PHYSICAL REVIEW LETTERS **124,** 215501 (2020)

Calculation of Mode Grüneisen Parameters Made Simple

David Cuffari[1,2] and Angelo Bongiorno[1,2]
[1]*Department of Chemistry, College of Staten Island, Staten Island, New York 10314, USA*
[2]*The Graduate Center of the City University of New York, New York, New York 10016, USA*

(Received 19 January 2020; accepted 2 April 2020; published 27 May 2020)

A novel method to calculate mode Grüneisen parameters of a material from *first principles* is presented. This method overcomes the difficulties and limitations of existing approaches, based on the calculation of either third-order force constants or phonon frequencies at different volumes. Our method requires the calculation of phonon frequencies of a material at only the volume of interest, it is based on the second-order differentiation of a corrected stress tensor with respect to normal mode coordinates, and it yields simultaneously all the components of the mode Grüneisen parameters tensor. In this work, after discussing conceptual and technical aspects, the method is applied to silicon, aluminum, scandium fluoride, and a metallic alloy. These calculations show that our method is straightforward and it is suited to be applied to the broad class of materials prone to exhibit structural instabilities, or presenting anisotropy, or chemical and/or structural disorder.

DOI: 10.1103/PhysRevLett.124.215501

In thermodynamics, the Grüneisen parameter (γ) quantifies the rate at which thermal pressure (p) at constant volume (V) changes with internal energy (U) [1–4], which in turn can be expressed in terms of the following macroscopic thermodynamic parameters,

$$\gamma = V\frac{\partial p}{\partial U}\bigg|_V = \frac{V\alpha_V B_T}{C_V}, \tag{1}$$

where C_V is the isochoric heat capacity, B_T is the isothermal bulk modulus, and α_V is the coefficient of volumetric thermal expansion. The Grüneisen parameter can be measured by combining inelastic x-ray (or neutron) scattering and x-ray diffraction experiments [5,6] or by probing the elastic-stress pulses resulting from the heating induced by brief bursts of MeV electrons or laser radiation [2,7]. Although the general relevance of the Grüneisen parameter stems from Eq. (1) and its relation to the thermoelastic properties of a substance [6], in fields such as geophysics and biomedicine, this parameter has become important in itself, to predict the phase behavior of solids at high pressure [5] and for imaging and characterization of biological tissues [7], respectively. Because of its importance and ubiquity, atomistic calculations of the Grüneisen parameter are carried out routinely, to investigate thermal properties of materials [8–12], and also to characterize liquids [13] and their behaviors near critical points [14].

First principles calculations of the thermodynamic Grüneisen parameter rely on the quasiharmonic approximation and the following equation [3,9]:

$$\gamma = \frac{\sum_k c_V^k \gamma_k}{C_V}, \tag{2}$$

where c_V^k is the specific heat capacity of a harmonic oscillator with frequency ω_k, and γ_k is the mode Grüneisen parameter defined as

$$\gamma_k = -\frac{V}{\omega_k}\frac{\partial \omega_k}{\partial V}. \tag{3}$$

Two approaches are used to calculate the mode Grüneisen parameters. The first one relies on perturbation theory [3], yielding γ_k's expressed in terms of normal mode coordinates and third-order force constants [3,10,15], and for this reason this cumbersome approach is not used regularly. The second method stems directly from Eq. (3), and it is based on the numerical differentiation of phonon frequencies of a material with respect to volume [8]. This second approach is straightforward, and it is used routinely to calculate γ_k's and thermal expansion coefficients [via Eq. (1)] [8,11,16]. However, this latter method suffers from two major technical limitations. First, it involves a reindexing operation of the phonon frequencies to establish the correspondence between frequencies computed at different volumes. This task is trivial in the case of simple solids described by using primitive unit cells (and hence requiring the reordering of only a few phonon branches per k point), but it can lead to erroneous assignments and results in the case of complex materials described by large supercells. Second, carrying out the numerical derivative in Eq. (3) requires the calculation of phonon frequencies at (at least three) different volumes, within an interval of dynamical stability of the material of interest [8,11,16]. The smaller this interval is, the more difficult and less accurate this numerical operation becomes [11,16]. Because of the two issues above, it remains a challenge to apply

Eqs. (1)–(3) and quasiharmonic approximation calculations to study materials exhibiting anisotropy or disorder, or anharmonic materials prone to exhibit structural instabilities upon expansion or compression [11,16,17].

In this work, we present a novel method to calculate mode Grüneisen parameters that overcomes the difficulties and limitations of existing approaches. In contrast to current techniques (based on calculating either third-order force constants or phonon frequencies at different volumes), our method requires the calculation of phonon frequencies of a material at only the volume of interest, and it is based on the second-order differentiation of a corrected stress tensor with respect to normal mode coordinates. For each mode, this operation yields simultaneously all the components of the generalized mode Grüneisen parameter tensor, and it involves one or a few total energy calculations with ions at fixed positions. In comparison with current techniques (which can be used with both primitive and large unit cells to estimate mode parameters of a phonon with a wave vector), our method necessitates the use of large supercells to accommodate normal mode displacements, and it yields values of mode Grüneisen parameters of the $3N-3$ phonon modes with wave vectors constrained by periodic boundary conditions. For the reasons above, our method is suitable to be applied to materials systems exhibiting anisotropy, or chemical or structural disorder, i.e., systems requiring the use of large supercells to obtain a proper description of their structure. As demonstrated herein, for such systems our method surpasses existing techniques in both computational efficiency and reliability of results.

The generalized mode Grüneisen parameters are defined as follows:

$$\gamma_k^{(\nu\mu)} = -\frac{1}{\omega_k}\frac{\partial\omega_k}{\partial\varepsilon_{\nu\mu}} = -\frac{1}{2\omega_k^2}\frac{\partial\omega_k^2}{\partial\varepsilon_{\nu\mu}}, \tag{4}$$

where $\varepsilon_{\nu\mu}$ is a component of the strain tensor, and the indexes ν and μ are equal to x, y, or z. In the framework of the Bohr-Oppenheimer (BO) approximation and, for instance, periodic density functional theory (DFT) calculations, we can write the nuclear Hamiltonian of a material system as

$$H = \sum_n \frac{\mathbf{p}_n^2}{2M_n} + V_{\mathrm{BO}}(\vec{R}, \{\vec{a}_i\}), \tag{5}$$

where V_{BO} is the BO energy surface, M_n and $\mathbf{p}_n$ are the mass and momentum of the nth atom, $\vec{R}$ is the collective set of all ionic positions in the periodic cell, and $\vec{a}_i$ are the cell vectors. In the harmonic approximation, Eq. (5) becomes

$$H \approx \sum_{n=1}^{N} \frac{\mathbf{p}_n^2}{2M_n} + \frac{1}{2}\sum_{n,m}\sum_{\nu,\mu} u_n^\nu \Phi_{nm}^{\nu\mu} u_m^\mu, \tag{6}$$

where $\Phi_{nm}^{\nu\mu}$ is a matrix element of the real space force constant matrix, and $u_n^\nu = \vec{R}_n^\nu - \vec{\mathcal{R}}_n^\nu$ is the displacement of the nth atom along the ν direction with respect to the equilibrium position $\vec{\mathcal{R}}_n$. In particular, using a compact matrix notation, we can write

$$\begin{aligned} V_h(\vec{R}_0+\vec{u},\{\vec{a}_i\}) &= \frac{1}{2}\sum_{n,m}\sum_{\nu,\mu} u_n^\nu \Phi_{nm}^{\nu\mu} u_m^\mu \\ &= \frac{1}{2}\vec{u}^{+}\mathbf{\Phi}\vec{u} = \frac{1}{2}\sum_k \omega_k^2 q_k^2 = \frac{1}{2}\vec{q}^{+}\mathbf{\Omega}\vec{q}, \end{aligned} \tag{7}$$

where q_k are the normal mode coordinates and $\vec{q}$ and $\vec{u}$ are the collective variables of normal coordinates and Cartesian displacements, respectively. In Eq. (7), $\mathbf{\Omega}$ is the diagonal matrix of second-order derivatives over the normal modes of V_h,

$$\mathbf{\Omega} = \mathbf{L}^{+}\mathbf{M}^{-1/2}\mathbf{\Phi}\mathbf{M}^{-1/2}\mathbf{L}, \tag{8}$$

where $\mathbf{M}$ is the diagonal matrix of atomic masses and $\mathbf{L}$ is the matrix of columnwise eigenvectors of the mass weighted Cartesian force constant matrix, $\mathbf{M}^{-1/2}\mathbf{\Phi}\mathbf{M}^{-1/2}$, and normal modes coordinates and atomic displacements are related to each other as

$$\vec{q} = \mathbf{L}^{+}\mathbf{M}^{1/2}\vec{u}, \tag{9}$$

with $\vec{u}$ vanishing at the reference ionic configuration $\vec{R}_0$, i.e., the collective variable of equilibrium ionic positions $\vec{\mathcal{R}}_n$. Using the notation introduced above, and considering that a mode Grüneisen parameter measures the deformation-induced shift of a phonon frequency with respect to that of a pure harmonic oscillator, we can write Eq. (4) as

$$\begin{aligned} \gamma_k^{(\nu\mu)} &= -\frac{1}{2\omega_k^2}\frac{\partial}{\partial\varepsilon_{\nu\mu}}\frac{\partial^2[V_{\mathrm{BO}}-V_h]}{\partial q_k^2} \\ &= \frac{1}{2\omega_k^2}\frac{\partial^2}{\partial q_k^2}\left[-\frac{\partial V_{\mathrm{BO}}}{\partial\varepsilon_{\nu\mu}} + \frac{\partial V_h}{\partial\varepsilon_{\nu\mu}}\right] = \frac{V}{2\omega_k^2}\frac{\partial^2 P_{\nu\mu}}{\partial q_k^2}, \end{aligned} \tag{10}$$

with $P_{\nu\mu}$ a "corrected" stress tensor having the following expression,

$$P_{\nu\mu} = P_{\nu\mu}^0 - \frac{1}{2V}\sum_n (f_n^\nu u_n^\mu + f_n^\mu u_n^\nu), \tag{11}$$

where $P_{\nu\mu}^0(\vec{R}_0+\vec{u},\{\vec{a}_i\})$ is the static contribution of the stress tensor, computed in the absence of quantum and thermal fluctuations with ions fixed at positions $\vec{R}_0+\vec{u}$ within a rigid supercell with volume V and cell vectors $\{\vec{a}_i\}$, whereas the summation on the right-hand side corresponds to the harmonic stress tensor, with f_n^ν being the Cartesian components of the harmonic force acting on the nth ion due to the collective displacement $\vec{u}$, equal to

$$f_n^\nu = -\sum_{m,\mu} \Phi_{nm}^{\nu\mu} u_m^\mu. \tag{12}$$

We remark that in the case of a pure harmonic crystal, the summation in Eq. (11) cancels the term $P^0_{\nu\mu}$, leading to the correct result of mode Grüneisen parameters identical to zero. We also remark that the corrected stress tensor in Eq. (11) is identical (besides terms included to improve numerical accuracy) to the one derived within a self-consisted harmonic approximation formalism by Monacelli *et al.* in Ref. [18].

Equations (10) and (11) constitute the basis of our new method to calculate mode Grüneisen parameters of a material. These equations show that mode Grüneisen parameters can be obtained by carrying out atomistic calculations of a solid at a fixed V, without the need of computing harmonic frequencies and normal modes at volumes larger and smaller than V. In practice, our method to calculate mode Grüneisen parameters involves the following operations. First, optimization of supercell geometry and ionic positions, defining the static equilibrium configuration of a solid at zero pressure or subjected to an external stress. Second, calculation of the normal mode frequencies and coordinates. Third, for each mode and an amplitude q_k, calculation of the energy and internal stress tensor with ions fixed in a configuration accommodating displacements along the selected normal mode. Equation (11) is then used to calculate the "corrected" stress tensor $P_{\nu\mu}$, and the mode Grüneisen parameter is obtained by approximating Eq. (10) with a second-order central finite difference formula, as follows:

$$\gamma_k^{(\nu\mu)} \approxeq 2V \frac{P_{\nu\mu}[\zeta_k] - P_{\nu\mu}[0]}{\zeta_k^2}, \tag{13}$$

where $\zeta_k = \sqrt{2} q_k \omega_k$. It is to be noted that the formula above is written accounting that $P_{\nu\mu}[\zeta_k] = P_{\nu\mu}[-\zeta_k]$, and that $P_{\nu\mu}[0]$ reduces to the component of the internal stress tensor at equilibrium $P^0_{\nu\mu}$. Equation (13) thus shows that, after computing the normal modes and phonon frequencies, each mode Grüneisen parameter can be calculated by carrying out a single total energy fixed-point calculation (Fig. 1).

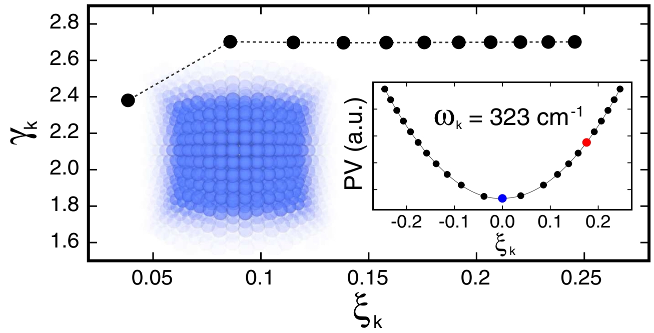

FIG. 1. Values of a mode Grüneisen parameter obtained from Eq. (13) using increasing values of $\zeta_k = \sqrt{2} q_k \omega_k$. Inset: Values of the "corrected" pressure times V (in atomic units of energy) versus ζ_k. The colored disks indicate that a mode parameter can be calculated by carrying out a single total energy calculation (red disk) with ions fixed in a configuration accommodating displacements resulting from a normal mode coordinate equal to q_k. These results were obtained by considering a large supercell of fcc Al (inset) described by using a classical energy scheme.

To demonstrate the correctness and validity of our method to calculate mode Grüneisen parameters, we first considered an energy scheme employing embedded-atom interatomic potentials [19] to describe a cubic supercell containing 864 Al atoms with the face-centered-cubic structure. Then, we calculated the isotropic mode Grüneisen parameters using both our method [Eqs. (10)–(13) and Fig. 1] and the conventional approach based on calculating phonon frequencies at different volumes, sorting and assigning normal modes by using the standard $k \cdot p$-based approach, and using first-order finite difference formulas to compute the γ_k [Eq. (4)]. The two sets of parameters shown in Fig. 2 demonstrate that our method gives results in excellent agreement with those obtained by using conventional methods.

To further corroborate the validity of our method, we considered a 216-atom cubic cell of cubic Si, and we used a periodic DFT approach [20] to calculate isotropic mode Grüneisen parameters by using both our method and the conventional approach (based on calculating phonon frequencies at different volumes). In detail, we used density functional perturbation theory [20] to calculate normal mode frequencies and coordinates, and all Γ-point calculations were carried out by using an energy cutoff of 50 Ry, a norm-conserving pseudopotential [21], and the Perdew-Burke-Ernzerhof (PBE) parametrization of the exchange and correlation energy functional [22]. Also in this case,

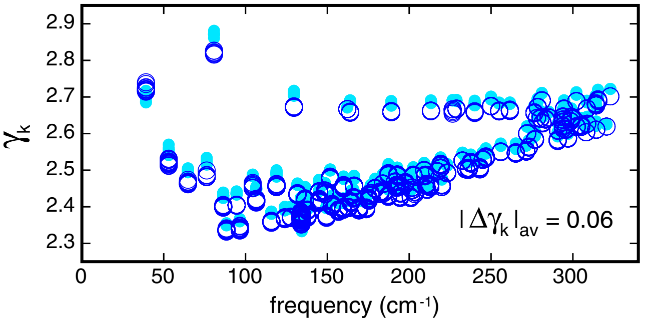

FIG. 2. Mode Grüneisen parameters of fcc Al computed by using classical interatomic potentials and a cubic supercell containing 864 atoms. Light blue disks show results obtained by using the conventional method based on numerical differentiation of phonon frequencies computed at different volumes, whereas blue circles show parameters computed by using our method. The absolute average difference between these two sets of data is 0.06.

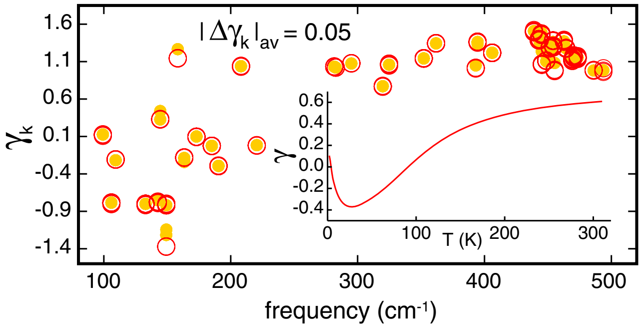

FIG. 3. Mode Grüneisen parameters of Si calculated by using a periodic DFT approach and a cubic supercell containing 216 atoms. Dark yellow disks are used to show parameters obtained by using the conventional method, whereas red circles show results obtained by using our method. The absolute average difference between the two sets of values is 0.05. Inset: Average Grüneisen parameter versus temperature calculated by using Eq. (2).

our calculations showed that our method gives results in excellent agreement with parameters computed by using the conventional approach (Fig. 3). The mode parameters shown in Fig. 3 were used to calculate the thermodynamic Grüneisen parameter as a function of temperature using Eq. (2). This result shown in Fig. 3 is in agreement with experimental data of γ obtained from measurements of the inertial thermoelastic stress produced by pulse heating [2]. Overall, the results in Figs. 2 and 3 demonstrate that our method to calculate mode Grüneisen parameters is valid, whereas Eq. (13) and Fig. 1 show that our method is straightforward and involves simple numerical tasks. In terms of computational efficiency, the overall computational cost our method to calculate isotropic mode parameters is equivalent to approximately 1.5 phonon calculations, whereas the conventional approach required 3 phonon calculations.

To demonstrate the advantages of our novel method over existing approaches, we first considered the case of ScF_3, a cubic material exhibiting negative thermal expansion up to a temperature of 1100 K [23]. The origin of the negative expansion of ScF_3 has been attributed to the thermally induced rocking motions of the rigid ScF_6 units, corresponding to phonon modes at and near the R^{4+} and M^{3+} points in the Brillouin zone [23]. As discussed by Oba *et al.* in Ref. [17], the Grüneisen parameters associated to these modes cannot be calculated by using the conventional approach based on numerical differentiation of phonon frequencies [Eq. (3)]. Small changes of the volume near equilibrium induce large frequency variations of the R^{4+} and M^{3+} modes, which become rapidly unstable upon compression [17]. For this reason, calculation of these mode Grüneisen parameters based on differentiation of phonon frequencies can lead to unreliable or questionable values [17,24,25].

We used our method to calculate the isotropic Grüneisen parameters of the triply degenerate R^{4+} and M^{3+} modes of ScF_3. In particular, we used a $2 \times 2 \times 2$ supercell containing 32 atoms, ultrasoft pseudopotentials for both Sc and F [20,26], the PBE functional, a $4 \times 4 \times 4$ uniform grid of k points to sample the Brillouin zone, energy cutoffs of 50 and 410 Ry for the wave functions and electronic charge density, respectively, and normal modes and phonon frequencies were calculated by using the finite-displacement approach. With these technical details, we obtained an equilibrium lattice parameter of 4.062 Å, a static bulk modulus of 86 GPa, and phonon frequencies of the R^{4+} and M^{3+} modes equal to 36 and 37 cm^{-1}, respectively. These results are in excellent agreement with recent DFT studies [17]. As for the mode Grüneisen parameters, our method yielded values equal to -45 (R^{4+}) and -43 (M^{3+}), in good agreement with values of about -35 estimated by using third-order force constants computed at 300 K by self-consistent *ab initio* lattice dynamical calculations [27].

To further show the advantages of our method, we calculated the mode Grüneisen parameters of a Mg-Li alloy, a light material with potential applications in aerospace, automobile, and portable electronics technologies [28,29]. In particular, we considered the case of a Mg-Li alloy containing a small amount of Li, and thus preserving the hexagonal-close-packed (hcp) structure [28]. In detail, we used a 72-atom $3 \times 4 \times 3$ hexagonal (folded into an orthorhombic) supercell of hcp Mg, with 8 Li atoms replacing Mg at random sites. We used norm-conserving pseudopotentials for both Mg and Li [20,21], the PBE functional [22], a $4 \times 3 \times 3$ uniform grid of k points to sample the Brillouin zone, an energy cutoff of 30 Ry, and fractional occupation numbers with a smearing temperature of 0.02 Ry. After a geometry optimization calculation (the lattice parameters a and c of the alloy reduced, with respect to those of pristine hcp Mg, by 0.5% and 1.1%, respectively), we used a finite-displacement approach to calculate normal modes and phonon frequencies, and our method to calculate mode Grüneisen parameters. The results in Fig. 4 show that at low temperatures, the hcp alloy is prone to exhibit a larger thermal expansion along the c axis, and that for temperatures larger than 100 K, the diagonal components of the thermodynamic Grüneisen parameters tensor assume the same value of about 1.4. Figure 4 shows that our method and Eqs. (10)–(13) allow us to calculate all the components of the mode-parameters tensor, at no additional computational cost and without the need of calculating phonon frequencies of deformed configurations of the supercell. We underline that to obtain the same results, conventional approaches would have required a minimum of 15 phonon calculations, i.e., about 10 times more computationally costly than our method. These results demonstrate that our method is suitable to be applied to large anisotropic materials presenting chemical or structural disorder, for the study of thermoelastic and even thermal conductivity [12] properties from first principles.

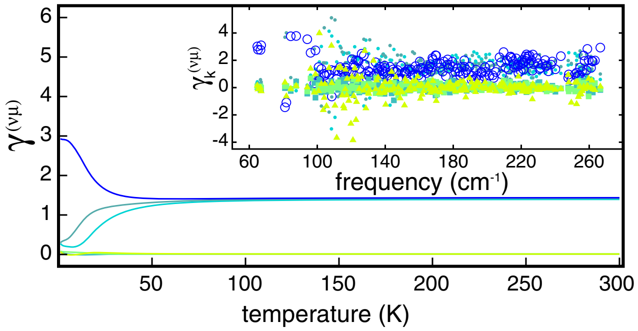

FIG. 4. Thermodynamic Grüneisen parameters tensor of a hcp Mg-Li alloy versus temperature derived from Eq. (2) and generalized mode parameters (shown in the inset) calculated by using our method. Aqua, dark green, and blue colored symbols and solid lines show the *xx*, *yy*, and *zz* components of the mode and thermodynamic Grüneisen parameters tensors, respectively. Light green colors are used to show the *yz*, *xz*, and *xy* components of the symmetric tensors.

In summary, we have presented a novel first principles method to calculate mode Grüneisen parameters. Our method is straightforward, accurate, and computationally efficient. It requires the use of large supercells to accommodate normal mode displacements, it can be easily applied to anharmonic materials prone to exhibit dynamical instabilities such as ScF_3, and it allows for the simultaneous calculation of all the components of the mode Grüneisen parameters tensor. For these reasons, our method has the potential to enable studies of thermoelastic properties (within the quasiharmonic approximation, and in combination with novel approaches to calculate linear and nonlinear elastic constants [30]) of anisotropic materials, presenting chemical or structural disorder, such as doped or defected crystals, metal alloys, and amorphous materials.

We acknowledge the support of the CUNY High Performance Computing Center and a PSC-CUNY grant (No. 62651-0050).

[1] O. L. Anderson, *Equation of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, New York, 1995).
[2] W. B. Gauster, Phys. Rev. B **4**, 1288 (1971).
[3] A. A. Maradudin, Phys. Status Solidi **2**, 1493 (1962).
[4] G. Dolling and R. A. Cowley, Proc. Phys. Soc. **88**, 463 (1966).
[5] C. A. Murphy, J. M. Jackson, W. Sturhahn, and B. Chen, Geophys. Res. Lett. **38**, L24306 (2011).
[6] D. S. Kim, H. L. Smith, J. L. Niedziela, C. W. Li, D. L. Abernathy, and B. Fultz, Phys. Rev. B **91**, 014307 (2015).
[7] S. Liang, B. Lashkari, S. S. S. Choi, V. Ntziachristos, and A. Mandelis, Photoacoustics **11**, 56 (2018).
[8] N. Mounet and N. Marzari, Phys. Rev. B **71**, 205214 (2005).
[9] Z. Wu and R. M. Wentzcovitch, Phys. Rev. B **83**, 184115 (2011).
[10] O. Hellman and I. A. Abrikosov, Phys. Rev. B **88**, 144301 (2013).
[11] L.-F. Huang, X.-Z. Lu, E. Tennessen, and J. M. Rondinelli, Comput. Mater. Sci. **120**, 84 (2016).
[12] C. H. Lee and C. K. Gan, Phys. Rev. B **96**, 035105 (2017).
[13] P. Mausbach, A. Köster, G. Rutkai, M. Thol, and J. Vrabec, J. Chem. Phys. **144**, 244505 (2016).
[14] G. O. Gomes, H. E. Stanley, and M. de Souza, Sci. Rep. **9**, 12006 (2019).
[15] J. Fabian and P. B. Allen, Phys. Rev. Lett. **79**, 1885 (1997).
[16] L.-F. Huang, N. Z. Koocher, M. Gu, and J. M. Rondinelli, Chem. Mater. **30**, 7100 (2018).
[17] Y. Oba, T. Tadano, R. Akashi, and S. Tsuneyuki, Phys. Rev. Mater. **3**, 033601 (2019).
[18] L. Monacelli, I. Errea, M. Calandra, and F. Mauri, Phys. Rev. B **98**, 024106 (2018).
[19] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[20] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009).
[21] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[23] B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman, and A. P. Wilkinson, J. Am. Chem. Soc. **132**, 15496 (2010).
[24] C. W. Li, X. Tang, J. A. Muñoz, J. B. Keith, S. J. Tracy, D. L. Abernathy, and B. Fultz, Phys. Rev. Lett. **107**, 195504 (2011).
[25] Y. Liu, Z. Wang, M. Wu, Q. Sun, M. Chao, and Y. Jia, Comput. Mater. Sci. **107**, 157 (2015).
[26] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[27] A. van Roekeghem, J. Carrete, and N. Mingo, Phys. Rev. B **94**, 020303(R) (2016).
[28] R. Wu, Y. Yan, G. Wang, L. E. Murr, W. Han, Z. Zhang, and M. Zhang, Int. Mater. Rev. **60**, 65 (2015).
[29] R. H. Taylor, S. Curtarolo, and G. L. W. Hart, Phys. Rev. B **81**, 024112 (2010).
[30] T. Cao, D. Cuffari, and A. Bongiorno, Phys. Rev. Lett. **121**, 216001 (2018).