

# Multiphonon diffuse scattering in solids from first principles: Application to layered crystals and two-dimensional materials

Marios Zacharias<sup>1,\*</sup>, Hélène Seiler<sup>2</sup>, Fabio Caruso<sup>3</sup>, Daniela Zahn<sup>2</sup>, Feliciano Giustino<sup>4,5</sup>,  
Pantelis C. Kelires<sup>2,1</sup>, and Ralph Ernstorfer<sup>2,6,†</sup>

<sup>1</sup>*Department of Mechanical and Materials Science Engineering, Cyprus University of Technology, P.O. Box 50329, 3603 Limassol, Cyprus*

<sup>2</sup>*Fritz-Haber-Institut, Physical Chemistry Department, Berlin, 14195, Germany*

<sup>3</sup>*Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany*

<sup>4</sup>*Oden Institute for Computational Engineering and Sciences, The University of Texas at Austin, Austin, Texas 78712, USA*

<sup>5</sup>*Department of Physics, The University of Texas at Austin, Austin, Texas 78712, USA*

<sup>6</sup>*Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin, Germany*



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Time-resolved diffuse scattering experiments have gained increasing attention due to their potential to reveal nonequilibrium 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 multiphonon excitations. In Ref. [M. Zacharias, H. Seiler, F. Caruso, D. Zahn, F. Giustino, P. C. Kelires, and R. Ernstorfer, *Phys. Rev. Lett.* **127**, 207401 (2021)], 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 multiphonon interactions are captured efficiently by exploiting translational and time-reversal symmetries of the crystal. We demonstrate its predictive power by calculating the scattering patterns of monolayer molybdenum disulfide (MoS<sub>2</sub>), bulk MoS<sub>2</sub>, and black phosphorus (bP), and we obtain excellent agreement with our measurements of thermal electron diffuse scattering. Remarkably, our results show that multiphonon excitations dominate in bP across multiple Brillouin zones, while in MoS<sub>2</sub> they play a less pronounced role. We expand our analysis for each system and examine the effect of individual atomic and interatomic vibrational motion on the diffuse scattering signals. We further demonstrate the high-throughput capability of our approach by reporting all-phonon scattering maps of two-dimensional MoSe<sub>2</sub>, WSe<sub>2</sub>, WS<sub>2</sub>, graphene, and CdI<sub>2</sub>, rationalizing in each case the effect of multiphonon processes. As a side point, we show that the special displacement method reproduces the thermally distorted configuration that generates precisely the all-phonon diffuse pattern. The present methodology opens the way for systematic calculations of the scattering intensity in crystals and the accurate interpretation of static and time-resolved inelastic scattering experiments.

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## I. INTRODUCTION

Nonequilibrium phenomena as diverse as phase transitions, polaron formation, and 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]. 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 wave vector 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 scattering pattern  $\Delta I(\mathbf{Q}, t)$  [13,15]. In Figs. 1(a) and 1(b) we present a schematic illustration of FEDS and a typical  $\Delta I(\mathbf{Q}, t)$  of bulk molybdenum disulfide (MoS<sub>2</sub>). The left subplot in Fig. 1(b) simply shows the 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 wave vectors  $\mathbf{q}$ . The right subplot shows  $\Delta I(\mathbf{Q}, 100 \text{ ps})$  and displays a hot but quasithermalized distribution of phonons in the MoS<sub>2</sub> sample. The blue/red features represent a decrease/increase in the signal due to Bragg/diffuse scattering. The higher intensity of the red features indicates regions of the reciprocal space with higher phonon scattering probability. Recent works have shown that  $\Delta I(\mathbf{Q}, t)$  can change profoundly and

\*marios.zacharias@cut.ac.cy

†ernstorfer@fhi-berlin.mpg.de

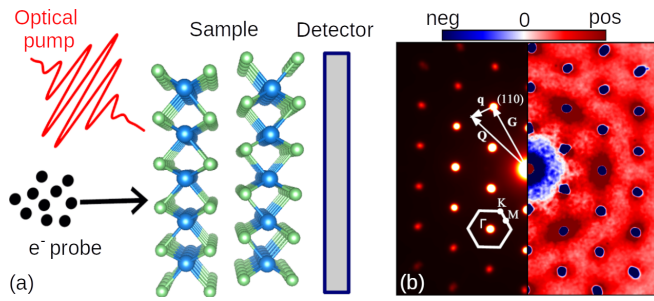


FIG. 1. (a) Schematic illustration of FEDS experiment on bulk MoS<sub>2</sub>. More details about the setup can be found in Sec. III A and Ref. [16]. (b) Typical scattering pattern of bulk MoS<sub>2</sub>. The left subplot shows the raw pattern as collected on the detector.  $\mathbf{G}$  indicates the Bragg peak vector (110),  $\mathbf{q}$  the reduced phonon wave vector, and  $\mathbf{Q} = \mathbf{G} + \mathbf{q}$  the scattering vector. A hexagonal Brillouin zone with the high-symmetry points  $\Gamma$ ,  $K$ , and  $M$  is also shown. The right subplot shows the difference scattering 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 intensity prior to photoexcitation.

qualitatively as time evolves, reflecting nonthermal lattice dynamics [7,9,13]. Phonon populations typically evolve towards a hot but thermal distribution [see, e.g., the 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 analyzing the highly nonequilibrium 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 phonon-diffuse scattering [10,12–14,17–19] rely on the quantum theory of the one-phonon structure factor [20,21]. Despite their great success in explaining some of the main features in the diffuse pattern, one-phonon interactions are considered inadequate to explain scattering signals at large  $|\mathbf{Q}|$  and/or high temperatures [21,22]. In these cases, the intensity contributed by multiphonon scattering can become comparable with, and even larger than, that of one-phonon excitations. A multiphonon process occurs when the momentum transfer to the beam in a single scattering event is specified by more than one phonon. This principle is well described in the literature [23–28]. Other mechanisms that contribute to diffuse signals are multiple interactions (i.e., more than one electron scattering event [21]), inelastic scattering on plasmons and defects, or surface imperfections, making the role of multiphonon scattering inconclusive [29]. This situation highlights the need for computational tools that directly probe multiphonon contributions and, in essence, go a step forward to extract phonon population dynamics across the entire Brillouin zone [12].

In the parallel paper, 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 interactions, and thus isolate their scattering signatures. In the present work, we further validate our implementation by first calculating one-phonon and multi-

phonon scattering patterns of monolayer MoS<sub>2</sub>. Using the same system, we also demonstrate that the special displacement method (SDM) [30,31] can provide an alternative route for the assessment of all-phonon contributions. We then apply our technique for the calculation of bulk MoS<sub>2</sub> and black phosphorus (bP) scattering patterns and obtain excellent agreement with experiment. Importantly, our results reveal that multiphonon interactions are more manifested in bP than in MoS<sub>2</sub>. We also demonstrate the efficiency of our technique by evaluating phonon-induced scattering patterns of several two-dimensional (2D) materials. 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 the manuscript is as follows: In Secs. II A and II B we describe the theory of quantum-mechanical scattering in solids, and we derive the main equations used to evaluate the respective phonon contributions. In Sec. II C and Appendix 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 the experimental and computational details of the measurements and calculations performed in this work. In Sec. IV we present our results for several 2D materials, bulk MoS<sub>2</sub>, and bP. Specifically, in Sec. IV A we report scattering intensity calculations of 2D MoS<sub>2</sub> using the exact theory, special displacements, and the Einstein model. In Secs. IV C and IV D we report the phonon scattering intensities of bulk MoS<sub>2</sub> and bP, respectively, and we compare our calculations of the difference patterns with experiment. The results are accompanied by an analysis of the multiphonon contribution across multiple Brillouin zones, as well as of the scattering signatures of individual atomic and interatomic thermal motion. In Sec. IV E we further validate our approach on monolayers MoSe<sub>2</sub>, WSe<sub>2</sub>, WS<sub>2</sub>, graphene, and CdI<sub>2</sub>. Our conclusions and outlook are presented in Sec. V.

## II. THEORY

In this section we present the theoretical framework underpinning the evaluation of multiphonon scattering intensity. Starting from the Laval-Born-James [32–34] theory, we derive the zero-phonon, one-phonon, and all-phonon scattering intensities in the harmonic approximation. We also demonstrate that exact phonon-diffuse 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 limit [21]. In this limit, also known as the Born-approximation, the Lippmann-Schwinger quantum formulation for particle scattering [35] is truncated up to the first order in the interaction potential, thus neglecting multiple scattering events. That amounts to assume weak interactions where the incident beam is scattered only once by the crystal.

In the following, we adopt a similar notation as in Ref. [36].

### A. Scattering intensity

In the adiabatic formulation and kinematic limit of the quantum-mechanical scattering theory, originally developed by Laval [32], Born [33], and James [34] (LBJ), the intensity of the wave scattered by the atoms in a crystal is given by [37]

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

Here the many-body electron-nuclear system is described in terms of the Born-Huang expansion [38], 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  $\alpha$  and  $\beta$ . The summations run over all atoms  $\kappa$  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  $\kappa$  from its equilibrium position vector  $\boldsymbol{\tau}_{\kappa}$  is represented by  $\Delta\boldsymbol{\tau}_{p\kappa}$ . For generality and brevity reasons, the intensity  $I(\mathbf{Q})$  is expressed in scattering units depending on the probe-sample interaction [37].

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  $\sum_m |X_{0m}\rangle \langle X_{0m}| = \mathbb{I}$ , 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 [33].

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 [39,40] 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. [31], considering no electronic excitations, and integrating over the energy transfer to the crystal [20]. An alternative interpretation is that Eq. (4) represents, essentially, the static limit of the dynamic structure factor [27], accounting for an average of all initial and final vibrational states accessible at thermal equilibrium.

### 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 multiphonon (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 wave vector  $\mathbf{q}$  and branch index  $\nu$ ,  $M_{\kappa}$  is the mass of the  $\kappa$ 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 wave function  $|X_{0n}\rangle$  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 Mehler's sum rule [41] leads to the following integral form for the LBJ scattering intensity [31,42]:

$$I(\mathbf{Q}, T) = \langle I^{(\tau)}(\mathbf{Q}) \rangle_T = \prod_{\mathbf{q}\nu} \int \frac{dz_{\mathbf{q}\nu}}{\pi u_{\mathbf{q}\nu}^2} e^{-|z_{\mathbf{q}\nu}|^2/u_{\mathbf{q}\nu}^2} I^{(\tau)}(\mathbf{Q}). \quad (6)$$

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 as a Williams-Lax observable in the harmonic approximation [43]. 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  $\omega_{\mathbf{q}\nu}$  at thermal equilibrium, but can depart significantly from this value under nonequilibrium conditions [4,13]. We note that Eq. (7) is indefinite for the zero-frequency translational modes (acoustic modes at  $\Gamma$ ). 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  $\langle z_{\mathbf{q}\nu} z_{\mathbf{q}'\nu'}^* \rangle_T = u_{\mathbf{q}\nu}^2 \delta_{\mathbf{q}\mathbf{q}'} \delta_{\nu\nu'}$ , we

obtain the following compact form for the LBJ (or *all-phonon*) scattering intensity [44]:

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

We emphasize that this formula is identical to Van Hove's dynamical structure factor for inelastic scattering [45] when integrated over phonon energies, thus accounting precisely

for all phonon absorption and emission processes. Here, the exponent of the Debye-Waller factor is defined as

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

and the exponent of the phononic factor is defined as

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

The summations are restricted to (i) the group  $\mathcal{B}$  containing phonons with wave vectors 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 [31].  $\text{Re}[\cdot]$  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 assessment of multiphonon 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 [45].

Physically, the Debye-Waller factor,  $e^{-W_{\kappa}}$ , determines the attenuation of the scattering intensity at temperature  $T$  due to the vibrational motion of atom  $\kappa$ . 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  $\kappa$  and  $\kappa'$  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 we observe that  $I_0(\mathbf{G}, T) = I_0(-\mathbf{G}, T)$ , we can write the zero-phonon, or Bragg scattering, term as

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

This expression is directly related to Laue's interference condition and has very sharp maxima whenever  $\mathbf{Q} = \mathbf{G}$ , and it 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

$$I_1(\mathbf{Q}, T) = M_0 N_p \sum_{\kappa\kappa'} f_{\kappa}(\mathbf{Q}) f_{\kappa'}^*(\mathbf{Q}) \frac{e^{-W_{\kappa}(\mathbf{Q}, T)} e^{-W_{\kappa'}(\mathbf{Q}, T)}}{\sqrt{M_{\kappa} M_{\kappa'}}} \times \sum_v \text{Re}[\mathbf{Q} \cdot \mathbf{e}_{\kappa, v}(\mathbf{Q}) \mathbf{Q} \cdot \mathbf{e}_{\kappa', v}^*(\mathbf{Q}) e^{i\mathbf{Q} \cdot [\mathbf{r}_{\kappa'} - \mathbf{r}_{\kappa}]}] u_{\mathbf{Q}v}^2. \quad (14)$$

One can continue the analysis and derive explicit expressions for the intensity of each higher-order process. Notably, each expression is positive-definite, and thus multiphonon scattering contributes constructively so that  $I_{\text{all}}(\mathbf{Q}, T) \geq I_0(\mathbf{Q}, T) + I_1(\mathbf{Q}, T)$ .

### 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) [30,31]. SDM amounts to applying ZG displacements on the nuclei away from their equilibrium positions given by [31]

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

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

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

The above formula 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 [31]. More details about the allocation of the signs  $S_{\mathbf{q}v}$ , 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 nonperturbative error in the calculation of the temperature-dependent observable is eliminated, and (ii) the quantum-mechanical



anisotropic displacement tensor of the atoms, defined as [46]

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

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 us 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. [31]. In Appendix, 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 they 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 [47]. These approximations allow one to replace (i) the mode-resolved mean-square displacement of the atoms  $u_{\mathbf{q}v}^2$  by a constant  $u_E^2 = \hbar/(2M_0\omega_E)[2n_E(T) + 1]$ , where  $\omega_E$  is the average phonon frequency of the crystal and  $n_E$  is the associated Bose-Einstein occupation, and (ii) the phonon polarization vectors  $\mathbf{e}_{\kappa, v}(\mathbf{q})$  with a normalized isotropic eigenvector [48]. Applying (i) and (ii) to Eq. (10), the scattering intensity within the Einstein model reads

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

where  $C_{\kappa\kappa'}(\mathbf{Q}, T) = M_0 u_E^2 \mathbf{Q}^2 / \sqrt{4M_\kappa M_{\kappa'}}$ . 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 first order in  $C_{\kappa\kappa'}(\mathbf{Q}, T)$  yields the Einstein model's analog 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 femtosecond laser system (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 noncollinear optical parametric amplifier (NOPA) and subsequent photoemission from a gold photocathode. The photoemitted electron bunches are accelerated towards the anode to reach 60–90 keV as they exit the gun. Each electron bunch is estimated to contain  $\sim 10^3$  electrons. Scattering patterns are recorded with a phosphor screen fiber-coupled to a CMOS detector (brand TVIPS, model TemCam-F416).

For sample preparation, bulk black phosphorus and MoS<sub>2</sub> 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 [49]. Due to their air-sensitivity, the bP flakes were transferred to vacuum immediately after preparation to prevent degradation of the bulk film.

The bP data were acquired at a base temperature of  $T = 100$  K, whereas the MoS<sub>2</sub> data were acquired at a base temperature of  $T = 300$  K. All data were processed using the open-source python module *scikit-ued* [50]. In particular, a sixfold (twofold) symmetrization operation was performed on the raw MoS<sub>2</sub> (bP) scattering patterns. The symmetrization operations were carried out for visualization purposes only. Prior to symmetrization, it was verified that the signals in corresponding Bragg orders (Friedel pairs) match in intensity within error, defined as the standard error of the mean signal over multiple independent acquisitions of the scattering pattern. In the symmetrized experimental patterns, we observe double peaks at large scattering vectors. These double peaks are artefactual and arise from magnetic field distortions of the electrons lens, which induce aberrations at large scattering vectors.

### B. Computational details

*Ab initio* calculations were performed using plane wave basis sets and the PBE generalized gradient approximation [51] to density-functional theory (DFT), as implemented in the QUANTUM ESPRESSO software package [52,53]. We used the primitive cells of 2D transition-metal dichalcogenides (MoS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, and WS<sub>2</sub> with space group  $P\bar{6}m2$ ), CdI<sub>2</sub> ( $P\bar{3}m1$ ), graphene ( $P6/mmm$ ), bulk MoS<sub>2</sub> ( $P6_3/mmc$ ), and bP ( $Cmce$ ), which contain three, three, two, six, and 4 atoms, respectively. We employed Goedecker-Hartwigsen-Hutter-Teter norm-conserving pseudopotentials [54,55] for all monolayers, and bulk MoS<sub>2</sub>, and Troullier-Martins [56] norm-conserving pseudopotentials for bP. The plane-wave kinetic energy cutoff was set to 80 Ry for graphene, 90 Ry for bP, 100 Ry for CdI<sub>2</sub>, 120 Ry for MoS<sub>2</sub>, 130 Ry for MoSe<sub>2</sub>, WSe<sub>2</sub>, and WS<sub>2</sub>. Self-consistent-field calculations were performed using Brillouin zone  $\mathbf{k}$ -grids of  $10 \times 10 \times 1$  (monolayers MoS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, WS<sub>2</sub>, and graphene),  $14 \times 14 \times 1$  (monolayer CdI<sub>2</sub>),  $10 \times 10 \times$

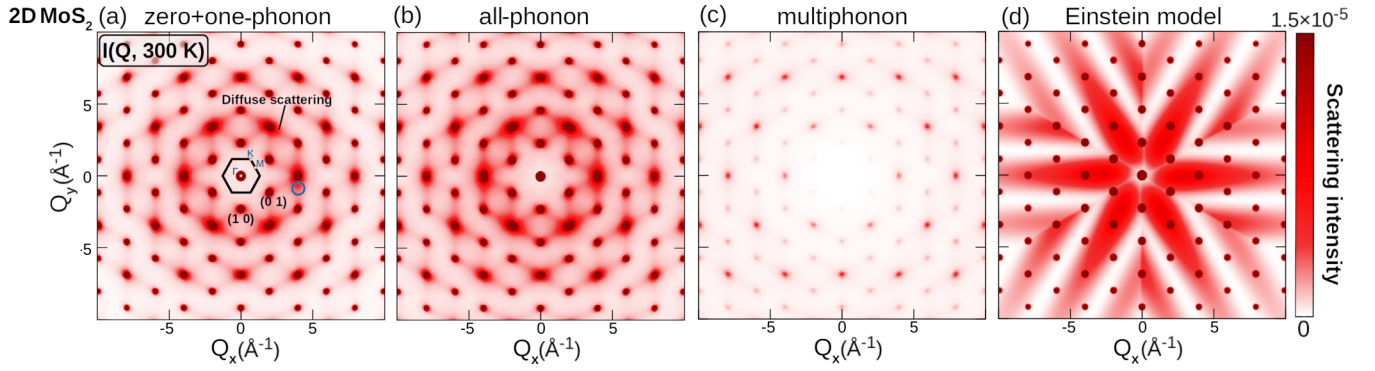


FIG. 2. (a) Zero-plus-one-phonon, (b) all-phonon, (c) multiphonon, and (d) Einstein model scattering intensity of monolayer MoS<sub>2</sub> calculated for  $T = 300$  K. In plot (a) we show the fundamental Brillouin zone together with the high-symmetry points  $\Gamma$ ,  $K$ , and  $M$ . We also show the  $(1\ 0)$  and  $(0\ 1)$  Bragg peaks. The blue circle indicates a rapid decrease in the diffuse scattering intensity. The sampling of the Brillouin zone was performed using a  $50 \times 50$   $\mathbf{q}$ -grid. For all plots, the scattering intensity is divided by the maximum Bragg intensity, i.e., with  $I_0(\mathbf{Q} = \mathbf{0}, T)$ .

3 (bulk MoS<sub>2</sub>), and  $12 \times 10 \times 10$  (bP) points. To avoid interactions between periodic replicas of the monolayers, we used an interlayer vacuum larger than  $15\ \text{\AA}$  and a truncated Coulomb interaction [57]. The optimized lattice parameters for monolayers are  $a = 3.17\ \text{\AA}$  (MoS<sub>2</sub>),  $3.32\ \text{\AA}$  (MoSe<sub>2</sub>),  $3.31\ \text{\AA}$  (WSe<sub>2</sub>),  $3.18\ \text{\AA}$  (WS<sub>2</sub>),  $2.47\ \text{\AA}$  (graphene),  $4.33\ \text{\AA}$  (CdI<sub>2</sub>);  $a = 3.191\ \text{\AA}$  and  $c = 12.43\ \text{\AA}$  for bulk MoS<sub>2</sub>; and  $a = 3.307\ \text{\AA}$ ,  $b = 4.554\ \text{\AA}$ , and  $c = 11.256\ \text{\AA}$  for bP. We determined the interatomic force constants by means of density-functional perturbation theory [58] using Brillouin zone  $\mathbf{q}$ -grids of  $8 \times 8 \times 1$  (monolayers),  $8 \times 8 \times 2$  (bulk MoS<sub>2</sub>), and  $5 \times 5 \times 5$  (bP) points.

The zero ( $I_0$ ), one ( $I_1$ ), and all ( $I_{\text{all}}$ ) -phonon scattering intensities were calculated employing 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 sets of phonon eigenmodes and eigenfrequencies were obtained by using standard Fourier interpolation of dynamical matrices on  $\mathbf{q}$ -grids of  $50 \times 50 \times 1$  (monolayers) and  $50 \times 50 \times 50$  (bulk systems) points, unless specified otherwise.  $\mathbf{Q}$ -grids of the same size were employed to sample the scattering pattern per Brillouin zone of each system. We must emphasize that it is erroneous to compute the all-phonon scattering intensity using  $\mathbf{Q}$ - and  $\mathbf{q}$ -grids of different density, since this violates the momentum selection rule and gives rise to artefacts in the phonon-diffuse pattern. For MoS<sub>2</sub> systems we show 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  $\mathbf{Q}$ . bP patterns are obtained as the average of the scattering intensities at  $Q_z = 0$  and  $Q_z = 2\pi/c = 0.56\ \text{\AA}^{-1}$  planes. Simulating the zero-order Laue zone ( $Q_z = 0$  plane) and the first-order Laue zone ( $Q_z = 2\pi/c$  plane) reproduces more Bragg peaks observed in the experiment, which we attribute to stacking faults in the sample [59–61]. The atomic scattering amplitudes  $f_k(\mathbf{Q})$  for each atom were obtained analytically as a sum of Gaussians [62] using the parameters in Ref. [63]. For the calculation of the full maps of hexagonal (monolayers and bulk MoS<sub>2</sub>) and orthorhombic (bP) systems, we applied a sixfold and fourfold rotation symmetry around the  $\Gamma$ -point.

The set of special displacements [Eq. (15)] were generated via the ZG executable (ZG.X) of the EPW software package [64].

The general procedure for applying SDM is described in Ref. [31]. In short, here we (i) used the same  $\mathbf{q}$ -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  $\mathbf{q}$ -points, (iii) ensured similarity by enforcing a smooth Berry connection between the phonon eigenmodes at adjacent  $\mathbf{q}$ -points, and (iv) assigned  $2^{n-1}$  unique combinations of  $n$  signs  $\{S_{q_v}, \dots, S_{q_v'}\}$  to every  $2^{n-1}$   $\mathbf{q}$ -point, where  $n$ , here, 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  $\mathbf{Q}$ -grid as for the LBJ scattering intensity. Notably, implementing Eq. (18) is much more straightforward than Eq. (10). Hence, SDM serves as a guide for validating our calculations of the LBJ diffuse scattering intensity.

The code (`disca.x`) used for the calculation of all phonon contributions to diffuse scattering is available at the EPW/ZG tree. 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 postprocessing steps and allow for the rapid evaluation of the (ZG or LBJ) scattering intensity of any material, provided that the interatomic force constants have already been 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 [58], the frozen-phonon method [65], the self-consistent harmonic approximation [66], or *ab initio* molecular dynamics [67].

## IV. RESULTS

### A. 2D MoS<sub>2</sub>

Figures 2(a), 2(b), and 2(c) show the zero-plus-one-phonon, multiphonon, and all-phonon scattering intensities at  $T = 300$  K in the reciprocal space of monolayer MoS<sub>2</sub>. 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.

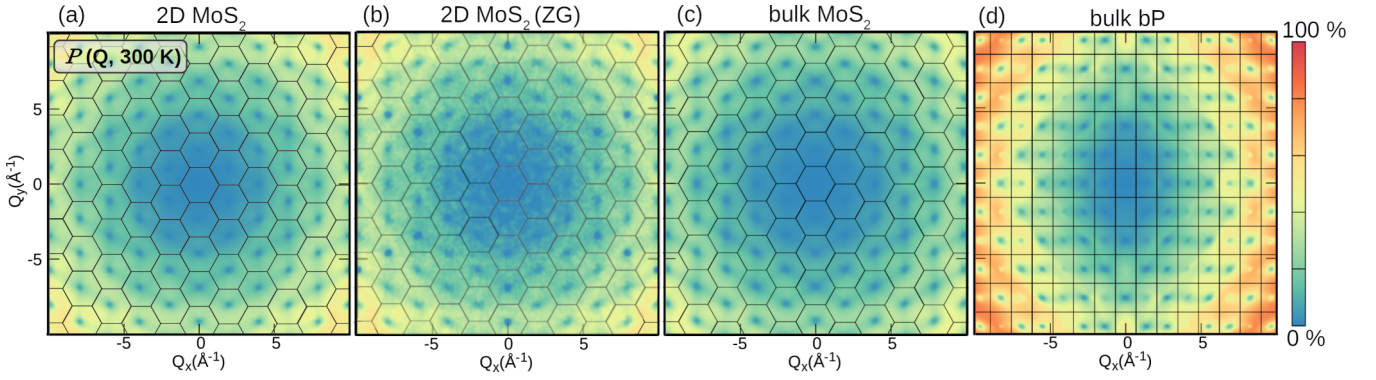


FIG. 3. Percentage contribution of multiphonon interactions to diffuse scattering of (a),(b) monolayer MoS<sub>2</sub>, (c) bulk MoS<sub>2</sub>, and (d) bulk black phosphorus (bP) calculated as  $\mathcal{P} = I_{\text{multi}}/(I_1 + I_{\text{multi}}) \times 100$  at  $T = 300$  K. Parts (a), (c), and (d) represent calculations within the LBJ theory and (b) using ZG displacements. Maps are separated into Brillouin zones to highlight the extent of multiphonon interactions.

Both sets of data have been normalized such that the scattering intensity at the zone center is equal to 1. The multiphonon scattering intensity was obtained from  $I_{\text{multi}} = I_{\text{all}} - I_0 - I_1$ . Our results show that the diffuse pattern of monolayer MoS<sub>2</sub> is determined to a large extent by one-phonon scattering, while multiphonon interactions play a secondary role without introducing new features. To quantitatively assess the effect of multiphonon processes on the diffuse pattern, we report in Fig. 3(a) the percentage  $\mathcal{P} = I_{\text{multi}}/(I_1 + I_{\text{multi}}) \times 100$  as a function of  $\mathbf{Q}$ . The response of the scattering intensity to multiphonon 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  $\omega_E = 287.4 \text{ cm}^{-1}$ . Not surprisingly, the Einstein model fails completely to explain diffuse scattering in 2D MoS<sub>2</sub> resembling scattering patterns calculated for isotropic systems [68]. However, this approximation can provide a rough prediction of the multiphonon contributions to diffuse scattering by evaluating the total energy transfer to the crystal,  $\Delta\mathcal{E}$ , as defined in the parallel paper, 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 noting that a corresponding calculation of the percentage  $\mathcal{P}$  will miss the reduced contribution of multiphonon interactions at the Bragg peaks [22].

To understand the main features in the scattering pattern of monolayer MoS<sub>2</sub>, we examine the individual atomic ( $\kappa = \kappa'$ ) and interatomic ( $\kappa \neq \kappa'$ ) terms entering Eq. (14). Figures 4(a) and 4(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 scattering concentrated in the vicinity of the Bragg peaks. Within the first Brillouin zone, the patterns exhibit a relatively weak intensity as a result of the small transferred momenta.

Figures 4(c) and 4(d) show the response of the all-phonon scattering intensity to each inequivalent distinct pairing: MoS and S<sub>1</sub>S<sub>2</sub>. 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  $\mathbf{Q} = (hk)$ , 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 by the blue circle

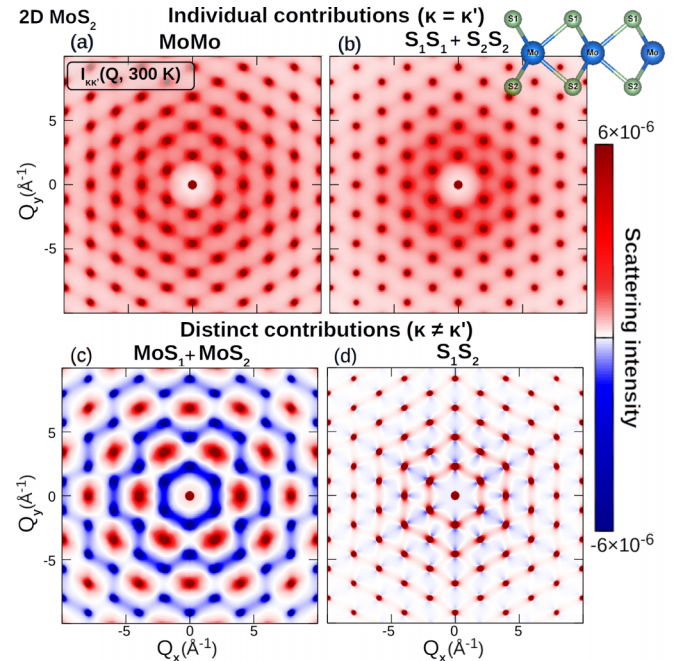


FIG. 4. Individual and distinct atomic contributions to the all-phonon scattering intensity of monolayer MoS<sub>2</sub> calculated for  $T = 300$  K. Parts (a) and (b) are for the Mo and S individual scattering terms. Parts (c) and (d) are for the MoS and S<sub>1</sub>S<sub>2</sub> distinct scattering terms. The Brillouin zone sampling was performed using a  $50 \times 50$   $\mathbf{q}$ -grid. Data are divided by the Bragg intensity at the center of the Brillouin zone, i.e., with  $I_0(\mathbf{Q} = \mathbf{0}, T)$ .



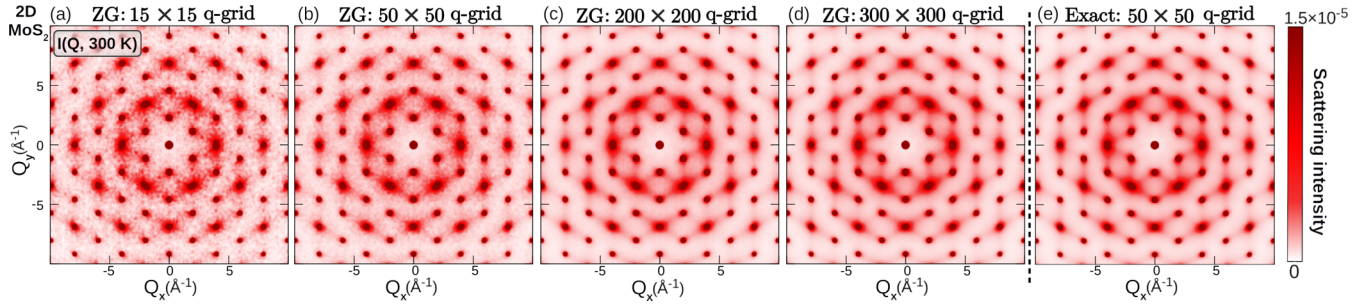


FIG. 5. (a)–(d) Convergence of the ZG scattering intensity of monolayer MoS<sub>2</sub> at  $T = 300$  K with respect to the Brillouin zone sampling. (e) Exact all-phonon scattering intensity calculated using Eq. (10). All data are divided by the Bragg peak at the center of the Brillouin zone, i.e., with  $I_0(\mathbf{Q} = \mathbf{0}, T)$ .

in Fig. 2(a). For  $S_1S_2$  distinct terms, the cosine modulation factor simplifies to 1 due to the trigonal prismatic coordination of the S atoms, thereby enhancing Bragg scattering. The correlated vibrational motion between sulfide atoms tends to reduce phonon-induced scattering in such a way that the intensity of the starlike domain formed within the first- and second-order Brillouin zones of monolayer MoS<sub>2</sub> is enhanced.

### B. Evaluation of the all-phonon scattering intensity using the ZG displacement

As described in Secs. II C and III B, SDM constitutes an alternative way to evaluate the scattering intensity, and it 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 MoS<sub>2</sub>, and we demonstrate that the two approaches give identical results in the limit of dense Brillouin zone sampling.

To analyze the convergence behavior of the SDM, in Figs. 5(a)–5(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. 5(e) we also present the data obtained using the exact expression in Eq. (10). The ZG scattering intensity calculated for a  $15 \times 15$   $\mathbf{q}$ -grid, commensurate with the supercell size of realistic ZG DFT-calculations, compares well with the exact result and reveals all the main features in the patterns. Deviations from the Bragg and inelastic scattering appear as statistical background noise and are explained by the error in the evaluation of the ZG observable. We remark that calculations of the difference images between ZG and exact patterns show that discrepancies are more prominent at the Bragg peaks, as a result of the two extra terms entering the function  $\Delta_{\kappa\kappa'}(\mathbf{Q}, T)$  when  $\mathbf{Q} = \mathbf{G}$  [Eq. (A7) of the Appendix]. As shown in Figs. 5(b)–5(d), the error is alleviated by using finer  $\mathbf{q}$ -grids, and it vanishes in the limit of dense Brillouin sampling, i.e., for a  $300 \times 300$   $\mathbf{q}$ -grid. The agreement between the two methods is further substantiated in the Appendix (Fig. 11), where the multiphonon 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. 3(a) and 3(b). This successful comparison provides a 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 to in Refs. [30,31,69–83]. 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 multiphonon effects, including carrier-multiphonon coupling. On top of that, SDM can be upgraded straightforwardly for the calculation of ultrafast phonon-diffuse data [13] and other nonequilibrium electron-phonon mediated properties. 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). This will, in turn, significantly simplify the interpretation of ultrafast phenomena, providing a physical picture with respect to real-space displacements.

### C. Bulk MoS<sub>2</sub>

Figures 6(a)–6(c) show the zero-plus-one phonon, all-phonon, and ZG scattering patterns of bulk MoS<sub>2</sub> at  $T = 300$  K. All sets of data have been normalized such that the intensity at the zone-center is equal to 1. The scattering pattern of bulk MoS<sub>2</sub> is qualitatively identical to that of its monolayer counterpart, shown in Fig. 2. Quantitatively, the major difference is that the intensity of Bragg scattering in bulk MoS<sub>2</sub> is about two orders of magnitude higher. These findings suggest that collective displacements between any two atoms that lie in separate MoS<sub>2</sub> 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 MoS<sub>2</sub>, the main characteristics in the diffuse pattern arise from the MoS correlated displacements.

In Fig. 6(d) we present the multiphonon structure factor map of bulk MoS<sub>2</sub>, obtained as the difference between the all-phonon and zero-plus-one-phonon diffuse 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



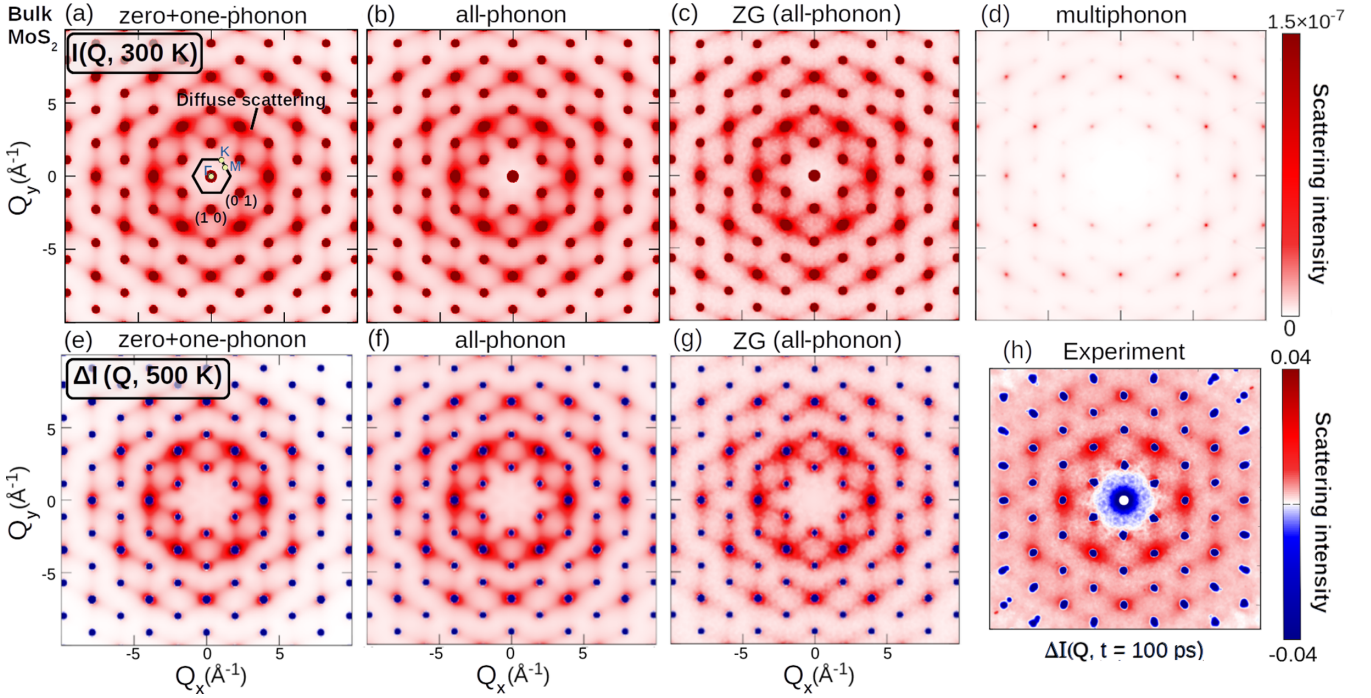


FIG. 6. (a) Zero-plus-one-phonon, (b) all-phonon, (c) ZG (all-phonon), and (d) multiphonon scattering intensity of bulk MoS<sub>2</sub> calculated for  $T = 300$  K. The calculated intensities are divided by the Bragg intensity at the center of the Brillouin zone, i.e., with  $I_0(\mathbf{Q} = \mathbf{0}, T)$ . In plot (a) we show the fundamental Brillouin zone together with the high-symmetry points  $\Gamma$ ,  $K$ , and  $M$ . We also show the (1 0) and (0 1) Bragg peaks. 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) diffuse maps of bulk MoS<sub>2</sub> calculated as  $\Delta I(\mathbf{Q}, 500 \text{ K}) = I(\mathbf{Q}, 500 \text{ K}) - I(\mathbf{Q}, 300 \text{ K})$ , corresponding to the temperature difference estimated from the experiments. (h) Experimental scattering signals of bulk MoS<sub>2</sub> measured at 100 ps. Signals are divided by the maximum count due to elastic scattering. For comparison purposes, the simulated data are multiplied by 500 000 to match the experiment. The sampling of the Brillouin zone was performed using a  $50 \times 50 \times 50$   $\mathbf{q}$ -grid.

observation is further supported by Fig. 3(c), which shows that the multiphonon 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)–6(h) we compare the zero-plus-one-phonon, all-phonon, and ZG difference scattering patterns of bulk MoS<sub>2</sub> 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 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,  $-W_k(\mathbf{Q}, T)$ , 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 multiphonon interactions via Eq. (10), or ZG displacements, are accounted for. Despite multiphonon scattering, the background observed experimentally can be due to many others factors, such as multiple scattering events and inelastic scattering on plasmons [15,21,84].

#### D. Bulk black phosphorus

Figures 7(a) and 7(b) show the scattering 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 tem-

perature in Fig. 7(c). In Fig. 7(d), we show the multiphonon scattering pattern of bulk bP. Unlike 2D and bulk MoS<sub>2</sub>, multiphonon processes in bP strongly enhance diffuse scattering away from the zone center, revealing, essentially, new diamondlike patterns. In Fig. 3(d), we also disclose the percentage contribution of multiphonon excitations to diffuse scattering intensity,  $\mathcal{P}$ . We find that higher-order processes play the primary role in 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. 3 that  $\mathcal{P}$  is much more prominent in bP than in MoS<sub>2</sub> crystals. Using our toy model developed in the parallel paper, Ref. [22], and observing that the mean frequencies of the three crystals are similar, we can then attribute this different behavior to the lighter mass of phosphorus.

For completeness, in Figs. 6(e)–6(h) we reproduce the results of the parallel paper, Ref. [22], and compare the zero-plus-one-phonon, all-phonon, and ZG difference scattering 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 a 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 analyzing the interatomic correlations (see below). In the experimental diffraction pattern of bP, however, we observe the presence of additional forbidden reflections

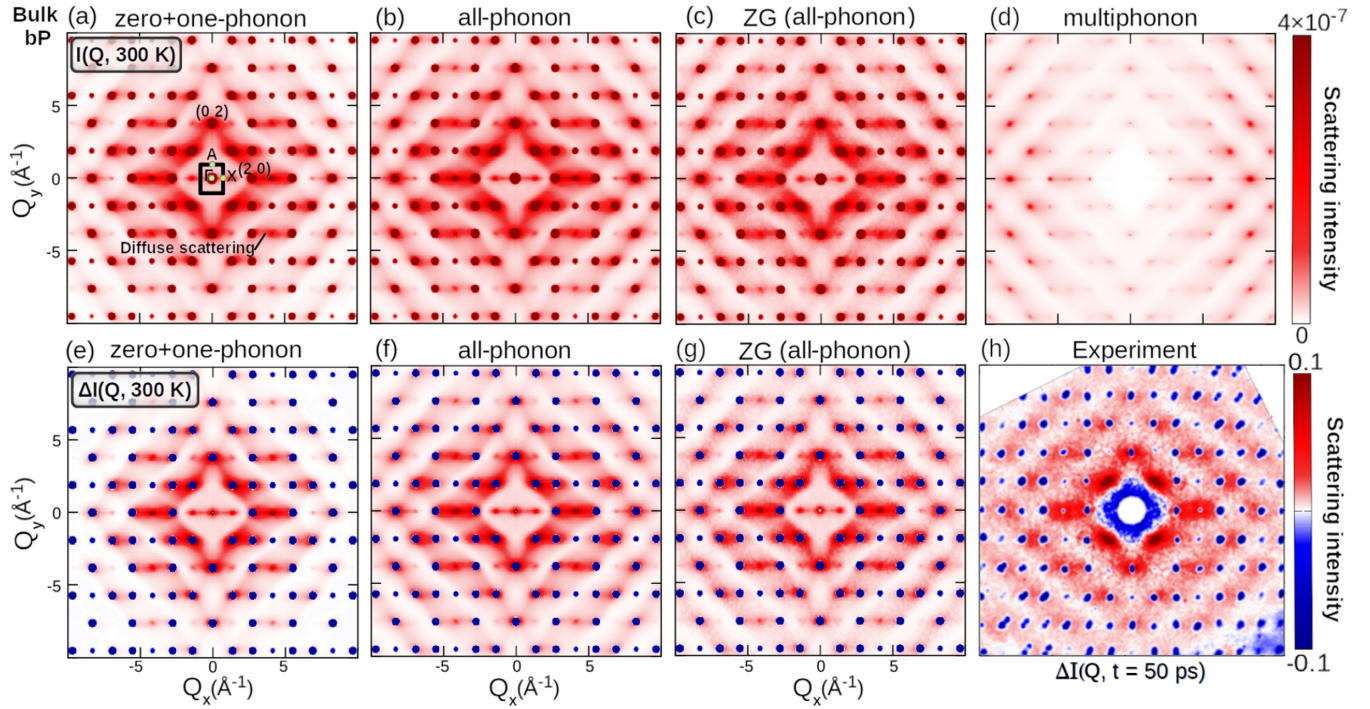


FIG. 7. (a) Zero-plus-one-phonon, (b) all-phonon, (c) ZG (all-phonon), and (d) multiphonon scattering intensity of bulk black phosphorus (bP) calculated for  $T = 300$  K. The calculated intensities are divided by the elastic scattering at the central Bragg peak,  $I_0(\mathbf{Q} = \mathbf{0}, T)$ . In plot (a) we show the fundamental Brillouin zone together with the high-symmetry points  $\Gamma$ , A, and X. We also show the (2 0) and (0 2) Bragg peaks. (e) Zero-plus-one-phonon, (f) all-phonon, and (g) ZG (all-phonon) difference scattering maps of bulk black phosphorus calculated as  $\Delta I(\mathbf{Q}, 300 \text{ K}) = I(\mathbf{Q}, 300 \text{ K}) - I(\mathbf{Q}, 100 \text{ K})$ , compatible with experimental conditions. (h) Experimental difference scattering signals measured at 50 ps. Signals are divided by the maximum count due to elastic scattering. Simulations are multiplied by 400 000 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.

for  $h + k = 2n + 1$ . Such reflections were also observed in previous works [61]. They may be caused by stacking faults or structural deviations at the surface, as bP is well-known to oxidize rapidly. These additional reflections do not alter the overall picture. In fact, the agreement between the all-phonon theory and experiment is striking, confirming that multiphonon excitations change diffuse signals qualitatively and quantitatively [22]. In essence, scattering beyond one-phonon is the main mechanism of the formation of the outer diamondlike domains. These features are also present in the ZG scattering difference pattern, validating once again the physical meaning of the ZG distorted structure. Given the unprecedented agreement between our sets of calculated all-phonon data and measurements [22], we exclude a large redistribution of diffuse intensity from lower-order into higher-order Brillouin zones due to Bragg-Bragg and Bragg-diffuse multiple scattering [85]. Our additional analysis, based on the method described in Ref. [86], also guarantees that multiple scattering is not a critical issue in our measurements.

In Figs. 8(a) and 8(b) we report the all-phonon scattering intensity coming from the displacements of individual phosphorus atoms. The diffuse pattern is mostly structureless, and the total signal fades out with the distance from the central Bragg peak due to 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)–8(f) show the response of the all-phonon scattering intensity to displacements between pairs of P atoms. The ball and 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 the characteristic diffuse 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.

### E. 2D materials

In this section, we evaluate the diffuse scattering patterns of five more 2D materials in order to gain further insight into the role of multiphonon processes, and we demonstrate the high-throughput capability of our method.

Figure 9 shows the zero-plus-one-phonon, all-phonon, and multiphonon scattering intensities of (a) MoS<sub>2</sub>, (b) MoSe<sub>2</sub>, (c) WSe<sub>2</sub>, (d) WS<sub>2</sub>, (e) graphene, and (f) CdI<sub>2</sub> all calculated at  $T = 300$  K within the LBJ theory. We also show the percentage  $\mathcal{P} = I_{\text{multi}} / (I_1 + I_{\text{multi}}) \times 100$  to provide a quantitative hierarchy between one-phonon and multiphonon processes. To support our subsequent analysis, we report the calculated energy transfer from multiphonon processes,  $\Delta\mathcal{E}$  [22], the total atomic mass per unit cell,  $M_T = \sum_{\kappa} M_{\kappa}$ , and the Einstein



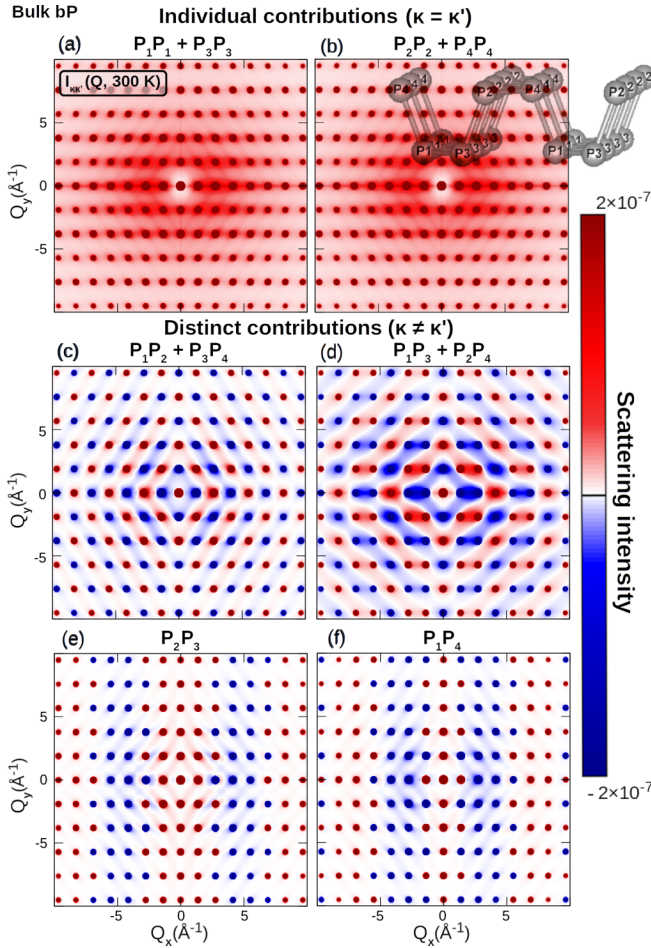


FIG. 8. Individual and distinct atomic contributions to the all-phonon scattering intensity of bulk black phosphorus calculated for  $T = 300$  K. Plots (a) and (b) are for the individual  $P_1$ ,  $P_2$ ,  $P_3$ , and  $P_4$  contributions. Plots (c), (d), (e), and (f) are for the distinct (and inequivalent)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

phonon frequency  $\omega_E$  of each 2D material. At this point, we recall that  $\Delta\mathcal{E}$  scales inversely proportional with the atomic masses and phonon frequencies of the system. All transition-metal dichalcogenides ( $\text{MoS}_2$ ,  $\text{MoSe}_2$ ,  $\text{WSe}_2$ , and  $\text{WS}_2$ ) share the same space group ( $P\bar{6}m2$ ) and exhibit similar diffraction and phonon-diffuse patterns. Importantly, when the sulfide atoms are replaced by the heavier selenium in  $\text{WX}_2$  and  $\text{MoX}_2$  (where  $X$  indicates the chalcogen atom), we obtain a subtle enhancement of the phonon-induced scattering intensities and  $\Delta\mathcal{E}$  by 2%. In both cases,  $M_T$  becomes larger by more than 35%, but  $\omega_E$  is reduced by  $\sim 33\%$ , indicating that the change in the phonon frequencies is the primary measure for estimating the extent of multiphonon processes.

This conclusion can be further justified by our analysis for graphene, shown in Fig. 9(e). Our results reveal almost identical one-phonon and all-phonon diffuse patterns, as well as a small percentage  $\mathcal{P}$  across the reciprocal space. We find the energy transfer due to multiphonon excitations  $\Delta\mathcal{E}$  to be as low as 5%. Our value comes as no surprise, despite

the light mass of carbon atoms. In particular, the small  $\Delta\mathcal{E}$  is driven by the relatively large Einstein phonon frequency ( $\omega_E = 917.4 \text{ cm}^{-1}$ ) of graphene, being three to four times larger than  $\omega_E$  reported for transition-metal dichalcogenides. It is also evident that employing the one-phonon structure factor is an accurate and reliable practice for investigating diffuse scattering signals in materials exhibiting large mean phonon frequencies [12].

At variance with graphene, multiphonon processes have a prominent impact on the diffuse pattern of 2D  $\text{CdI}_2$  (space group  $P\bar{3}m1$ ), as shown in Fig. 9(f). We can readily see that the one-phonon scattering theory reveals negligible diffuse scattering for  $|\mathbf{Q}| > 5 \text{ \AA}^{-1}$ , missing important features of the all-phonon scattering map. It is also striking that multiphonon excitations dominate inelastic scattering beyond the fundamental Brillouin zone, giving  $\Delta\mathcal{E} = 63\%$ . Based on our previous discussion, this value is consistent with the relatively small mean phonon frequency of  $\text{CdI}_2$ ,  $\omega_E = 70.6 \text{ cm}^{-1}$ . The value of  $\omega_E$  also explains the rapid Debye-Waller damping of the Bragg intensities at large scattering wave vectors [see Eq. (11)]. Unlike the diffraction patterns of transition-metal dichalcogenides, we observe that for a Bragg scattering vector  $\mathbf{Q} = (hk)$ , the total intensity is reduced when  $|h - k| \neq 3n$ . To shed light on this result, we report the individual and distinct atomic contributions to the all-phonon scattering pattern of monolayer  $\text{CdI}_2$ , as shown in Fig. 10. Apart from the pronounced Debye-Waller damping in  $\text{CdI}_2$ , the main difference between the diffraction patterns of  $\text{MoS}_2$  and  $\text{CdI}_2$  is due to the distinct contributions from  $S_1S_2$  [Fig. 4(d)] and  $I_1I_2$  [Fig. 10(d)] pairs. In fact, electrons scattered by the collective motion between I atoms will interfere destructively, instead of constructively, when  $|h - k| \neq 3n$ . This different response is attributed to the fact that  $\text{CdI}_2$  (space group  $P\bar{3}m1$ ) lacks mirror symmetry with respect to the plane containing Cd atoms.

## V. CONCLUSIONS

In this manuscript, we have benchmarked a first-principles theory for the calculation of diffuse scattering in solids, as introduced in the parallel paper, Ref. [22]. In a nutshell, we have demonstrated that our method can calculate efficiently and accurately multiphonon scattering processes using as test cases bulk  $\text{MoS}_2$  and bP, as well as several 2D materials.

Starting from 2D  $\text{MoS}_2$ , we have validated our methodology by comparing successfully our results obtained within the LBJ and SDM theories. These theories enable one to calculate scattering 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 [31] which can be extended to study nonequilibrium dynamics [13]; here we have simply demonstrated the physical significance of SDM in reproducing all-phonon diffuse patterns. We have also shown that the Einstein model fails completely at describing diffuse scattering, but it can provide a good estimate for the contribution of multiphonon interactions.

We further demonstrate our implementation of the all-phonon LBJ theory by evaluating scattering patterns of 2D

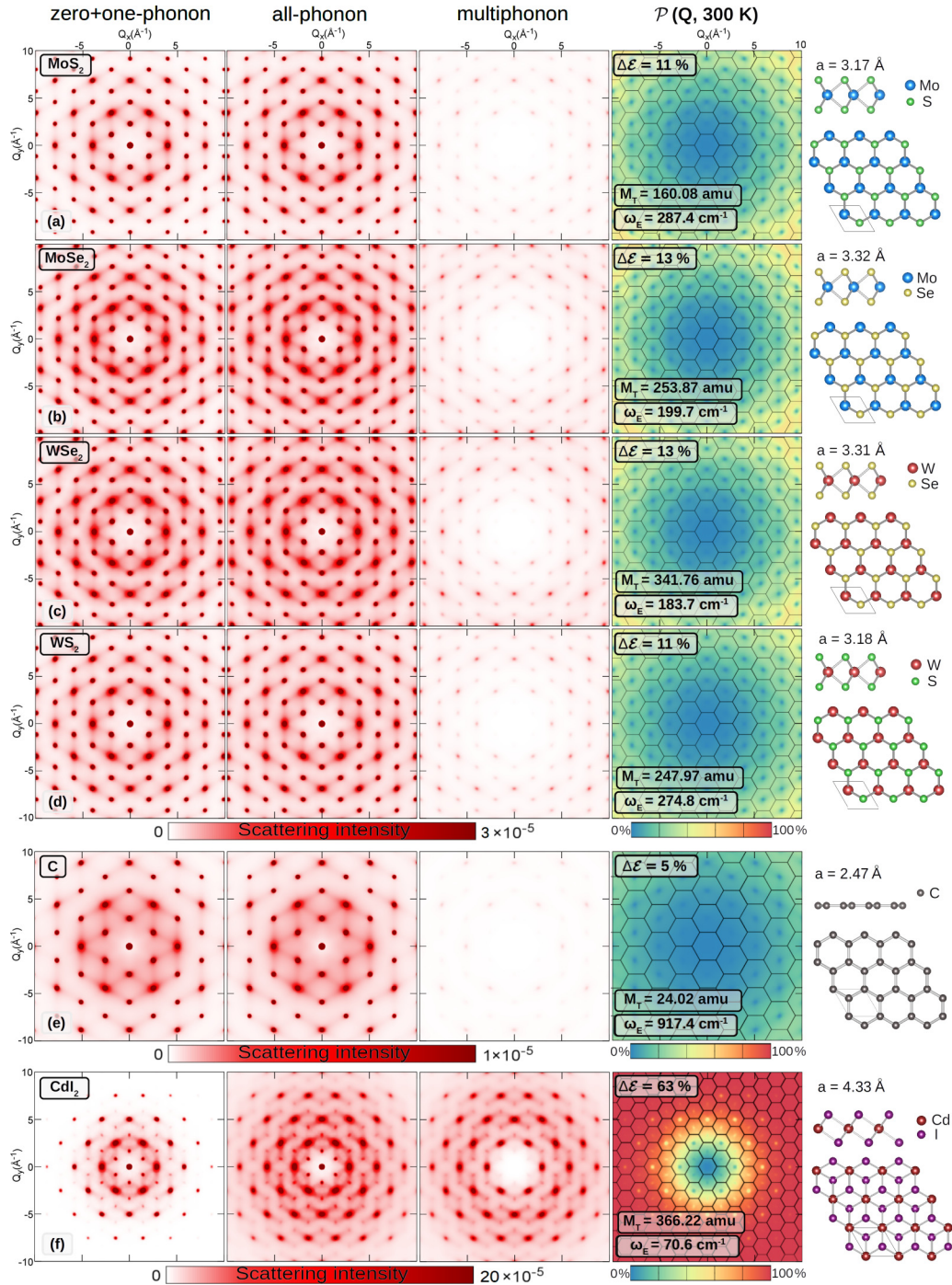


FIG. 9. Zero-plus-one-phonon, all-phonon, and multiphonon scattering intensities, and percentage contribution of multiphonon processes to diffuse scattering intensity  $\mathcal{P}$  calculated for 2D (a) MoS $_2$ , (b) MoSe $_2$ , (c) WSe $_2$ , (d) WS $_2$ , (e) graphene, and (f) CdI $_2$  all at  $T = 300$  K. The energy transfer to the crystal from multiphonon scattering,  $\Delta E$ , the total atomic mass per unit cell in atomic mass units (amu),  $M_T$ , and the mean phonon frequency,  $\omega_E$ , are indicated on each plot. The sampling of the Brillouin zone was performed using a  $50 \times 50$   $\mathbf{q}$ -grid, and data are divided by the maximum Bragg intensity, i.e., with  $I_0(\mathbf{Q} = \mathbf{0}, T)$ . We also provide the ball and stick model, primitive-cell, and optimized lattice parameter  $a$  of each structure.

transition-metal dichalcogenides (MoSe $_2$ , WSe $_2$ , and WS $_2$ ), graphene, and 2D CdI $_2$ . Remarkably, for 2D CdI $_2$  we find that multiphonon processes contribute above 60% to diffuse scattering. We clarify that this result should not be viewed as a limiting case, but rather a plausible outcome expected for several 2D materials sharing similar Einstein phonon frequencies [87].

The present work helps to understand the quality of experimental measurements and investigate primary, or secondary, features in the scattering patterns of solids. For example, our results for bulk MoS $_2$  reveal that the measured diffuse background signals can be mainly explained by multiphonon interactions. Furthermore, our multiphonon calculations for bP demonstrate clearly the emergence of



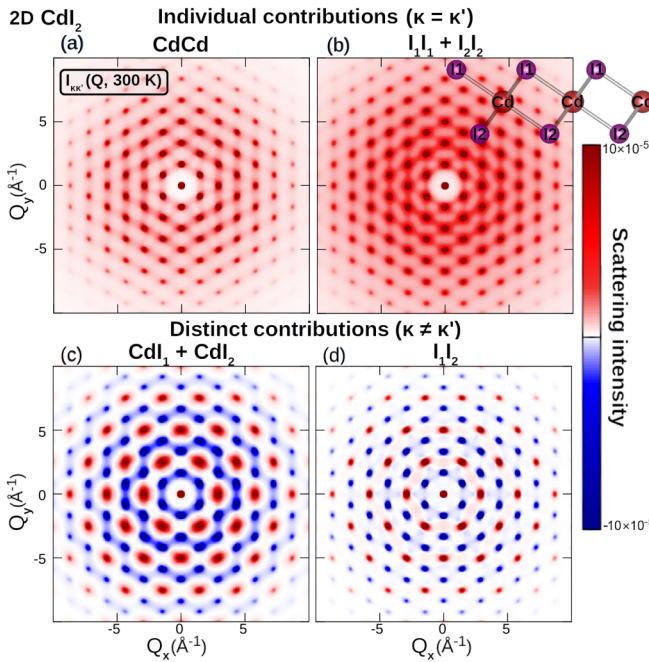


FIG. 10. Individual and distinct atomic contributions to the all-phonon scattering intensity of monolayer  $\text{CdI}_2$  calculated for  $T = 300$  K. Parts (a) and (b) are for the Cd and I individual contributions. Parts (c) and (d) are for the CdI and  $\text{I}_1\text{I}_2$  distinct terms. The Brillouin zone was sampled using a  $50 \times 50$   $\mathbf{q}$ -grid. Data are divided by the maximum Bragg intensity, i.e., with  $I_0(\mathbf{Q} = \mathbf{0}, T)$ .

new primary features. Importantly, our finding 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 diffuse 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 is responsible for the main fine structures observed experimentally. Clarifying the origin of these distinct features may help to interpret the data from a bonds perspective [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 multiphonon 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 multiphonon excitations can be dominant. We clarify that even if the occupancy of a single phonon mode is affected by photoexcitation in pump-probe experiments, the multiphonon theory is still necessary to describe accurately the changes induced in diffuse scattering signals.

The present approach is as simple as it is efficient, and it can be implemented straightforwardly in any software package dealing with phonon properties of materials. Given the generality of our methodology, it should be pos-

sible to apply it in a large-scale 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 [66,88], or combine Eq. (4) with *ab initio* molecular dynamics [89]. For special cases, including (i) doped graphene [90] or heavily boron doped diamond [91], and (ii) undoped semiconductors whose band-gap energy is comparable to their phonon energies, a breakdown of the adiabatic approximation is to be expected. In these cases, approaches beyond static density-functional perturbation theory and the frozen-phonon method are necessary to account for nonadiabatic phonon dispersions via the calculation of the phonon self-energy [36].

Electronic structure calculations performed in this study are available on the NOMAD repository [92].

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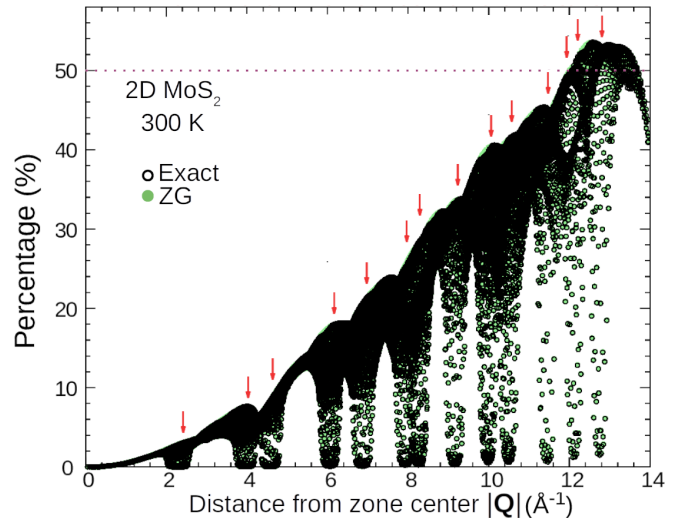


FIG. 11. Percentage contribution of multiphonon processes to the all-phonon scattering intensity,  $I_{\text{multi}}/I_{\text{all}}$ , of monolayer  $\text{MoS}_2$  as a function of the scattering vector's distance  $|\mathbf{Q}|$  from the zone center. Black circles represent calculations using the exact formula in Eq. (10) and a Brillouin zone  $\mathbf{q}$ -grid of size  $50 \times 50$ . The green disks represent calculations using ZG displacements and a Brillouin zone  $\mathbf{q}$ -grid of size  $300 \times 300$ . 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%.

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## APPENDIX: EQUIVALENCE BETWEEN EQS. (18) AND (10)

In this Appendix, we show the equivalence between Eqs. (18) and (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 [31].

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

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

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

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

where

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

and

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

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  $\kappa, p$  and  $\kappa', p'$  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

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

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.,  $I_{\text{ZG}}(\mathbf{Q}, T) = I_{\text{ZG}}(-\mathbf{Q}, T)$ . Hence, the ZG scattering intensity simplifies to

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

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

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

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  $E(\{S_{\mathbf{q}\nu}\}, T)$  due to the choice of signs made for the ZG displacement. 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 Eqs. (18) and (10) are equivalent in the thermodynamic limit. As a numerical demonstration, in Fig. 11 we show that multiphonon contributions calculated with Eqs. (18) and (10) are indeed identical.

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