **26**, 365503 (2014).
- [36] M. Zacharias, C. E. Patrick, and F. Giustino, *Phys. Rev. Lett.* **115**, 177401 (2015).
- [37] R. Xu and T. C. Chiang, *Z. Kristallogr. Cryst. Mater.* **220** (2005).
- [38] L. Van Hove, *Phys. Rev.* **95**, 249 (1954).
- [39] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of lattice dynamics in the harmonic approximation* (Academic Press, New York, 1963) p. 240.
- [40] C. R. Hall and P. B. Hirsch, *Proc. R. Soc. Lond. A* **286**, 158 (1965).
- [41] C. R. Hall, *Philos. Mag.* **12**, 815 (1965).
- [42] J. R. Dwyer, R. E. Jordan, C. T. Hebeisen, M. Harb, R. Ernstorfer, T. Dartigalongue, and R. J. D. Miller, *J. Mod. Opt.* **54**, 923 (2007).
- [43] L. P. R. de Cotret, M. R. Otto, M. J. Stern, and B. J. Siwick, *Adv. Struct. Chem. Imaging* **4** (2018).
- [44] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [45] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **21**, 395502 (2009).
- [46] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **29**, 465901 (2017).
- [47] C. Hartwigsen, S. Goedecker, and J. Hutter, *Phys. Rev. B* **58**, 3641 (1998).
- [48] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [49] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- [50] V. Vand, P. F. Eiland, and R. Pepinsky, *Acta Crystallogr.* **10**, 303 (1957).
- [51] L.-M. Peng, S. Dudarev, and M. Whelan, *High-energy Electron Diffraction and Microscopy* (Oxford University Press, 2004).
- [52] S. Poncé, E. Margine, C. Verdi, and F. Giustino, *Comput. Phys. Commun.* **209**, 116 (2016).
- [53] G. J. Ackland, M. C. Warren, and S. J. Clark, *J. Phys. Condens. Matter.* **9**, 7861 (1997).
- [54] I. Errea, M. Calandra, and F. Mauri, *Phys. Rev. B* **89**, 064302 (2014).
- [55] O. Hellman, I. A. Abrikosov, and S. I. Simak, *Phys. Rev. B* **84**, 180301 (2011).
- [56] D. A. Muller, B. Edwards, E. J. Kirkland, and J. Silcox, *Ultramicroscopy* **86**, 371 (2001).
- [57] T. Biswas, P. Ravindra, E. Athresh, R. Ranjan, S. Avasthi, and M. Jain, *J. Phys. Chem. C* **121**, 24766 (2017).
- [58] T. Gunst, T. Markussen, M. L. N. Palsgaard, K. Stokbro, and M. Brandbyge, *Phys. Rev. B* **96**, 161404 (2017).
- [59] X.-W. Zhang, E.-G. Wang, and X.-Z. Li, *Phys. Rev. B* **98**, 134110 (2018).
- [60] Y. Kang, H. Peelaers, K. Krishnaswamy, and C. G. Van de Walle, *Appl. Phys. Lett* **112**, 062106 (2018).
- [61] F. Karsai, M. Engel, G. Kresse, and E. Flage-Larsen, *New J. Phys.* **20**, 123008 (2018).
- [62] F. Karsai, M. Humer, E. Flage-Larsen, P. Blaha, and G. Kresse, *Phys. Rev. B* **98**, 235205 (2018).
- [63] M. Palsgaard, T. Markussen, T. Gunst, M. Brandbyge, and K. Stokbro, *Phys. Rev. Appl.* **10**, 014026 (2018).
- [64] T. Huang, D. K. Lewis, and S. Sharifzadeh, *J. Phys. Chem. Lett.* **10**, 2842 (2019).
- [65] D. Novko and M. Kralj, *NPJ 2D Mater. Appl.* **3**, 48 (2019).
- [66] Y. Zhang, Z. Wang, J. Xi, and J. Yang, *J. Phys. Condens. Matter.* **32**, 475503 (2020).
- [67] V.-A. Ha, B. Karasulu, R. Maezono, G. Brunin, J. B. Varley, G.-M. Rignanes, B. Monserrat, and G. Hautier,

- Phys. Rev. Materials **4**, 065401 (2020).
- [68] A. Tal, P. Liu, G. Kresse, and A. Pasquarello, Phys. Rev. Research **2**, 032019 (2020).
- [69] M. Zacharias and P. C. Kelires, Phys. Rev. B **101**, 245122 (2020).
- [70] K. Liu, X. Shi, R. Mohan, J. Gorchon, S. Coh, and R. B. Wilson, (2021), arXiv:2103.06337.
- [71] S. Schafer, W. Liang, and A. H. Zewail, J. Chem. Phys. **135**, 214201 (2011).
- [72] C. E. Patrick, K. W. Jacobsen, and K. S. Thygesen, Phys. Rev. B **92**, 201205 (2015).
- [73] M. Zacharias, M. Scheffler, and C. Carbogno, Phys. Rev. B **102**, 045126 (2020).