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# Electronic, vibrational, and electron-phonon coupling properties in SnSe<sub>2</sub> and SnS<sub>2</sub> under pressure

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The tin-selenide and tin-sulfide classes of materials undergo multiple structural transitions under high pressure leading to periodic lattice distortions, superconductivity, and topologically non-trivial phases, yet a number of controversies exist regarding the structural transformations in these systems. We perform first-principles calculations within the framework of density functional theory and a careful comparison of our results with available experiments on SnSe<sub>2</sub> reveals that the apparent contradictions among high-pressure results can be attributed to differences in experimental conditions. We further demonstrate that under hydrostatic pressure a  $\sqrt{3} \times \sqrt{3} \times 1$  superstructure can be stabilized above 20 GPa in SnS<sub>2</sub> via a periodic lattice distortion as found recently in the case of SnSe<sub>2</sub>, and that this pressure-induced phase transition is due to the combined effect of Fermi surface nesting and electron-phonon coupling at a momentum wave vector  $\mathbf{q} = (1/3, 1/3, 0)$ . In addition, we investigate the contribution of nonadiabatic corrections on the calculated phonon frequencies, and show that the quantitative agreement between theory and experiment for the high-energy  $A_{1g}$  phonon mode is improved when these effects are taken into account. Finally, we examine the nature of the superconducting state recently observed in SnSe<sub>2</sub> under nonhydrostatic pressure and predict the emergence of superconductivity with a comparable critical temperature in SnS<sub>2</sub> under similar experimental conditions. Interestingly, in the periodic lattice distorted phases, the critical temperature is found to be reduced by an order of magnitude due to the restructuring of the Fermi surface.

## I. INTRODUCTION

Tin-based binary compounds, Sn<sub>x</sub>Se<sub>y</sub> and Sn<sub>x</sub>S<sub>y</sub>, have emerged as promising candidates for electronic, optoelectronic, photovoltaic, and thermoelectric applications<sup>1-8</sup> as well as platforms for exploring exotic states of matter<sup>9-13</sup>. Similar to other layered metal chalcogenide materials<sup>14-21</sup>, it has been found that under increased pressure and/or temperature these compounds undergo substantial changes in their structural and electronic properties, special interest being paid to those materials that can host charge density wave (CDW), superconducting, or topologically non-trivial phases<sup>9-13,19,22-28</sup>.

In the dichalcogenide systems, pressure-induced structural phase transitions have been reported for both SnSe<sub>2</sub> and SnS<sub>2</sub>. For example, two theoretical studies have predicted that SnSe<sub>2</sub> becomes thermodynamically unstable above 18-20 GPa and then decomposes into Sn<sub>3</sub>Se<sub>4</sub> (space group  $I\bar{4}3d$ ) and Se<sup>10,22</sup>. A similar decomposition has been theoretically shown to take place in the sister compound SnS<sub>2</sub>, which remains thermodynamically stable up to approximately 28 GPa<sup>23</sup>. We would like to note in passing that both 3:4 compounds have been recently predicted to be superconducting with  $T_c$  values of 3.3-4.7 K at 10 GPa<sup>10,11</sup>, and 21.9 K at 30 GPa<sup>23</sup>, respectively. Although the formation of Sn<sub>3</sub>Se<sub>4</sub> and Sn<sub>3</sub>S<sub>4</sub> has been reported in experiments<sup>10,29</sup>, the presence of a superconducting state in these materials still awaits experimental confirmation.

While SnSe<sub>2</sub> is no longer on the convex hull tie-line at

higher pressures and also becomes dynamically unstable, we have shown in a previous study<sup>19</sup> that it can be stabilized in a  $\sqrt{3} \times \sqrt{3} \times 1$  supercell through a periodic lattice distortion (PLD) and that it can, in fact, be realized in experiments. In particular, under applying pressure, SnSe<sub>2</sub> becomes metallic in the 8-13 GPa range, with a typical metallic behavior above 17 GPa, and transitions to the PLD phase at around 17 GPa. The agreement between theory and experiment was very good, and the experimentally observed phase transition has been successfully ascribed to a combined effect of electron-phonon (e-ph) coupling and Fermi surface (FS) nesting. This is in contrast to transitional metal dichalcogenides (TMDs), where FS nesting is found to only play a minor role in creating the CDW instability<sup>20,30-33</sup>. Interestingly, in another recent high-pressure experimental study<sup>28</sup>, neither the proposed theoretical decomposition<sup>10,22</sup> nor the transformation to the PLD phase<sup>19</sup> were detected up to 46 GPa. Instead, electrical resistance measurements in compressed SnSe<sub>2</sub> showed an insulator-to-metallic transition above 15.2 GPa and the appearance of a superconducting state around 18.6 GPa.

In the present study, we first address the apparent contradiction among high-pressure experimental results in SnSe<sub>2</sub> above 20 GPa. Next, we explore whether a  $\sqrt{3} \times \sqrt{3} \times 1$  superstructure can also be stabilized in SnS<sub>2</sub> via a PLD by providing a detailed comparison of the electronic, vibrational, and e-ph properties of the two compounds. We expand on our previous work<sup>19</sup> to improve the quantitative agreement between theory and experi-

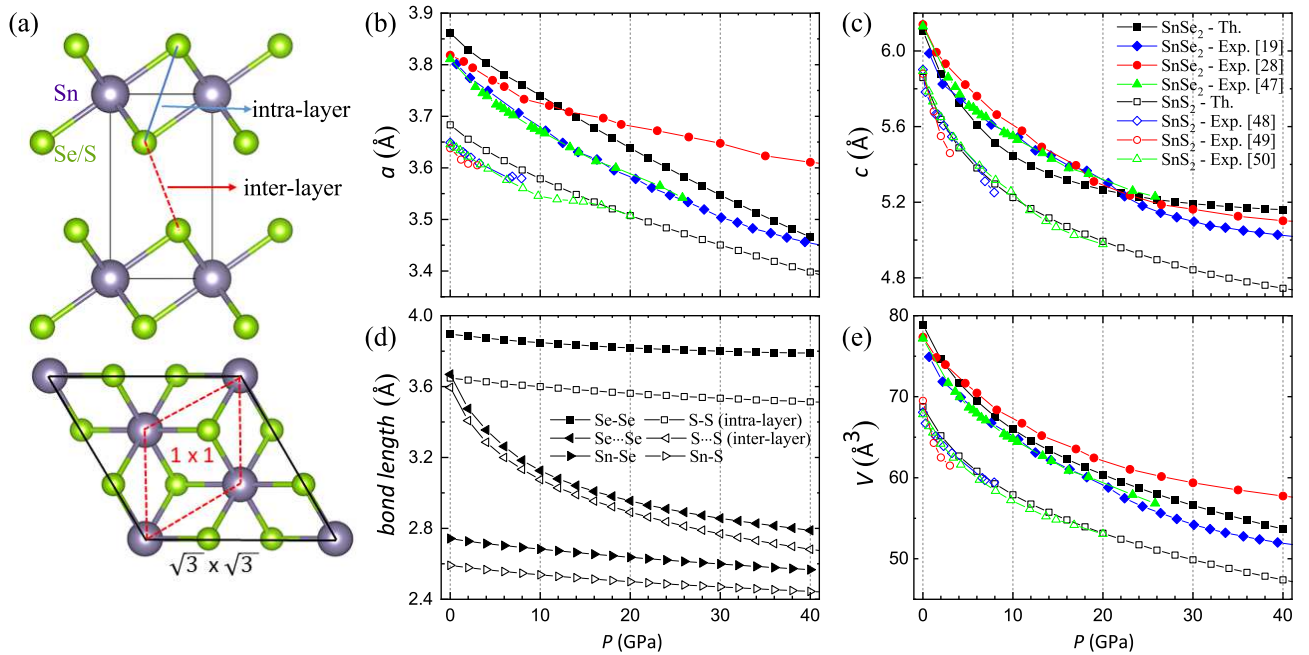


FIG. 1: (a) Crystal structures showing the intra-layer (Se-Se/S-S) and inter-layer (Se···Se/S···S) distances (top figure) and  $1 \times 1$  and  $\sqrt{3} \times \sqrt{3}$  unit cells (bottom figure). Pressure dependence of (b), (c) the lattice parameters  $a$  and  $c$ , (d) the average bond lengths, and (e) the volume per one formula unit for SnSe<sub>2</sub> and SnS<sub>2</sub>. Theoretical results are shown as black symbols and are compared with available experimental data<sup>19,28,47–50</sup>. Data for SnSe<sub>2</sub> and SnS<sub>2</sub> are presented with solid and open symbols.

ment with respect to the pressure dependence of the  $A_{1g}$  phonon mode. In particular, we investigate the effect of LO-TO splitting and nonadiabatic corrections on the calculated phonon frequencies. Finally, we investigate the origin of the superconducting state recently observed in SnSe<sub>2</sub> under nonhydrostatic pressure, and shed light on the superconducting properties of SnS<sub>2</sub> and the PLD phases of the two systems at higher pressures.

## II. METHODS

First-principles calculations were performed within the density functional theory (DFT) using the Quantum ESPRESSO (QE)<sup>34</sup> code. We employed optimized norm-conserving Vanderbilt (ONCV) pseudopotentials<sup>35</sup> with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in the generalized gradient approximation<sup>36</sup>, where the Sn  $4d^{10}5s^25p^2$ , Se  $4s^24p^4$ , and S  $3s^23p^4$  orbitals were included as valence electrons. To properly treat the long-range dispersive interactions, we used the non-local van der Waals (vdW) density functional optB86b-vdW<sup>37,38</sup>. A plane wave kinetic-energy cutoff value of 60 Ry, a Marzari-Vanderbilt cold smearing<sup>39</sup> value of 0.01 Ry, and a  $\Gamma$ -centered  $24 \times 24 \times 16$  Monkhorst-Pack<sup>40</sup>  $\mathbf{k}$ -mesh for the three-atom unit cell and  $12 \times 12 \times 16$   $\mathbf{k}$ -mesh for the nine-atom  $\sqrt{3} \times \sqrt{3} \times 1$  supercell were used for the Brillouin-zone (BZ) integration. The atomic positions and lattice parameters were optimized until the self-consistent energy was converged within  $2.7 \times 10^{-5}$  eV and

the maximum Hellmann-Feynman force on each atom was less than  $0.005$  eV/Å. The dynamical matrices and the linear variation of the self-consistent potential were calculated within density-functional perturbation theory (DFPT)<sup>41</sup> on the irreducible set of a regular  $6 \times 6 \times 4$   $\mathbf{q}$ -mesh for the three-atom unit cell and  $3 \times 3 \times 4$   $\mathbf{q}$ -mesh for the nine-atom  $\sqrt{3} \times \sqrt{3} \times 1$  supercell.

The EPW code<sup>42,43</sup> was used to compute e-ph interactions and related properties. The electronic wavefunctions required for the Wannier-Fourier interpolation<sup>44,45</sup> were calculated on a uniform  $\Gamma$ -centered  $12 \times 12 \times 4$   $\mathbf{k}$ -grid for the three-atom unit cell. Ten maximally localized Wannier functions (one  $s$  and three  $p$  orbitals for each Sn atom and three  $p$  orbitals for each chalcogen atom) were used to describe the electronic structure near the Fermi level ( $E_F$ ). A uniform  $300 \times 300 \times 200$   $\mathbf{k}$ -mesh was used to evaluate the adiabatic phonon self-energy and static bare susceptibility, while 2 million random  $\mathbf{k}$  points were used to estimate the phonon spectral function in the nonadiabatic regime. Both sets of calculations were performed along a high-symmetry path in  $\mathbf{q}$ -space with smearings of 25 meV (electrons) and 0.05 meV (phonons). Uniform  $120 \times 120 \times 40$   $\mathbf{k}$ -point and  $60 \times 60 \times 20$   $\mathbf{q}$ -point grids were used for the superconductivity calculations in the three-atom unit cell (the in-plane meshes were reduced by a factor of three in the nine-atom supercell). The Matsubara frequency cutoff was set to 0.4 eV and the Dirac deltas were replaced by Lorentzians of width 25 meV (electrons) and 0.1 meV (phonons) when solving the isotropic Migdal-Eliashberg equations.

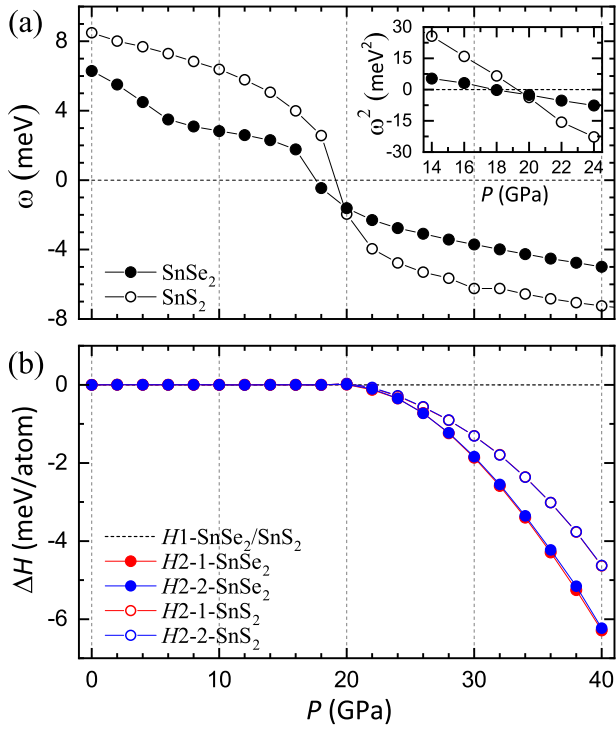


FIG. 2: (a) Calculated softening of the lowest-energy (degenerate) phonon modes in the  $\sqrt{3} \times \sqrt{3} \times 1$   $H1$  superlattice for  $\text{SnSe}_2$  and  $\text{SnS}_2$ , where imaginary phonon frequencies are shown as negative, illustrating the pressure-induced destabilization of the  $H1$  phase. The inset shows the squared frequency of the modes. (b) Enthalpy difference for the considered  $H2$  structures as function of pressure for  $\text{SnSe}_2$  and  $\text{SnS}_2$ , where the  $H1$  phase was chosen as a reference.

### III. RESULTS

#### A. Crystal structure evolution under pressure

At ambient conditions, bulk  $\text{SnSe}_2$  and  $\text{SnS}_2$  crystallize in the hexagonal, close-packed  $\text{CdI}_2$ -type structure with space group  $P\bar{3}m1$  (No. 164)<sup>19,46</sup>. The unit cell contains three atoms, where every Sn atom occupies the center of an octahedron formed by six chalcogen atoms (Se or S) [see Fig. 1(a)]. We refer to this high-symmetry structure as the  $H1$  phase. Fig. 1(b)-(e) presents the optimized structural parameters as a function of pressure, together with available experimental data for comparison<sup>19,28,47–50</sup>.

As pointed out in previous studies<sup>48–50</sup>, the contraction of the unit cell under compression is highly anisotropic. According to our theoretical results for hydrostatic pressure, the lattice parameter along the  $a$  axis decreases almost linearly with increasing pressure, while that along the  $c$  axis shrinks quickly before beginning a slower descent. This anisotropic compression can be related to the rapid decrease in the inter-layer  $\text{Se}\cdots\text{Se}/\text{S}\cdots\text{S}$  distance (i.e., the distance between the chalcogen atoms in adjacent layers) versus the intra-layer  $\text{Se-Se}/\text{S-S}$  and

$\text{Sn-Se}/\text{Sn-S}$  distances due to the weaker vdW inter-layer interaction relative to the stronger covalent intra-layer bonding.

Up to 10 GPa, there are no appreciable differences seen in the compressibility rates in the two systems. For instance, the lengths of the  $a$  and  $c$  axes at 10 GPa are reduced by about 3% and 11% with respect to their zero-pressure values in both cases. As the pressure increases, the compressibility rate along the  $a$  axis becomes slightly smaller in  $\text{SnS}_2$  than in  $\text{SnSe}_2$ , following the expected trend that a more covalent intra-layer bond is less compressible<sup>47</sup> [see Supplemental Fig. S1<sup>51</sup>]. The compressibility rate along the  $c$  axis, on the other hand, displays the opposite behavior. This can be empirically understood from the relatively more localized nature of the  $3p$  orbitals of  $\text{S}^{-2}$  compared to the  $4p$  orbitals of  $\text{Se}^{-2}$ , which gives rise to a weaker interaction across the vdW gap in  $\text{SnS}_2$  and thus increased compressibility.

The present theoretical results for the pressure dependence of the cell parameters are in very good agreement with all experimental data in the low pressure region between 0 and 10 GPa [see Fig. 1]. Beyond this point, the pressure transmitting medium used in various experiments can cause considerable differences between the compressed lattice parameters. The largest deviation is observed for the compression of the  $a$  axis in  $\text{SnSe}_2$  beyond 10 GPa in Ref. [28] and is attributed to nonhydrostatic pressure conditions in the experimental setup. A similar, but smaller effect, was also found in  $\text{SnS}_2$ <sup>48,50</sup>.

We next discuss the thermodynamic and dynamic stability of  $\text{SnSe}_2$  and  $\text{SnS}_2$  under compression. With respect to the full phase diagram, our calculations agree well with the findings reported in literature, namely that  $\text{SnSe}_2$  and  $\text{SnS}_2$  lie above the convex hull tie-line for pressures above approximately 20 and 40 GPa, respectively [see Supplemental Fig. S2<sup>51</sup>]. The occurrence of a lattice instability is established by calculating the full phonon dispersion relations in the harmonic approximation in the three-atom  $H1$  unit cell. As shown in Supplemental Fig. S3<sup>51</sup>, the lowest-energy vibrational mode has an imaginary frequency at the  $K$  point of the BZ at 20 GPa, indicating that the two systems have become dynamically unstable. Based on the above results, it would be expected that the systems will either decompose into more stable products or undergo a crystal transformation into a nearby minima in the configuration space by following the eigenvector of a soft phonon mode.

The successful synthesis of  $\text{Sn}_3\text{Se}_4$  in laser-heated diamond anvil cells<sup>10</sup> points towards the first scenario, but no traces of the  $\text{Sn}_3\text{Se}_4$  phase were detected in the high-pressure synchrotron x-ray diffraction (XRD) patterns measured at room temperature in two other recent studies<sup>19,28</sup>. This implies that a relatively large activation barrier needs to be overcome for the system to decompose, requiring not only high pressures but also high temperatures.

Evidence for the second scenario has also been provided in our combined experimental and theoretical work

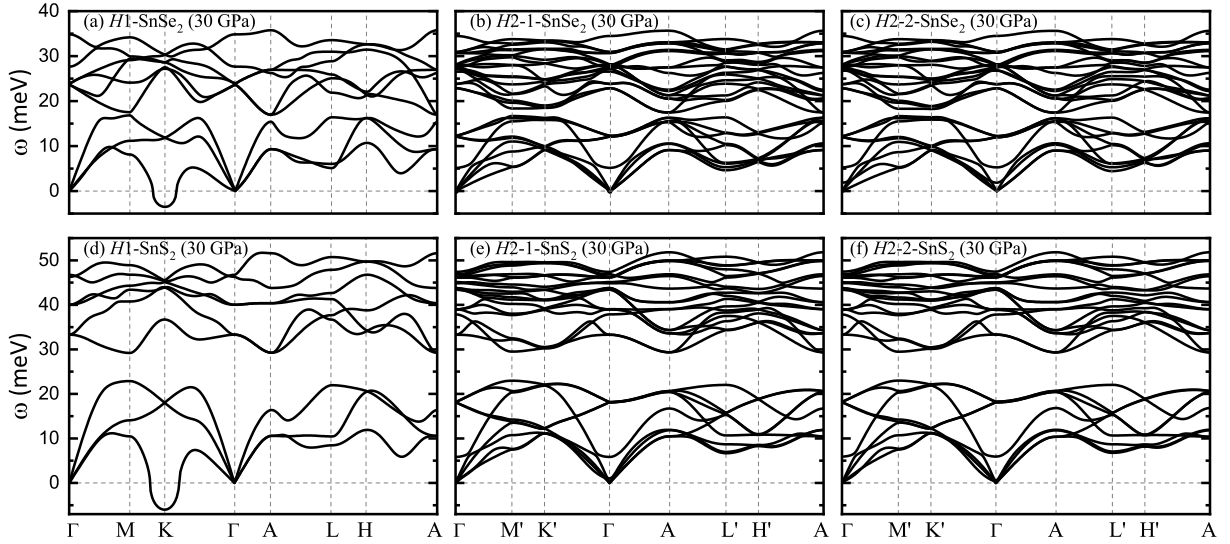


FIG. 3: Calculated phonon dispersion for the (a), (d)  $H1$  structure in the  $1 \times 1 \times 1$  unit cell and (b), (c), (e), (f)  $H2$  structures in the  $\sqrt{3} \times \sqrt{3} \times 1$  supercell of  $\text{SnSe}_2$  (top row) and  $\text{SnS}_2$  (bottom row) at 30 GPa. The  $H2-1$  and  $H2-2$  structures are derivatives of the undistorted  $\sqrt{3} \times \sqrt{3} \times 1$   $H1$  structure created via a PLD.

on  $\text{SnSe}_2$ <sup>19</sup>. Namely, the formation of a  $\sqrt{3} \times \sqrt{3} \times 1$  superlattice has been revealed through the sudden appearance of several reflections at  $(1/3, 1/3, 0)$  in XRD patterns and of two new peaks in the Raman spectra above 17 GPa. In addition, it has been shown that energetically more stable structures with lower symmetry can be constructed as detailed below. Here we will refer to the derivatives of the undistorted  $\sqrt{3} \times \sqrt{3} \times 1$   $H1$  structure created via a PLD as  $H2$ . The fact that  $\text{SnSe}_2$  has not been synthesized in the  $H2$  structure in the study by Zhou *et al.*<sup>28</sup> suggests that the formation of this metastable phase is strongly dependent on the experimental conditions. While the NaCl powder used in our high-pressure XRD experiments ensured a quasi-hydrostatic pressure environment below 40 GPa<sup>19</sup>, the silicone oil used as a pressure transmitting medium by Zhou *et al.* produced nonhydrostatic pressures above 13.2 GPa<sup>28</sup>. A similar situation has been observed for TMDs, where different pressure conditions give rise to variations in the structural and electronic properties.<sup>52,53</sup> For instance, in the case of  $\text{WS}_2$ , the transition from the  $2H_c$  to  $2H_a$  phase occurred under nonhydrostatic, but not under hydrostatic pressure<sup>53</sup>.

We now focus our attention on understanding whether a  $\sqrt{3} \times \sqrt{3} \times 1$  superstructure can also be stabilized in  $\text{SnS}_2$  via a PLD. Since the  $K$  point of the  $1 \times 1 \times 1$  unit cell folds onto the  $\Gamma$  point in the  $\sqrt{3} \times \sqrt{3} \times 1$  supercell, dynamical stability calculations can be performed by determining the phonon frequencies at the  $\Gamma$  point of the nine-atom  $H1$  structure. As pressure is increased, the two nearly degenerate lowest-energy phonon modes with  $A_{2g}$  and  $A_{2u}$  symmetry soften and become imaginary as shown in Fig. 2(a). The linear evolution of  $\omega^2$  with pressure [Fig. 2(a) inset] is a characteristic feature of a soft-mode phase transition<sup>54,55</sup>, enabling us to estimate

the critical transition pressure when  $\omega^2$  goes to zero. In this case, we obtain 18 GPa for  $\text{SnSe}_2$  and 19 GPa for  $\text{SnS}_2$ , respectively.

To construct the energetically preferred structural derivatives of the original  $H1$  phase, we follow the same strategy employed in our previous work on  $\text{SnSe}_2$ <sup>19</sup>. We displace the atomic coordinates according to the eigenvectors of  $A_{2g}$  ( $H2-1$  phase) and  $A_{2u}$  ( $H2-2$  phase) modes as well as a linear combination of the two eigenvectors ( $H2-3$  phase) to better explore the adiabatic potential energy surface. As for  $\text{SnSe}_2$ , the resulting distorted structures for the  $\sqrt{3} \times \sqrt{3} \times 1$  supercell are fully relaxed and found to converge to three distinct configurations based on the structure analysis performed with the MAISE package<sup>56</sup>. The lattice parameters, space groups, and Wyckoff positions of  $H2$  structures at 30 GPa are given in Table. S1 and the crystal structures are shown in Fig. S4<sup>51</sup>. Since  $H2-3$  is an intermediate phase along the pathway that transforms  $H2-1$  into  $H2-2$ , we will only concentrate on the  $H2-1$  and  $H2-2$  structures in our further discussion.

As can be appreciated from the pressure dependence plots of the relative enthalpy in Fig. 2(b), the  $H2$  phases are energetically more favorable above 18 and 20 GPa for  $\text{SnSe}_2$  and  $\text{SnS}_2$ , respectively. This is in good agreement with our phonon calculations at 30 GPa, showing no imaginary frequencies and demonstrating the dynamical stability of the predicted  $H2$  phases [Fig. 3]. We find the  $H2$  derivatives to be virtually degenerate in enthalpy and no distinguishable differences between their phonon spectra. A comparison of the radial distribution functions (RDFs) shown in Fig. 4 along with an estimate of the similarity factor (defined as the RDF dot product between two structures) provide further evidence that the  $H2-1$  and  $H2-2$  configurations are indeed distinct

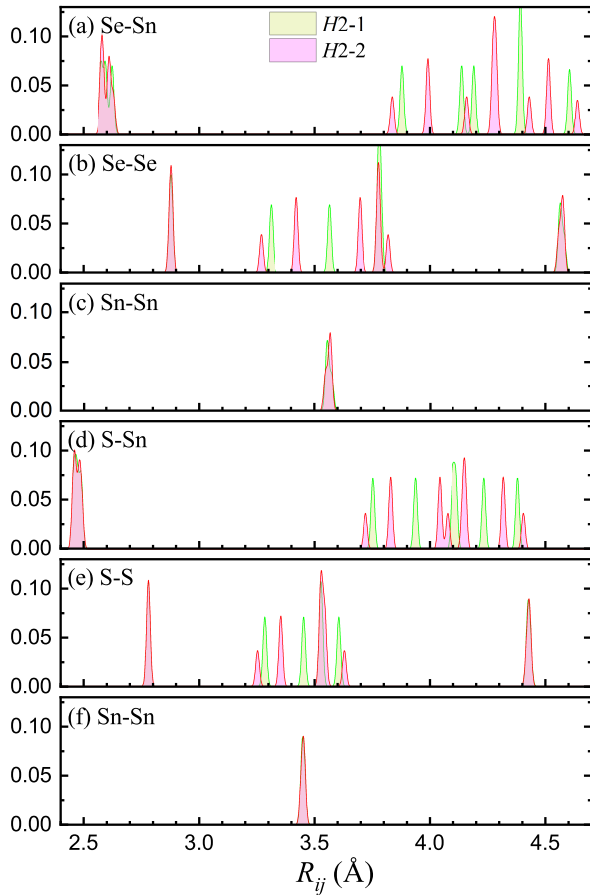


FIG. 4: Calculated radial distribution function of the  $H2$  structures for (a)-(c)  $\text{SnSe}_2$  and (d)-(f)  $\text{SnS}_2$  at 30 GPa with MAISE<sup>56</sup>.

despite having similar enthalpies. In this case, using a Gaussian spread of 0.008<sup>56</sup>, we find a similarity factor of 0.5358 and 0.6102 between the  $H2-1$  and  $H2-2$  structures for the  $\text{SnSe}_2$  and  $\text{SnS}_2$  systems, respectively. Noticeably, the main difference in the RDFs comes from the second-nearest neighbor, explaining the similar covalent network and, therefore, the very similar vibrational and low-energy electron properties of the  $H2$  derivatives. Based on the RDF analysis, we can establish that the distorted configurations are nearby local minima, a situation encountered in other systems<sup>57</sup>.

## B. Electronic properties

In this section we systematically analyze the band structure of  $\text{SnSe}_2$  and  $\text{SnS}_2$  under hydrostatic and non-hydrostatic pressure. At zero pressure, both systems are found to be semiconducting with an indirect band gap of 0.62 eV in  $\text{SnSe}_2$  and 1.35 eV in  $\text{SnS}_2$ , respectively. As for bulk TMDs consisting of the same transition metal, the compound with the most electronegative chalcogen has the largest band gap<sup>58–61</sup>. While this is the correct

trend, we need to keep in mind in our following discussion that the size of the band gaps are underestimated relative to those extracted from experiments<sup>62–66</sup> or calculated with the  $GW$  approximation or the HSE06 hybrid functional<sup>65,67</sup>.

Figure 5 shows the calculated hydrostatic band structures for the  $H1$  phase in the three-atom unit cell at 0, 6, and 20 GPa; band structures at other pressures are given in Supplemental Fig. S5<sup>51</sup>. The bottom of the conduction band displays a mixture of Sn  $s$  with chalcogen (Se or S)  $p_{xy}$  orbitals along the in-plane directions and with chalcogen  $p_z$  orbitals along the out-of-plane directions. The top of the valence band, on the other hand, consists almost entirely of chalcogen  $p_z$  orbitals. Under compression, the orbital character of the bands remains largely unaffected, but the bandwidths expand as indicated by the increase in the slope of the dispersion curves. Near the Fermi level, the most significant change takes place in the lowest conduction band level along the  $\Gamma - K$  segment. Due to a greater overlap between the chalcogen  $p_{xy}$  and Sn  $s$  orbitals, the band energy at the  $K$  point decreases, eventually dropping below the valence band maximum and closing the band gap. As a result, a pressure-induced semiconductor-to-metal transition is estimated to occur at 6 and 20 GPa in  $\text{SnSe}_2$  and  $\text{SnS}_2$ , respectively.

The predicted metallization pressures are consistent with available theoretical results<sup>19,22,50</sup>, but lower than the experimental values as anticipated from the underestimation of the band gaps in the PBE approximation. Additional changes in the metallization pressure are also expected under nonhydrostatic pressure conditions. DFT results show that a transition at a higher (lower) pressure is favored under in-plane (out-of-plane) uniaxial compressive strain [see Supplemental Fig. S6<sup>51</sup>]. This trend is in agreement with experimental resistivity measurements in  $\text{SnSe}_2$  where a semiconductor-to-metal transition was observed between 8–13 GPa under quasi-hydrostatic pressure<sup>19</sup> compared to a transition above 15.2 GPa under nonhydrostatic pressure<sup>28</sup>. As can be seen in Fig. 1(b), the in-plane compression in the latter study is considerable smaller, thus pushing the metallization point to a higher pressure.

To get a better understanding of how the internal structural parameters of the layers, the inter-layer distance, and the choice of chalcogen atom affect the electronic transition, we calculate the electronic dispersions of (i)  $\text{SnSe}_2$  structure at 0 GPa in which the Se atoms are substituted with S and the atomic coordinates are either kept unchanged (labeled as  $\text{SnSe}_2\text{-str-S}$ ) or allowed to relax (labeled as  $\text{SnSe}_2\text{-str-S-relaxed}$ ), and (ii)  $\text{SnS}_2$  structure at 0 GPa in which the S atoms are substituted with Se and the atomic coordinates are either kept unchanged (labeled as  $\text{SnS}_2\text{-str-Se}$ ) or allowed to relax (labeled as  $\text{SnS}_2\text{-str-Se-relaxed}$ ).

As shown in Supplemental Fig. S7<sup>51</sup>, the effect of replacing Se with S is an up-shift of the lowest conduction band states and, consequently, a slight increase in the band gap from 0.62 to 0.75 eV. Allowing the atoms to

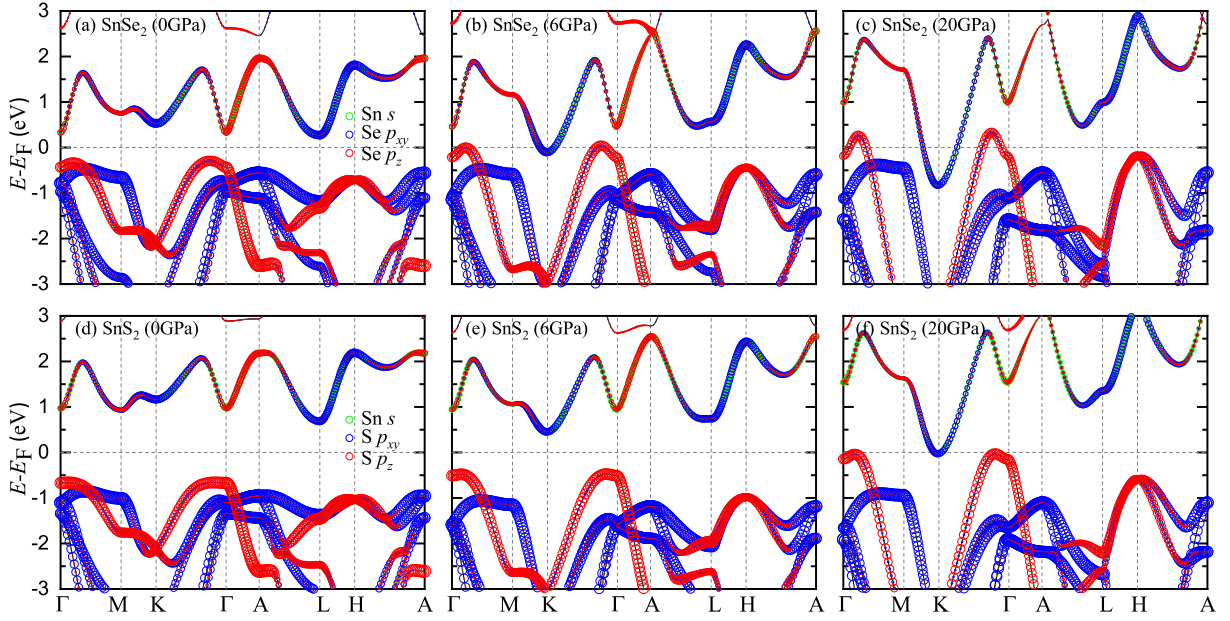


FIG. 5: Calculated band structure for the  $H1$  structure in the  $1 \times 1 \times 1$  unit cell of (a)-(c)  $\text{SnSe}_2$  and (d)-(f)  $\text{SnS}_2$  at 0, 6, and 20 GPa. The size of the symbols is proportional to the contribution of each orbital character.

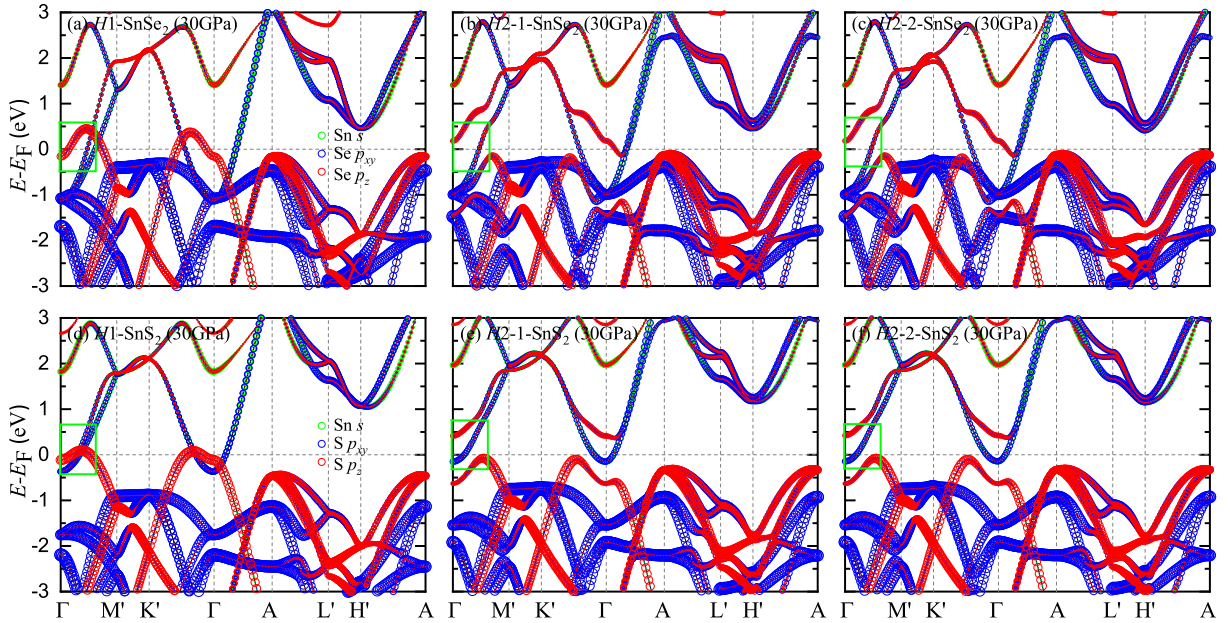


FIG. 6: Calculated band structure for the (a), (d)  $H1$  and (b), (c), (e), (f)  $H2$  structures in the  $\sqrt{3} \times \sqrt{3} \times 1$  supercell of  $\text{SnSe}_2$  (top row) and  $\text{SnS}_2$  (bottom row) at 30 GPa. The  $H2-1$  and  $H2-2$  structures are derivatives of the undistorted  $\sqrt{3} \times \sqrt{3} \times 1$   $H1$  structure created via a PLD. The area indicated by the green box in (a), (d) is to be compared to (b), (e) and (c), (f) where avoided crossing near the Fermi level can be observed in the  $H2$  structures.

relax gives an additional up-shift of 0.15 eV since the intra-layer distance is reduced to almost the ideal value in  $\text{SnS}_2$ . However this up-shift is still not large enough to reach the band gap value of  $\text{SnS}_2$ . If, on the other hand, we use the  $\text{SnS}_2$  structure with the Se pseudopotential, as in calculation (ii), we see an opposite trend since now the

lowest conduction band states move down in energy. The band gap reduces from 1.35 to 0.90 eV without atomic relaxation and further to 0.22 eV once the atoms are allowed to relax. The reduction by a factor of almost three of the band gap relative to the value in ideal  $\text{SnSe}_2$  can be ascribed to the presence of slightly more charge in the

vdW gap as the inter-layer distance is compressed by almost 10%. Supplemental Figs. S8 and S9<sup>51</sup> show total charge and charge redistribution plots for the configurations described above. Overall, the metallization process is driven by the cooperative effect of both chemical and structural factors.

We further study the evolution of the charge density with pressure. Similar to TMDs, we find that under compression more electronic charge moves away from the Sn atoms and accumulates along the intra-layer bonds formed by Sn with the chalcogen atoms and in the inter-layer region between the chalcogen atoms<sup>68–70</sup> [Supplemental Figs. S10<sup>51</sup>]. This view is also supported by the increase in the in-plane average charge at the middle of the vdW gap under applied pressure [see Supplemental Figs. S11<sup>51</sup> showing the in-plane average charge as a function of the perpendicular direction with respect to the layer]. This behavior is in contrast to intercalated carbon and boron layered compounds where, under applied pressure, the inter-layer charge from the intercalant atoms is forced out to the covalent sheets<sup>71–73</sup>.

Finally, in Fig. 6 we compare the electronic structure of  $H1$  and  $H2$  phases in the  $\sqrt{3} \times \sqrt{3} \times 1$  supercell for the two systems. As shown in our previous study on  $\text{SnSe}_2$ <sup>19</sup>, the main difference lies in the lifting of electronic degeneracy near the Fermi level along the  $\Gamma - M$  and  $K - \Gamma - A$  directions in the  $H2$  structures. Compared to the parent  $H1$  phase, there is an out-of-plane displacement of the Sn atoms resulting in a slight buckling of the Sn layers and a shift of the chalcogen atoms with respect to the center of the octahedron [see Supplemental Fig. S4<sup>51</sup>]. This modulation of atomic positions leads to the avoidance of crossings between the bands with mixed Sn  $s$  and chalcogen  $p_{xy}$  orbitals and the band with chalcogen  $p_z$  character. Similarly to the phonon spectra in Fig. 3, there are no noticeable differences between the band structure plots of the  $H2$  derivatives.

### C. Vibrational properties

In low-dimensional or layered systems, the appearance of a superlattice is often the signature of a CDW transition, as for example in TMDs<sup>31,32</sup>. In these materials, it has been established that the wave vector dependence of the e-ph coupling is crucial in understanding the CDW formation, while the FS nesting has been found to only play a minor role<sup>20,30–33</sup>. As presented in our previous study on  $\text{SnSe}_2$ <sup>19</sup>, the breaking of electronic degeneracies by a phonon-modulated lattice distortion, the reduction of the density of states (DOS) at the Fermi level, and the softening of a low-energy phonon are key signatures of a momentum-dependent e-ph coupling CDW instability. In this section, we want to investigate if the same reasoning is true for  $\text{SnS}_2$  as well.

To address the microscopic mechanism responsible for the phase transition and the origin of phonon softening at  $K$ , we calculate the adiabatic phonon self-energy

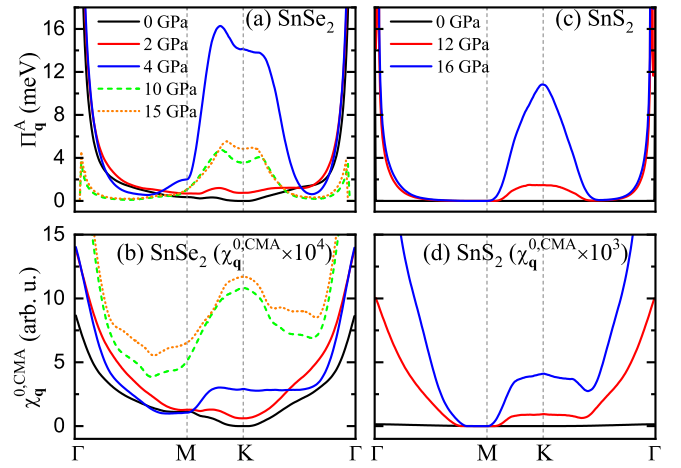


FIG. 7: The adiabatic phonon self-energy for the soft phonon mode and the static bare susceptibility in the constant matrix approximation for the  $H1$  structure in the  $1 \times 1 \times 1$  unit cell of (a)-(b)  $\text{SnSe}_2$  and (c)-(d)  $\text{SnS}_2$  as a function of pressure along a high-symmetry  $\mathbf{q}$ -path. The dashed and dotted lines for  $\text{SnSe}_2$  indicate pressures at which the material is in the metallic phase<sup>77</sup>. The  $\chi_{\mathbf{q}}^{0,CMA}$  values in (b) and (d) should be multiplied by a factor of  $10^4$  and  $10^3$ , respectively.

( $\Pi_{\mathbf{q}\nu}^A$ ) for the lowest-energy phonon mode and the static bare susceptibility in the constant matrix approximation ( $\chi_{\mathbf{q}}^{0,CMA}$ ) using the following equations<sup>43,74,75</sup>

$$\Pi_{\mathbf{q}\nu}^A = 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \left[ \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}} \right] \times \times g_{mn,\nu}^b(\mathbf{k}, \mathbf{q}) \times g_{mn,\nu}^*(\mathbf{k}, \mathbf{q}) \quad (1)$$

$$\chi_{\mathbf{q}}^{0,CMA} = 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \left[ \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}} \right] \quad (2)$$

Here, 2 is the spin degeneracy factor,  $\varepsilon_{n\mathbf{k}}$  and  $f_{n\mathbf{k}}$  represent single-particle energies and Fermi-Dirac occupation factors, respectively, and  $\Omega_{\text{BZ}}$  is the BZ volume. The screened e-ph matrix elements  $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$  were obtained as  $g_{mn,\nu}(\mathbf{k}, \mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V | \psi_{n\mathbf{k}} \rangle / \sqrt{\hbar/2\omega_{\mathbf{q}\nu}}$ , where  $\psi_{n\mathbf{k}}$  represents the Kohn-Sham single-particle eigenstates,  $\partial_{\mathbf{q}\nu} V$  is the derivative of the self-consistent potential, and  $\omega_{\mathbf{q}\nu}$  is the phonon frequency associated with phonon branch  $\nu$  and wave vector  $\mathbf{q}$ . The bare matrix element  $g_{mn,\nu}^b(\mathbf{k}, \mathbf{q})$  is calculated by multiplying the screened e-ph matrix elements  $g_{mn,\nu}(\mathbf{k}, \mathbf{q})$  with the electronic dielectric function at  $\omega=0$  [ $\varepsilon(\mathbf{q}, \omega=0)$ ]. Thus, the matrix elements  $g_{mn,\nu}^b(\mathbf{k}, \mathbf{q}) \times g_{mn,\nu}^*(\mathbf{k}, \mathbf{q})$  in Eqn. (1) can be replaced by  $|g_{mn,\nu}(\mathbf{k}, \mathbf{q})|^2 \times \varepsilon(\mathbf{q}, \omega=0)$ <sup>78</sup>.

Both  $\chi_{\mathbf{q}}^{0,CMA}$  and  $\Pi_{\mathbf{q}\nu}^A$  are properties of the FS bands and those electronic states close to them, yet  $\chi_{\mathbf{q}}^{0,CMA}$  is purely electronic, while  $\Pi_{\mathbf{q}\nu}^A$  includes the fully anisotropic e-ph interaction. As can be appreciated in Fig. 7, we observe an increasing response of  $\Pi_{\mathbf{q}\nu}^A$  and  $\chi_{\mathbf{q}}^{0,CMA}$  at the  $K$  point in both systems with increasing pressure, meaning that both FS nesting as well as the e-ph coupling strength



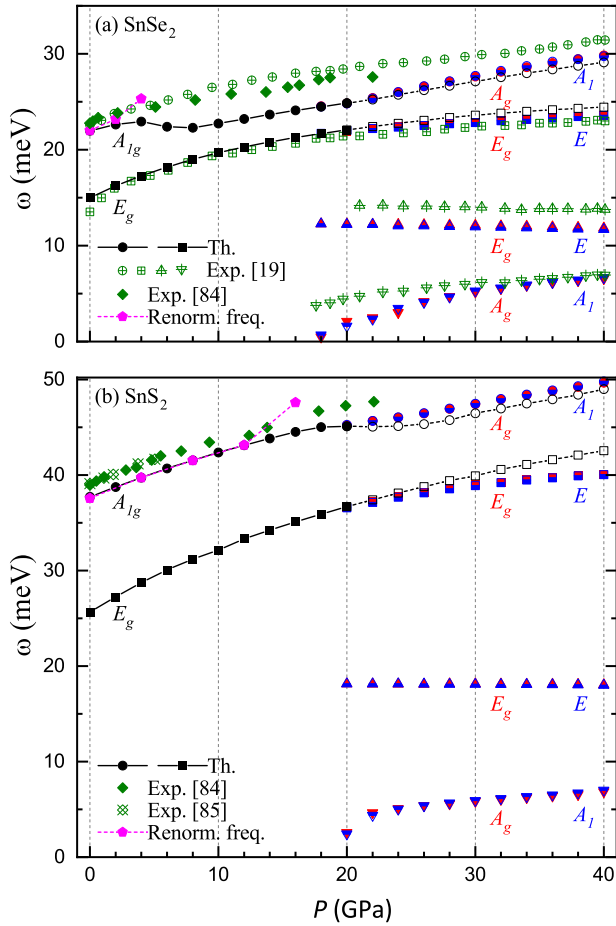


FIG. 8: Calculated frequency dependence of the Raman-active modes at  $\Gamma$  as a function of pressure for (a) SnSe<sub>2</sub> and (b) SnS<sub>2</sub>. The theoretical results are shown as black symbols (*H1*), red symbols (*H2-1*), and blue symbols (*H2-2*) while the experimental results<sup>19,84,85</sup> are shown as olive symbols. For *H1*, the data before and after the phase transition are shown as filled and open symbols. The nonadiabatically corrected frequency points are shown as filled magenta pentagons.

increase at the BZ regions close to *K* as the critical pressure for the phase transition is approached. This leads us to the conclusion that both FS nesting and strong e-ph interactions are providing important contributions in creating the PLD instability in SnS<sub>2</sub>, in close analogy to SnSe<sub>2</sub><sup>19,76,77</sup>.

Having identified the PLD instability in SnS<sub>2</sub> to be of the same origins as in SnSe<sub>2</sub>, we carry on to compare the materials' Raman-active modes' frequencies as a function of pressure, as shown in Fig. 8. The high energy *E<sub>g</sub>* mode increases monotonically as a function of pressure in both SnSe<sub>2</sub> and SnS<sub>2</sub>. The high energy *A<sub>1g</sub>* mode, on the other hand, shows a noticeable change of slope at approximately 6 and 20 GPa in the case of SnSe<sub>2</sub> and SnS<sub>2</sub>, respectively. This can be related to the semiconductor-to-metal transition in both systems as also supported by Supplemental Fig. S12<sup>51</sup>. After the phase transition, due

to the in-plane tripling of the unit cell, two additional Raman-active modes appear at 17 GPa for SnSe<sub>2</sub> and at 20 GPa for SnS<sub>2</sub>, in good agreement with available experimental data<sup>19</sup>.

The pressure dependence of the high-energy *E<sub>g</sub>* mode for SnSe<sub>2</sub> is in very good agreement with the experimental results, however, the high-energy *A<sub>1g</sub>* mode, while reproducing nicely the qualitative trend, underestimates the phonon energies by  $\sim 0.5$  meV at 0 GPa and  $\sim 3$  meV at 6 GPa (the metallization pressure) compared to experiments<sup>19</sup>. Recent studies on other insulators and semiconductors show that the underestimation of phonon energies with respect to experiments can be due to the neglect of nonadiabatic effects in the theoretical approach<sup>79–83</sup>. In order to assess the effect of nonadiabatic corrections on the phonon dispersions in our systems, we employed a field-theoretic framework<sup>74</sup>, where the phonon self-energy  $\Pi_{\mathbf{q}\nu}$  can be partitioned into adiabatic and nonadiabatic contributions, i.e.,  $\Pi(\omega) = \Pi^A + \Pi^{\text{NA}}(\omega)$ . Thus, the nonadiabatic corrections to the self-energy as a function of the phonon mode  $\nu$  and wave vector  $\mathbf{q}$  are given by:

$$\hbar\Pi_{\mathbf{q}\nu}^{\text{NA}}(\omega) = 2 \sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \times g_{mn,\nu}^b(\mathbf{k}, \mathbf{q}) \times g_{mn,\nu}^*(\mathbf{k}, \mathbf{q}) \times \left[ \frac{f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar(\omega + i\eta)} - \frac{f_{m\mathbf{k}+\mathbf{q}} - f_{n\mathbf{k}}}{\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}}} \right] \quad (3)$$

with  $\eta$  being a positive infinitesimal number. The nonadiabatic phonon spectral function<sup>86,87</sup> can then be calculated using

$$A_{\mathbf{q}\nu}^{\text{NA}}(\omega) = \frac{1}{\pi} \text{Im} \left[ \frac{2\hbar\omega_{\mathbf{q}\nu}}{(\hbar\omega)^2 - (\hbar\omega_{\mathbf{q}\nu})^2 - 2\hbar\omega_{\mathbf{q}\nu}\Pi_{\mathbf{q}\nu}^{\text{NA}}(\omega)} \right] \quad (4)$$

Equation (4) reveals that a strong response of the system is expected at the nonadiabatic phonon frequency,  $\Omega_{\mathbf{q}\nu}$ , when the denominator is very small or vanishes. The renormalized nonadiabatic phonon energy, that is, the phonon energy modified by the phonon self-energy of Eqn. (3) is thus given by

$$\Omega_{\mathbf{q}\nu}^2 \simeq \omega_{\mathbf{q}\nu}^2 + 2\omega_{\mathbf{q}\nu}\text{Re}\Pi_{\mathbf{q}\nu}^{\text{NA}}(\Omega_{\mathbf{q}\nu}) \quad (5)$$

The nonadiabatic spectral functions and the nonadiabatic phonon dispersions obtained via Eqns. (4) and (5) at various pressures along the  $\Gamma - M - K - \Gamma$  direction for SnSe<sub>2</sub> and SnS<sub>2</sub> are reported in Fig. 9. As can be appreciated from Fig. 9, the nonadiabatic effects are very small in both systems at ambient pressure. As the pressure increases (and the band gap decreases), the renormalization of the *A<sub>1g</sub>* mode energy becomes significant around 4 GPa in SnSe<sub>2</sub> and around 16 GPa in SnS<sub>2</sub>. In particular, the *A<sub>1g</sub>* mode in SnSe<sub>2</sub> hardens by  $\sim 2$  meV at 4 GPa

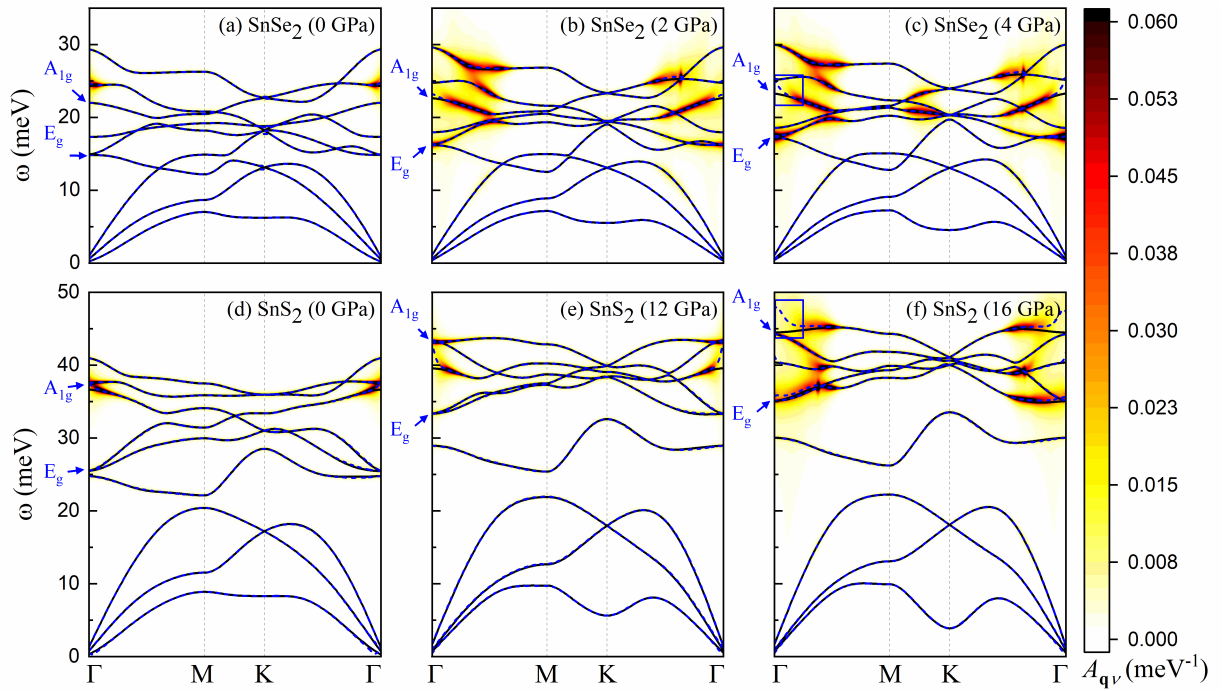


FIG. 9: Calculated nonadiabatic phonon spectral function and nonadiabatic renormalized phonon for the  $H1$  structure in the  $1 \times 1 \times 1$  unit cell of (a)-(c)  $\text{SnSe}_2$  and (d)-(f)  $\text{SnS}_2$  at various pressures. The solid black and dashed blue lines represent the DFPT phonon and renormalized phonon dispersions, respectively. The color map corresponds to the nonadiabatic phonon spectral function.

[Fig. 9(c)], improving the quantitative agreement of our calculations with the experiments<sup>19</sup> [see also Fig. 8]. Similarly, the  $A_{1g}$  mode in  $\text{SnS}_2$  hardens by  $\sim 3$  meV at 16 GPa as shown in Fig. 9(f). For the  $E_g$  mode, where the agreement between experiments and theory has already been very good, the nonadiabatic corrections are found to be very small.

As  $\text{SnSe}_2$  and  $\text{SnS}_2$  are polar semiconductors at ambient and low pressures, we also want to address the topic of LO-TO splitting. At ambient pressure, we observe a LO-TO splitting of 7 meV for  $\text{SnSe}_2$  and 11.8 meV for  $\text{SnS}_2$  [see Supplemental Fig. S13<sup>51</sup>]. With increasing pressure, the band gap decreases and the value for the dielectric function increases. In turn, the magnitude of the LO-TO splitting decreases, in accordance with experimental measurements in other polar semiconductors<sup>88,89</sup>. Interestingly, however, at the critical pressures above which our compounds become metallic, our calculations still yield finite values for the splitting (around 6.4 meV for  $\text{SnSe}_2$  and 10 meV for  $\text{SnS}_2$ ). A possible explanation for the residual LO-TO splitting is that in the pressure regions, where the materials pass through the semiconductor-metal phase transition, the charge carrier concentration is so low that the long-range Coulomb interactions are not fully screened, thus allowing for finite LO-TO splitting. In the fully metallic state at higher pressures, the long-range Coulomb interactions are screened completely leading to the degeneracy of LO and TO modes. Although highly interesting, resolving the intermediate bad

metal phase would go beyond the scope of this work and is therefore the focus of future investigations.

#### D. Superconducting properties

Experimental evidence of pressure-induced superconductivity in  $\text{SnSe}_2$  has been recently provided based on electrical transport and synchrotron XRD measurements<sup>28</sup>. The superconducting state is observed to emerge at 18.6 GPa and to reach a maximum  $T_c$  of about 6.1 K, which remains nearly constant in a large pressure range between 30.1 and 50.3 GPa. Earlier studies have demonstrated superconductivity in bulk and thin films  $\text{SnSe}_2$  through intercalation and gating<sup>13,90-92</sup> as well as interface superconductivity in  $\text{SnSe}_2$ /ion-liquid and  $\text{SnSe}_2$ /graphene<sup>93,94</sup>.

In this section we investigate the origin of the observed superconducting transition in  $\text{SnSe}_2$  using the Migdal-Eliashberg (ME) formalism implemented in the EPW code<sup>43,95</sup>. To facilitate the comparison with the experimental results of Zhou *et al.*<sup>28</sup>, the superconducting properties are calculated at the experimental unit cell parameters for nonhydrostatic pressure points at 23 and 30 GPa while allowing the atomic positions to relax. The resulting electronic structure and phonon dispersion are shown in Supplemental Figs. S14-S16<sup>51</sup>. A comparison with the plots under hydrostatic conditions at 20 and 30 GPa [Figs. 5, 6, and S3] demonstrate that the elec-

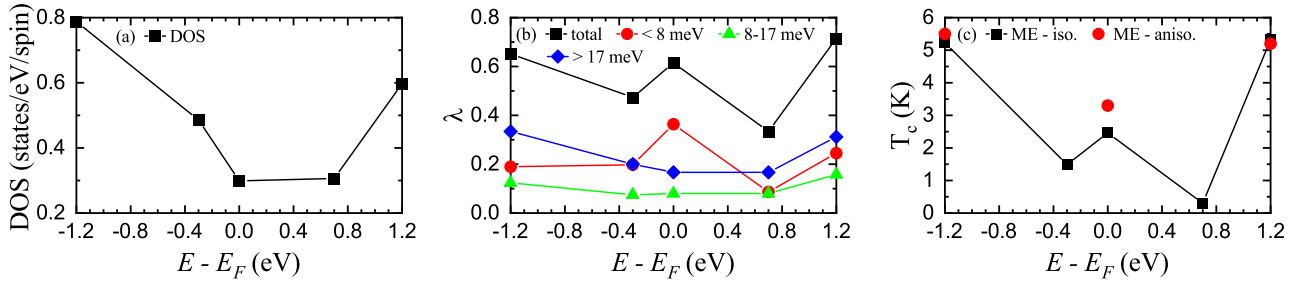


FIG. 10: Variations in (a) DOS at  $E_F$ , (b)  $\lambda$ , and (c)  $T_c$  as a function of a rigid shift of the Fermi level for the  $H1$  structure in the  $1 \times 1 \times 1$  unit cell of  $\text{SnSe}_2$  at the experimental unit cell parameters at 23 GPa. In (b), squares represent the total  $\lambda$ , while circles, triangles, and rhombuses represent the contribution of the low-, medium- and high-energy modes. In (c), circles and squares represent the  $T_c$  obtained from the numerical solutions of the anisotropic and isotropic ME equations.

tronic structure is highly insensitive to the crystal structure parameters while the phonon frequencies are slightly affected. For instance, according to our phonon calculations within the harmonic approximation a lattice instability starts developing at 20 and 30 GPa under hydrostatic and nonhydrostatic conditions, respectively. Since the pressure-dependence of the lowest acoustic mode at the  $K$  point is responsible for the dynamical instability in this compound, the reduced in-plane compressibility rate in the latter case leads to a decrease in the phonon softening rate and consequently an increase in the stability region up to 30 GPa. While this trend is in the right direction, the transition pressure is still underestimated compared to the nonhydrostatic experiments in Ref. [28] that showed no structural phase transition or decomposition up to 46 GPa. The situation is reminiscent of the one encountered in  $\text{NbSe}_2$  and  $\text{NbS}_2$ , where the instability found at the harmonic level has been shown to be weakened or even removed when quantum anharmonic effects are taken into account, and therefore suppress the formation of the CDW phase<sup>16,30</sup>. A similar scenario occurring in  $\text{SnSe}_2$  would extend the stabilization region to higher pressures as found in experiment. To check this point, we re-evaluated the phonons at the  $K$  point with a larger smearing value of 0.03 Ry and indeed found that the imaginary phonon mode is removed, thus preserving the dynamic stability [see dash line in Supplemental Fig. S16(a)<sup>51</sup>].

In order to understand the origin of the superconducting state, we evaluate the Eliashberg spectral function  $\alpha^2F(\omega)$  and the corresponding e-ph coupling strength  $\lambda$ . A comparative analysis of the  $\alpha^2F(\omega)$  and the atomically resolved phonon DOS (PHDOS) at the experimental lattice cell parameters at 23 GPa [Supplemental Fig. S15<sup>51</sup>] reveals that the low-frequency phonons below 8 meV associated with both Sn and Se vibrations contribute 60% of the total  $\lambda = 0.62$ , while the phonons in the high-frequency region between 17 and 32 meV dominated by Se atoms vibrations give approximately 30% of  $\lambda$  [Fig. 10(b)]. Using a typical value of  $\mu^* = 0.1$ , we predict a  $T_c$  of 2.5 and 3.3 K from the numerical solutions of the isotropic and anisotropic ME gap equations<sup>43,95</sup>,

slightly below the 4.0 K onset temperature ( $T_c^{\text{onset}}$ ) of electrical resistance drop at 22 GPa reported in Ref. [28]. The results are almost unchanged when the calculations are performed at the experimental lattice cell parameters at 30 GPa [Supplemental Fig. S16<sup>51</sup>]. For the  $K$  point phonons computed at the larger smearing value of 0.03 Ry, we get  $\lambda = 0.59$  and an isotropic  $T_c = 2.3$  K with  $\mu^* = 0.1$ .

Considering that superconductivity in  $\text{SnSe}_2$  has been achieved experimentally either in Se-deficient<sup>28</sup> or intercalated<sup>13,90–92</sup> samples, we further investigate the impact of doping on the predicted  $T_c$  via a rigid shift of  $E_F$ , chosen to match particular features either in the valence or in the conduction band, for the structure at the experimental lattice cell parameters at 23 GPa. The results summarized in Fig. 10 can be rationalized in terms of the changes taking place at the FS upon raising or lowering the Fermi level. In the undoped systems, the momentum-resolved e-ph coupling strength  $\lambda_{\mathbf{k}}$  on the FS displays a highly anisotropic distribution (between 0.3 and 1.1) where the lower and upper regions of the spectra can be associated with the  $\Gamma$  and  $K$ -centered pockets, respectively [Fig. 11(a),(c)]. A continuous distribution with a sizable anisotropy is also found for the superconducting gap on the FS as shown in Fig. 11(b),(d). When  $E_F$  is moved up by 0.7 eV, the spread in  $\lambda_{\mathbf{k}}$  is reduced to a much narrower range of 0.3–0.5 since the  $\Gamma$ -centered hole-like FS sheet vanishes. However, the spread goes back to the wider range once the system is doped until the Fermi level matches the first peak in the conduction band DOS as two additional FS sheets are introduced, thus opening extra scattering channels. This leads to an enhancement in both  $\lambda = 0.72$  and  $T_c \approx 5.2$  K, the latter in good agreement with the maximum  $T_c$  value found experimentally. Similar trends are also observed when the Fermi level is shifted down. It is also worth noting that the non-linear dependence of the total  $\lambda$  with doping correlates closely with that of the low-energy phonons [Fig. 10], indicating that these modes play a decisive role in raising the e-ph coupling strength and  $T_c$  in this system.

For completeness, we also analyze the superconducting properties of  $\text{SnS}_2$ . Assuming that the dynamical

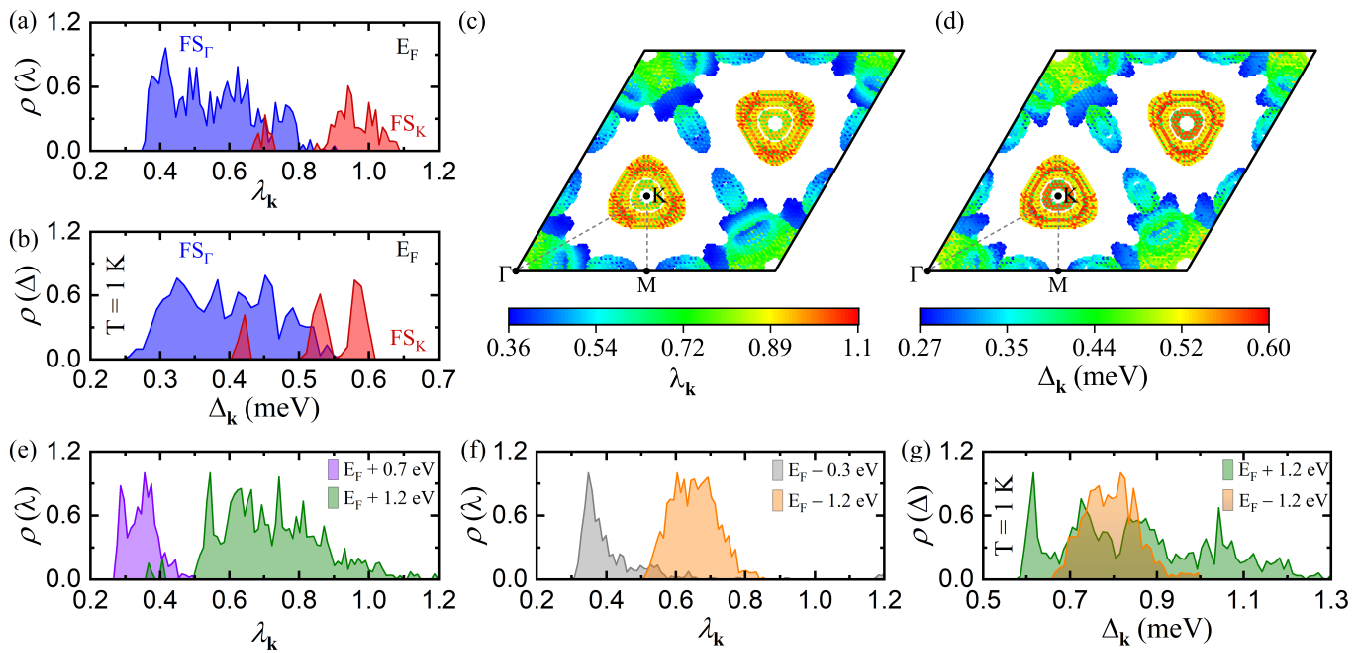


FIG. 11: Calculated superconducting properties for the *H1* structure in the  $1 \times 1 \times 1$  unit cell of  $\text{SnSe}_2$  at the experimental unit cell parameters at 23 GPa. Energy distribution of the (a) e-ph coupling strength  $\lambda_{\mathbf{k}}$  and (b) superconducting gap  $\Delta_{\mathbf{k}}$ ; color coded by FS sheets:  $\Gamma$ -centered holelike pocket  $\text{FS}_{\Gamma}$  (blue), and  $K$ -centered electronlike pocket  $\text{FS}_K$  (red). Momentum-resolved (c) e-ph coupling strength  $\lambda_{\mathbf{k}}$  and (d) superconducting gap  $\Delta_{\mathbf{k}}$  on the FS (top-view). Energy distribution of the (e) e-ph coupling strength  $\lambda_{\mathbf{k}}$ , and (f), (g) superconducting gap  $\Delta_{\mathbf{k}}$  at  $T = 1$  K at various rigid shifts of the Fermi level with respect to the original data as shown in Supplemental Fig. S14<sup>51</sup>.

stability of  $\text{SnS}_2$  can be extended to higher pressures under nonhydrostatic compression as for  $\text{SnSe}_2$ , we perform superconductivity calculations at 30 GPa and used a smearing value of 0.04 Ry for the phonons at the  $K$  point in order to remove the imaginary frequency. The calculated PHDOS and Eliashberg spectral function comprise of two well defined regions separated by a gap between the acoustic and optical branches [Supplemental Fig. S18<sup>51</sup>]. Integrating  $\alpha^2 F(\omega)$ , the strength of the e-ph coupling  $\lambda$  is estimated to be 1.08. From the solutions of the isotropic and anisotropic ME gap equations with  $\mu^* = 0.1$ , we obtain a  $T_c$  of 4.6 and 5.9 K, respectively [Supplemental Figs. S19-S20<sup>51</sup>]. The values of  $\lambda$  and  $T_c$  are twice larger than those in  $\text{SnSe}_2$  due to the enhanced coupling of the acoustic phonons dominated by Sn vibrations with the electronic state present at the Fermi level. Similar to  $\text{SnSe}_2$ , the strongest coupling takes place on the  $K$ -centered FS, but both  $\lambda_{\mathbf{k}}$  and  $\Delta_{\mathbf{k}}$  exhibit a much broader distribution profile. We also find that  $\lambda$  is strongly affected by changes in the FS topology when  $E_F$  is shifted up or down. Namely, the e-ph coupling drops significantly as the contribution of the low-energy acoustic modes is drastically reduced and large doping is required to raise back the  $T_c$ .

Finally, we investigate  $\text{SnSe}_2$  and  $\text{SnS}_2$  compounds in the *H2-1* structure as potential superconductors. The results are presented in Supplemental Figs. S21-S23<sup>51</sup>. Despite the close resemblance between the DOS and PH-

DOS of the parent and superlattice structures, the  $T_c$  in *H2-1* phase is found to be an order of magnitude lower than in the *H1* phase. This can be linked to a decrease in the e-ph coupling over the full phonon range due to the reorganization that takes place at the FS. Looking at the electronic band structure in the  $\sqrt{3} \times \sqrt{3} \times 1$  supercell [region enclosed by the green box in Fig. 6], it can be seen that the  $\Gamma$ -centered FS sheet disappears as a gap opens in the electronic band dominated by Se  $p_z$  orbitals. An increase in the DOS at  $E_F$  is expected to produce a marked enhancement in  $T_c$ , particularly under hole doping as multiple bands will cross the Fermi level. In  $\text{SnSe}_2$  a 0.3 eV down shift in  $E_F$  results in an isotropic  $T_c = 3.7$  K, while in  $\text{SnS}_2$  a 0.5 eV down shift leads to  $T_c = 3.5$  K.

#### IV. CONCLUSIONS

In this work, we have performed a comparative study of  $\text{SnSe}_2$  and  $\text{SnS}_2$  at ambient conditions and pressures up to 40 GPa. We show that the apparent contradictions among high-pressure results on  $\text{SnSe}_2$  can be attributed to differences in experimental conditions and that inclusion of nonadiabatic effects improves the quantitative agreement with the measured Raman-active phonon frequencies. We further demonstrate that a periodic lattice transition, of a similar origin to the one observed

in SnSe<sub>2</sub>, also occurs in SnS<sub>2</sub> above 20 GPa. In addition, we examine the nature of the superconducting state recently observed in SnSe<sub>2</sub> under nonhydrostatic pressure, and provide evidence that the superconducting transition can be explained within a standard phonon-mediated mechanism. The emergence of superconductivity with a comparable critical temperature in SnS<sub>2</sub> under similar experimental conditions is also predicted. Finally, we show that in the high pressure PLD *H2-1* phase the  $T_c$  is reduced by an order of magnitude compared to the high-symmetry *H1* phase in both systems, a fact that we attribute to a restructuring and suppression of large parts of the Fermi surface.

### Conflicts of interest

There are no conflicts to declare.

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- <sup>77</sup> In the case of those pressures, where  $\text{SnSe}_2$  is in the metallic phase,  $g_{mn,\nu}^b(\mathbf{k}, \mathbf{q}) \times g_{mn,\nu}^*(\mathbf{k}, \mathbf{q})$  has been approximated using the standard expression  $|g_{mn,\nu}(\mathbf{k}, \mathbf{q})|^2$  due to the fact that  $\varepsilon(\mathbf{q}, \omega = 0)$  diverges for metals.
- <sup>78</sup> Due to the layered structure of the considered compounds, the dielectric function exhibits a slight anisotropy with respect to its in-plane and out-of-plane components, as shown in Supplemental Fig. S13<sup>51</sup>. The differences between calculations using the in-plane, the out-of-plane or an average of the two are negligible. For simplicity and consistency, all results presented in the paper were therefore obtained using the in-plane value of the dielectric function.
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