

Unusual anisotropic thermal expansion in multilayer SnSe leads to positive-to-negative crossover of Poisson's ratio

Cite as: Appl. Phys. Lett. **116**, 083101 (2020); <https://doi.org/10.1063/1.5142639>

Submitted: 17 December 2019 . Accepted: 14 February 2020 . Published Online: 26 February 2020

Rui-Zi Zhang, Jian Liu , Yu-Yang Zhang , Shixuan Du, and Sokrates T. Pantelides



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Experimental investigation of buffer traps physical mechanisms on the gate charge of GaN-on-Si devices under various substrate biases](#)

Applied Physics Letters **116**, 083501 (2020); <https://doi.org/10.1063/1.5124871>

[Theoretical study of the structure and magnetism of \$Ga_{1-x}V_xSb\$ compounds for spintronic applications](#)

Applied Physics Letters **116**, 082105 (2020); <https://doi.org/10.1063/1.5140817>

[The effect on the optical modes of quaternary chalcogenides upon metal and chalcogen substitution](#)

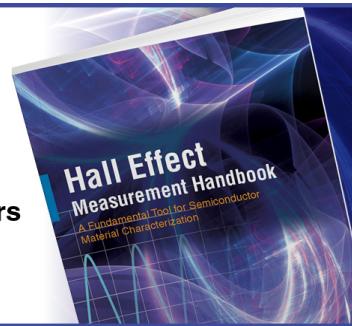
Applied Physics Letters **116**, 082103 (2020); <https://doi.org/10.1063/1.5143248>



Hall Effect Measurement Handbook

A comprehensive resource for researchers

Explore theory, methods, sources of errors, and ways to minimize the effects of errors



Request it here

Lake Shore
CRYOTRONICS

Unusual anisotropic thermal expansion in multilayer SnSe leads to positive-to-negative crossover of Poisson's ratio

Cite as: Appl. Phys. Lett. **116**, 083101 (2020); doi: [10.1063/1.5142639](https://doi.org/10.1063/1.5142639)

Submitted: 17 December 2019 · Accepted: 14 February 2020 ·

Published Online: 26 February 2020



Rui-Zi Zhang,^{1,2} Jian Liu,^{2,3} Yu-Yang Zhang,^{1,4} Shixuan Du,^{1,4,a)} and Sokrates T. Pantelides^{1,2}

AFFILIATIONS

¹Institute of Physics and University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

²Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

³Optics and Thermal Radiation Research Center, Shandong University, Qingdao, Shandong 266237, China

⁴CAS Centre for Excellence in Topological Quantum Computation, Beijing 100190, People's Republic of China

^{a)}Author to whom correspondence should be addressed: sxdu@iphy.ac.cn

ABSTRACT

Monolayer SnSe has been predicted to exhibit an unusual anisotropic thermal expansion—when heated, the long lattice parameter contracts, while the short one expands, resulting in a rectangular-to-square-lattice phase transformation at a critical temperature (T_c). Here, we employ density-functional-theory calculations to demonstrate an even more notable thermal-expansion behavior of SnSe from monolayer to bulk. We find that the unusual thermal expansion persists in multilayers, while the coefficients of thermal expansion of different numbers of layers are almost identical. This behavior results from a delicate interplay between the elastic stiffness coefficient and Grüneisen parameters. Finally, we find that the Poisson's ratio of multilayer SnSe, which is positive at $T = 0\text{ K}$, gets smaller with increasing temperature and even turns negative, signaling a zero Poisson's ratio at a particular temperature. Overall, the present results provide another perspective in understanding the unusual thermal properties of monochalcogenides.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5142639>

Materials usually expand when heated. Negative thermal expansion (NTE) has been found in two-dimensional materials, such as graphene,^{1,2} silicene,^{2,3} and germanene,^{2,3} and in bulk materials, such as ZrW_2O_8 ⁴ and ScF_3 .⁵ Layered materials with negative thermal expansion often exhibit distinct thermal expansion behavior in their monolayer and bulk forms. For example, the coefficient of thermal expansion (CTE) of graphene is three times as large as that of graphite.⁶ Monolayer^{7–9} and bulk^{10,11} group-IV monochalcogenides exhibit intriguing anisotropic thermal expansion behavior: the long lattice parameter a in the armchair direction contracts, while the short lattice parameter b in the zigzag direction expands with increasing temperature, until a critical temperature (T_c) is reached at which a and b become equal. Monolayer group-IV monochalcogenides have also been predicted to have a negative Poisson's ratio at $T = 0\text{ K}$ (the monolayer becomes thicker when stretched along the armchair direction).^{12,13} It was demonstrated that the Poisson's ratio is temperature-dependent in some cases.^{14–16} Given the unusual thermal-expansion properties of monolayer and bulk group-IV monochalcogenides, the

question remains open whether unusual thermal phenomena occur in their multilayer versions.

In this Letter, we investigate the thermal expansion behavior and Poisson's ratio of SnSe as a representative of group-IV monochalcogenides using Grüneisen's theory combined with density functional theory (DFT) calculations. We demonstrate that SnSe, from monolayer to bulk, exhibits similar anisotropic thermal-expansion behavior, namely, the short lattice parameter expands, while the long lattice parameter shrinks, with increasing temperature. Such thermal expansion behavior is indicative of a structural phase transition that occurs when the two lattice parameters become equal. On the other hand, the CTEs for the two in-plane directions barely vary with the thickness of multilayers, in sharp contrast to the case of graphene/graphite. This different behavior is due to the fact that the CTEs in SnSe are largely controlled by the difference of the Grüneisen parameters along two directions of *in-plane* phonon modes, which are not affected by the layer stacking in the *out-of-plane* direction. Associated with such large anisotropic thermal expansion, the Poisson's ratios of these materials

are found to be temperature-dependent as well. It is particularly noteworthy that the Poisson's ratios of few-layer SnSe, which are positive at $T = 0$ K, diminish with increasing temperature and turn negative at specific temperatures where the Poisson's ratio is zero.

We apply the Grüneisen theory within the quasiharmonic approximation to investigate thermal expansion

$$\begin{pmatrix} \alpha^i \\ \alpha^j \end{pmatrix} = \frac{1}{\det(C) \times A} \begin{pmatrix} C_{22} & -C_{12} \\ -C_{12} & C_{11} \end{pmatrix} \begin{pmatrix} \sum_{\vec{q}\lambda} \frac{dU_{\vec{q}\lambda}}{dT} \gamma_{\vec{q}\lambda}^i \\ \sum_{\vec{q}\lambda} \frac{dU_{\vec{q}\lambda}}{dT} \gamma_{\vec{q}\lambda}^j \end{pmatrix}, \quad (1)$$

where α^i and α^j are the CTEs in the x and y directions, $\det(C)$ is the determinant of the elastic stiffness coefficients, $C_{ij} = 1/A(\partial^2 E / \partial \epsilon_i \partial \epsilon_j)$, A is the area of the unit cell, E is the total energy, ϵ_i is strain in the i direction, $U_{\vec{q}\lambda} = \hbar\omega_{\vec{q}\lambda}(n_{\vec{q}\lambda} + \frac{1}{2})$ is the internal vibration energy of phonon mode $\vec{q}\lambda$ with frequency $\omega_{\vec{q}\lambda}$, $n_{\vec{q}\lambda}$ is the Bose-Einstein distribution function, and $\gamma_{\vec{q}\lambda}^i = -\frac{\partial \ln \omega_{\vec{q}\lambda}}{\partial \epsilon_i}$ are the Grüneisen parameters associated with phonon mode $\vec{q}\lambda$ for strain component ϵ_i .

We also define the specific-heat-weighted Grüneisen parameter $\tilde{\gamma}_\epsilon$ as

$$\tilde{\gamma}_\epsilon = \int d\omega [\gamma_\epsilon(\omega) \times \tilde{C}(\omega)], \quad \epsilon = i, j, \quad (2)$$

where $\gamma_\epsilon(\omega) = \sum_{\vec{q}\lambda} \gamma_{\vec{q}\lambda}^\epsilon \delta(\omega - \omega_{\vec{q}\lambda})$ is the generalized Grüneisen parameter. $\tilde{C}(\omega) = dU(\omega)/dT$ is the harmonic specific heat, and $U(\omega) = \sum_{\vec{q}\lambda} U_{\vec{q}\lambda} \delta(\omega - \omega_{\vec{q}\lambda})$. Substituting Eq. (2) into Eq. (1), the CTEs can also be expressed as

$$\begin{cases} \alpha^i = \frac{1}{\det(C) \times A} (C_{22}\tilde{\gamma}_i - C_{12}\tilde{\gamma}_j), \\ \alpha^j = \frac{1}{\det(C) \times A} (C_{11}\tilde{\gamma}_j - C_{12}\tilde{\gamma}_i). \end{cases} \quad (3)$$

The Poisson's ratio is defined as $\nu_{ji} = -\epsilon_i/\epsilon_j$, which corresponds to a resulting strain in direction i when an external strain is applied in direction j . We consider the temperature dependence of the Poisson's ratio arising solely from thermal expansion, i.e., Poisson's ratios at finite temperatures, $\nu_{ji}(T)$, are obtained by fitting $\epsilon_i = -\nu_{ji}(T)\epsilon_j + \nu_2(T)\epsilon_j^2 + \nu_3(T)\epsilon_j^3$ when the lattice constants are held at $a(T)$ and $b(T)$.

The calculations are performed using the QUANTUM ESPRESSO package.¹⁷ For the electronic-structure calculations, we use norm-conserving Martin-Troullier pseudopotentials¹⁸ within the generalized gradient approximation.¹⁹ The electronic wave-functions are expanded in a plane wave basis with a kinetic energy cut-off of 80 Ry. Lattice-dynamics calculations are performed using density-functional perturbation theory (DFPT).²⁰ For monolayer and multilayers, a vacuum spacing of at least 20 Å is used. For Brillouin-zone sampling, the k -point mesh is $6 \times 6 \times 2$ for bulk and $9 \times 9 \times 1$ for mono- and multilayers. The q -point mesh is $5 \times 5 \times 2$ for bulk and $9 \times 9 \times 1$ for mono- and multilayers. A series of total-energy calculations at strains ranging from -0.2% to $+0.2\%$ was performed in order to obtain values for $C_{ij} = 1/A(\partial^2 E / \partial \epsilon_i \partial \epsilon_j)$. For each strain value, we also

calculated the corresponding phonon spectra, which we used to obtain the Grüneisen parameters $\gamma_{\vec{q}\lambda}^i$. The CTEs along the two directions are then obtained using Eq. (1). The structure figures are produced with VESTA.²¹

Monolayer SnSe adopts an orthorhombic structure (space group *Pnma*) that is similar to that of phosphorene, with four threefold-coordinated atoms in the unit cell. The long axis x and the short axis y are in the armchair and zigzag directions, respectively, as shown in Fig. 1. The multilayers and bulk material adopt an *AB* stacking layered structure.

We start with the thermal expansion of bulk SnSe. Experimental studies have demonstrated that the long (short) lattice parameter contracts (expands) along the armchair (zigzag) direction with increasing temperature, until the two lattice parameters become equal at 826 K.¹¹ This behavior is reproduced by the calculations. The predicted T_c is 1040 K, as shown in Fig. 2(a), in reasonable agreement with the measurements.^{22,23} The present work is based on perturbation theory and therefore neglects anharmonic contributions, in contrast to quantum molecular dynamics (QMD) simulations.⁸ On the other hand, the key value of the present calculations is that they allow a detailed analysis of the origin of various features by tracing them to Grüneisen parameters and, through them, to contributions of different phonon modes. In addition, in the cases where QMD simulations are available, comparison of the two results allows us to deduce the contributions of anharmonic terms. Thus, the present work provides further insights into the peculiar thermal behavior of group-IV monochalcogenides and into the possible control of Poisson's ratios.

We find that the anisotropic thermal expansion behavior persists from bulk to monolayer, but the phase transition occurs at increasingly lower temperatures, where the phase transition temperatures T_c are identified as the cross points of the two lattice parameters,^{8,11} as shown in Fig. 2(a). The calculated T_c 's of monolayer and bilayer are 190 K and 590 K, respectively. This intriguing anisotropic thermal expansion behavior, which represents the different signs of CTEs along two directions, can be attributed to the delicate interplay of elastic stiffness coefficients C_{ij} and the specific-heat-weighted Grüneisen parameters $\tilde{\gamma}_\epsilon$, as manifested in Eq. (3). Here, we use the specific temperature 150 K to exhibit the interplay between $\gamma_\epsilon(\omega)$ and C_{ij} , as shown in Table I. α^i is negative and α^j is positive after the relevant C_{ij} and $\tilde{\gamma}_\epsilon$ are substituted into Eq. (3).

It is worth noting that the present T_c for monolayer SnSe, 190 K, is almost the same as the value obtained by QMD, 175 ± 11 K.⁸ The small difference can be attributed to the fact that the present

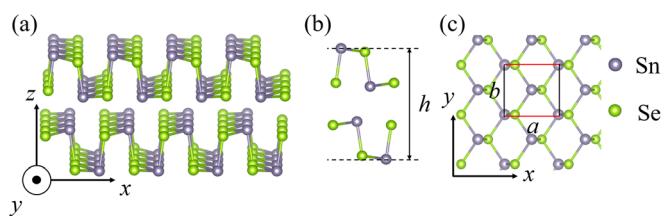


FIG. 1. (a) Overview and (b) sideview of bulk SnSe. The thickness h is defined as the vertical distance between the top and bottom atomic layers. (c) Top view of monolayer SnSe. Here, a is the long lattice parameter along the armchair (x) direction, b is the short lattice parameter along the zigzag (y) direction, and h is thickness of few layers SnSe.

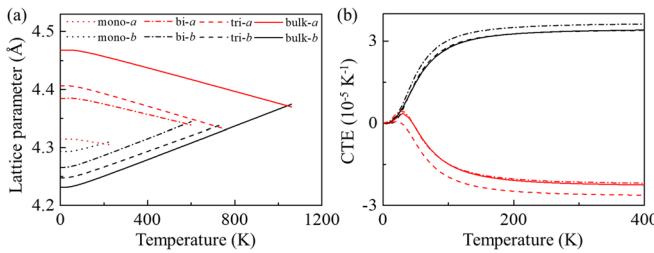


FIG. 2. (a) Thermal expansion curvature and (b) corresponding CTEs in the two directions of SnSe from monolayer to bulk. The red and black lines are along the armchair and zigzag directions, respectively. Anharmonic effects, not included in the present theory, would lower the values of T_c . The experimental value for bulk SnSe is 826 K for comparison.

perturbation-theoretic approach neglects anharmonic contributions. We can infer that the latter are relatively small. On the other hand, the present T_c for bilayer SnSe, 590 K, is significantly larger than the value obtained by QMD, 225 \pm 9. This large difference, 300 K, is difficult to reconcile with the fact that the present value for bulk SnSe, 1040 K, is larger than the experimental value, 826 K, by much less (\sim 200° K). The anharmonic effect leads to different phonon frequencies at different temperatures²⁴ and increases the CTE absolute values,^{23,25} especially at higher temperatures. Hence, the neglect of anharmonic effects in the present calculations overestimates T_c 's. Addition QMD simulations are needed to clarify the magnitudes of anharmonic contributions to the thermal expansion coefficients of group-VI monochalcogenides.

It is generally believed that rigid-unit phonon modes with negative Grüneisen parameters $\gamma_\epsilon(\omega)$ play a significant role in giving rise to NTE.^{26,27} However, it is not true in few-layer SnSe. The net effect of $\tilde{\gamma}_\epsilon$ for both the monolayer and bilayer are positive along two directions. However, a NTE still occurs since C_{22} and C_{12} are almost identical and $\tilde{\gamma}_j$ is much larger than $\tilde{\gamma}_i$. Thus, we conclude that NTE occurs in few-layer SnSe because of a delicate interplay between $\gamma_\epsilon(\omega)$ and C_{ij} . This phenomenon has also been found in PbTiO₃.²⁸

As shown in Fig. 2(b), the two CTEs almost do not change from bulk to monolayer. This behavior is in sharp contrast to that of graphene/graphite, where the thermal expansion coefficient of graphene

TABLE I. The elastic stiffness coefficients C_{ij} and the specific heat weighted Grüneisen parameter $\tilde{\gamma}_\epsilon$ at 150 K of different numbers of layers. These two parameters control the CTEs of SnSe, as manifested in Eq. (3).

	C_{ij} (N/m)			$\tilde{\gamma}_\epsilon$ at 150 K (k _B)	
	C_{11}	C_{12}	C_{22}	$\tilde{\gamma}_i$	$\tilde{\gamma}_j$
Monolayer	44	19	24	117.6	1053.3
Bilayer	78	32	40	0.1	2248.1
Trilayer	116	43	60	-71.9	2980.1

is three times the value for graphite. As manifest in Eq. (3), the Grüneisen parameter difference $[\gamma_i(\omega) - \gamma_j(\omega)]$ has a significant influence in determining the CTEs. It is the *in-plane* phonon modes that have a relatively large Grüneisen parameter difference $[\gamma_i(\omega) - \gamma_j(\omega)]$, as can be seen in Fig. 3(d). Therefore, in strong contrast to the case of graphene/graphite, NTE is not suppressed by the layer stacking in SnSe.

To further understand the underlying mechanism responsible for the thermal expansion, the calculated generalized Grüneisen parameters $\gamma_\epsilon(\omega)$ together with the harmonic specific heat $\tilde{C}(\omega)$ are shown in Fig. 3. In the case of graphene/graphite, the CTE of graphene is negative and three times as large as that of graphite, where the *out-of-plane* phonon modes have negative Grüneisen parameters (known as the membrane effect).¹ The two CTEs almost remain constant as a function of the number of layers for SnSe. For a specific temperature, the main contribution of CTEs originates from the large Grüneisen parameter difference $[\gamma_i(\omega) - \gamma_j(\omega)]$, as mentioned in Eqs. (2) and (3). Hence, as shown in Figs. 3(a)-3(c), the frequencies corresponding to large $[\gamma_i(\omega) - \gamma_j(\omega)]$ mainly are 65 cm⁻¹, 100 cm⁻¹, and 125 cm⁻¹. As shown in Fig. 3(d), we analyze the atomic displacements of the phonon modes at these three frequencies. It is found that most of the atomic displacements are *in-plane* vibrations, which is less influenced by layer stacking.

Many properties of materials such as the bandgap of semiconductors,²⁹ ferroelectric-to-paraelectric phase transition,³⁰ metal-insulator transition,³¹ and magnetic order^{32,33} exhibit temperature

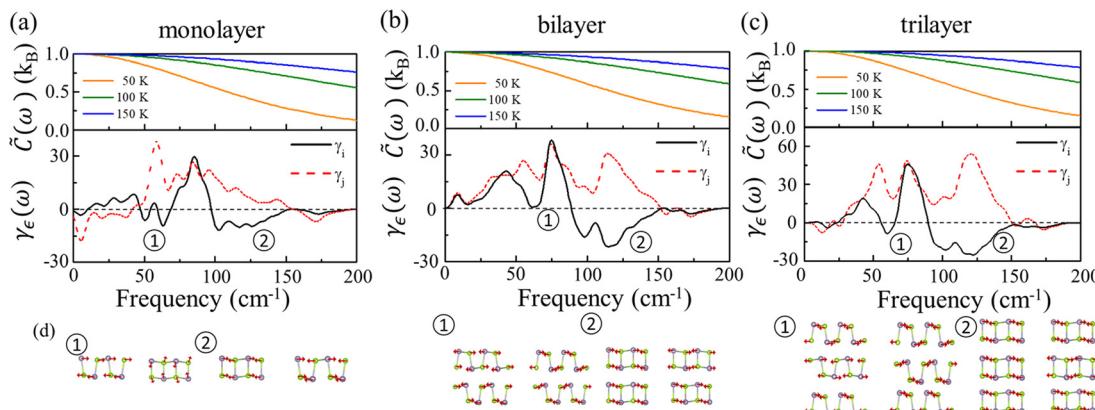


FIG. 3. Calculated frequency dependence of generalized Grüneisen parameters $\gamma_\epsilon(\omega)$ (bottom panel) and harmonic specific heat $\tilde{C}(\omega)$ (top panel) for the monolayer (a), bilayer (b), and trilayer (c). (d) The corresponding atomic displacements of the marked area.

dependence that is associated with thermal expansion. Poisson's ratio is a fundamental mechanical property of solids, which relates the resulting lateral strain to the applied axial strain. Contrary to many materials, monolayer monochalcogenides are found to exhibit negative Poisson's ratio (NPR)¹² (known as the auxetic effect³⁴). Previous theoretical studies reported that the monolayer SnSe exhibits a negative Poisson's ratio at $T = 0\text{ K}$ ($\nu_{ca} < 0$), namely, a SnSe monolayer becomes thicker when stretched along the armchair direction.¹³

Here, we investigate the Poisson's ratio ν_{ca} ($\nu_{ca} = -\epsilon_h/\epsilon_a$, where $\epsilon_h = \Delta h/h$) of multilayer SnSe without considering the finite temperatures. The calculated ν_{ca} of monolayer SnSe is -0.19 , consistent with previous studies,^{12,13} while the ν_{ca} values of a bilayer and a trilayer are 0.06 and 0.12 , as shown in the inset of Fig. 4(a). We further divide ν_{ca} into its intralayer ν_{ca}^{intra} and interlayer ν_{ca}^{inter} parts [$\nu_{ca} = \nu_{ca}^{intra} + \nu_{ca}^{inter}$, where $\nu_{ca}^{intra} = -\epsilon_{h,intra}/\epsilon_a$ and $\nu_{ca}^{inter} = -\epsilon_{h,inter}/\epsilon_a$, see Fig. 4(b)]. We find that, in the NPR of monolayers, the lattice is stretched along the armchair direction, as manifested in the negative values of ν_{ca}^{intra} . This can be attributed to the opposite direction of motion of the Sn atom and Se atoms, which form a hingelike structure.³⁵ Such a hingelike structure is hardly affected by the weak interlayer interaction.

The Poisson's ratio can be temperature dependent due to the thermal expansion. Hence, we then consider Poisson's ratio at finite temperatures. We find that the zero-point motion (ZPM)^{36,37} has a negligible influence on the calculated ν_{ca} and hence can be safely neglected, as shown in the inset of Fig. 4(a). At finite temperatures, however, the Poisson's ratio of SnSe exhibits distinct temperature dependence: with increasing temperature, while the ν_{ca} of monolayer SnSe remains negative, we find that the ν_{ca} values of multilayers (which are positive at zero temperature) decrease and even become negative at higher temperatures below T_c . This intriguing temperature dependence arises mainly from ν_{ca}^{intra} , while ν_{ca}^{inter} remains almost temperature independent. Hence, there is a specific temperature for each multilayer that exhibits zero Poisson's ratio. This provides a potential approach for the design of materials with zero Poisson's ratio.

In summary, we investigated the anisotropic thermal expansion of SnSe for different layers with Grüneisen's theory. In sharp contrast to the case of graphene/graphite, the CTEs of SnSe are not sensitive to the thickness, as they result from the *in-plane* phonon modes that predominantly contribute to the difference of the specific-heat-weighted Grüneisen parameters $\tilde{\gamma}_\epsilon$ along the two directions. The Poisson's ratio of multilayer SnSe, which is positive at $T = 0\text{ K}$, turns negative at higher temperatures. The temperature dependence arises from the decrease in the intralayer Poisson's ratio ν_{ca}^{intra} and the invariant

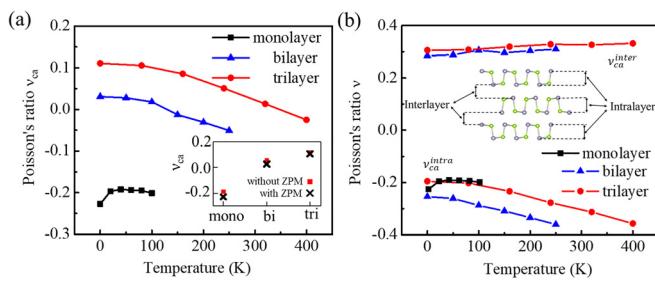


FIG. 4. (a) Finite-temperature Poisson's ratio ν_{ca} of SnSe. The inset shows the Poisson's ratio ν_{ca} with (black crossover) and without (red square) considering the zero-point motion. (b) Finite-temperature intralayer and interlayer Poisson's ratios.

interlayer Poisson's ratio ν_{ca}^{inter} with increasing temperatures. This result provides a possible approach to the design of materials with zero Poisson's ratio.

This work was supported by the National Key Research & Development Projects of China (Nos. 2016YFA0202300 and 2019YFA0308500), the National Natural Science Foundation of China (Nos. 61888102 and 51872284), the CAS Pioneer Hundred Talents Program, and the Strategic Priority Research Program of Chinese Academy of Sciences (Nos. XDB30000000 and XDB28000000). The work at Vanderbilt University was supported by the McMinn Endowment at Vanderbilt University. A portion of the research was performed in the CAS Key Laboratory of Vacuum Physics. Computational resources were provided by the Tianjin Supercomputer Center.

REFERENCES

- ¹N. Mounet and N. Marzari, "First-principles determination of the structural, vibrational and thermodynamic properties of diamond, graphite, and derivatives," *Phys. Rev. B* **71**, 205214 (2005).
- ²X.-J. Ge, K.-L. Yao, and J.-T. Lü, "Comparative study of phonon spectrum and thermal expansion of graphene, silicene, germanene, and blue phosphorene," *Phys. Rev. B* **94**, 165433 (2016).
- ³L.-F. Huang, P.-L. Gong, and Z. Zeng, "Phonon properties, thermal expansion, and thermomechanics of silicene and germanene," *Phys. Rev. B* **91**, 205433 (2015).
- ⁴T. A. Mary, J. S. O. Evans, T. Vogt, and A. W. Sleight, "Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW_2O_8 ," *Science* **272**, 90 (1996).
- ⁵C. W. Li, X. Tang, J. A. Muñoz, J. B. Keith, S. J. Tracy, D. L. Abernathy, and B. Fultz, "Structural relationship between negative thermal expansion and quartic anharmonicity of cubic ScF_3 ," *Phys. Rev. Lett.* **107**, 195504 (2011).
- ⁶N. Ferralis, "Probing mechanical properties of graphene with Raman spectroscopy," *J. Mater. Sci.* **45**, 5135 (2010).
- ⁷J. Liu and S. T. Pantelides, "Anisotropic thermal expansion of group-IV monochalcogenide monolayers," *Appl. Phys. Express* **11**, 101301 (2018).
- ⁸M. Mehboudi, B. M. Fregoso, Y. Yang, W. Zhu, A. van der Zande, J. Ferrer, L. Bellaiche, P. Kumar, and S. Barraza-Lopez, "Structural phase transition and material properties of few-layer monochalcogenides," *Phys. Rev. Lett.* **117**, 246802 (2016).
- ⁹R. X. Fei, W. Kang, and L. Yang, "Ferroelectricity and phase transitions in monolayer group-IV monochalcogenides," *Phys. Rev. Lett.* **117**, 097601 (2016).
- ¹⁰T. Chattopadhyay, A. Werner, H. G. Von Schnering, and J. Pannetier, "Temperature and pressure-induced phase transition in IV-VI compounds," *Rev. Phys. Appl.* **19**, 807 (1984).
- ¹¹T. Chattopadhyay, J. Pannetier, and H. G. Von Schnering, "Neutron-diffraction study of the structural phase transition in SnS and SnSe," *J. Phys. Chem. Solids* **47**, 879 (1986).
- ¹²X. Kong, J. K. Deng, L. Li, Y. L. Liu, X. D. Ding, J. Sun, and J. Z. Liu, "Tunable auxetic properties in group-IV monochalcogenide monolayers," *Phys. Rev. B* **98**, 184104 (2018).
- ¹³L.-C. Zhang, G. Qin, W.-Z. Fang, H.-J. Cui, Q.-R. Zheng, Q.-B. Yan, and G. Su, "Tinselenidene: A two-dimensional auxetic material with ultralow lattice thermal conductivity and ultrahigh hole mobility," *Sci. Rep.* **6**, 19830 (2016).
- ¹⁴E. Mozafari, N. Shulumba, P. Steneteg, B. Alling, and I. A. Abrikosov, "Finite-temperature elastic constants of paramagnetic materials within the disordered local moment picture from ab initio molecular dynamics calculations," *Phys. Rev. B* **94**, 054111 (2016).
- ¹⁵H. H. Pham, M. E. Williams, P. Mahaffey, M. Radovic, R. Arroyave, and T. Cagin, "Finite-temperature elasticity of FCC Al: Atomistic simulations and ultrasonic measurements," *Phys. Rev. B* **84**, 064101 (2011).
- ¹⁶K. V. Zakharchenko, M. I. Katsnelson, and A. Fasolino, "Finite-temperature lattice properties of graphene beyond the quasiharmonic approximation," *Phys. Rev. Lett.* **102**, 046808 (2009).

- ¹⁷P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, “QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials,” *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ¹⁸N. Troullier and J. L. Martins, “Efficient pseudopotentials for plane-wave calculations,” *Phys. Rev. B* **43**, 1993 (1991).
- ¹⁹J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²⁰S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, “Phonons and related crystal properties from density-functional perturbation theory,” *Rev. Mod. Phys.* **73**, 515 (2001).
- ²¹K. Momma and F. Izumi, “VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data,” *J. Appl. Crystallogr.* **44**, 1272 (2011).
- ²²G. Liu, J. Zhou, and H. Wang, “Anisotropic thermal expansion of SnSe from first-principles calculations based on Gruneisen’s theory,” *Phys. Chem. Chem. Phys.* **19**, 15187 (2017).
- ²³D. Bansal, J. Hong, C. W. Li, A. F. May, W. Porter, M. Y. Hu, D. L. Abernathy, and O. Delaire, “Phonon anharmonicity and negative thermal expansion in SnSe,” *Phys. Rev. B* **94**, 054307 (2016).
- ²⁴T. Tadano and S. Tsuneyuki, “Self-consistent phonon calculations of lattice dynamical properties in cubic SrTiO₃ with first-principles anharmonic force constants,” *Phys. Rev. B* **92**, 054301 (2015).
- ²⁵M. K. Gupta, B. Singh, R. Mittal, S. Rols, and S. L. Chaplot, “Lattice dynamics and thermal expansion behavior in the metal cyanides, MCN(M=Cu, Ag, Au): Neutron inelastic scattering and first-principles calculations,” *Phys. Rev. B* **93**, 134307 (2016).
- ²⁶M. G. Tucker, A. L. Goodwin, M. T. Dove, D. A. Keen, S. A. Wells, and J. S. O. Evans, “Negative thermal expansion in ZrW₂O₈: Mechanisms, rigid unit modes, and neutron total scattering,” *Phys. Rev. Lett.* **95**, 255501 (2005).
- ²⁷Y. Yamamura, S. Ikeuchi, and K. Saito, “Characteristic phonon spectrum of negative thermal expansion materials with framework structure through calorimetric study of Sc₂M₃O₁₂ (M = W and Mo),” *Chem. Mater.* **21**, 3008 (2009).
- ²⁸E. T. Ritz and N. A. Benedek, “Interplay between phonons and anisotropic elasticity drives negative thermal expansion in PbTiO₃,” *Phys. Rev. Lett.* **121**, 255901 (2018).
- ²⁹S. Wang, J. Ma, W. Li, J. Wang, H. Wang, H. Shen, J. Li, J. Wang, H. Luo, and D. Li, “Temperature-dependent band gap in two-dimensional perovskites: Thermal expansion interaction and electron-phonon interaction,” *J. Phys. Chem. Lett.* **10**, 2546 (2019).
- ³⁰H. Fang, Y. Wang, S. Shang, and Z.-K. Liu, “Nature of ferroelectric-paraelectric phase transition and origin of negative thermal expansion in PbTiO₃,” *Phys. Rev. B* **91**, 024104 (2015).
- ³¹M. Braden, G. Andre, S. Nakatsuji, and Y. Maeno, “Crystal and magnetic structure of Ca₂RuO₄: Magnetoelastic coupling and the metal-insulator transition,” *Phys. Rev. B* **58**, 847 (1998).
- ³²T. F. Qi, O. B. Korneta, S. Parkin, L. E. De Long, P. Schlottmann, and G. Cao, “Negative volume thermal expansion via orbital and magnetic orders in Ca₂Ru_{1-x}Cr_xO₄ (0 < x < 0.13),” *Phys. Rev. Lett.* **105**, 177203 (2010).
- ³³T. F. Qi, O. B. Korneta, S. Parkin, J. Hu, and G. Cao, “Magnetic and orbital orders coupled to negative thermal expansion in Mott insulators Ca₂Ru_{1-x}M_xO₄ (M = Mn and Fe),” *Phys. Rev. B* **85**, 165143 (2012).
- ³⁴K. E. Evans, M. A. Nkansah, I. J. Hutchinson, and S. C. Rogers, “Molecular network design,” *Nature* **353**, 124 (1991).
- ³⁵B. Liu, M. Niu, J. Fu, Z. Xi, M. Lei, and R. Quhe, “Negative Poisson’s ratio in puckered two-dimensional materials,” *Phys. Rev. Mater.* **3**, 054002 (2019).
- ³⁶L. Ortenzi, L. Pietronero, and E. Cappelluti, “Zero-point motion and direct-indirect band-gap crossover in layered transition-metal dichalcogenides,” *Phys. Rev. B* **98**, 195313 (2018).
- ³⁷E. Cannuccia and A. Marini, “Zero point motion effect on the electronic properties of diamond, trans-polyacetylene and polyethylene,” *Eur. Phys. J. B* **85**, 320 (2012).