Theoretical explanation of dynamical stability for two- and three-dimensional Lennard-Jones crystals

Shota Ono* and Tasuku Ito
Department of Electrical, Electronic and Computer Engineering, Gifu University, Gifu 501-1193, Japan

(Received 2 November 2020; revised 24 January 2021; accepted 26 January 2021; published 3 February 2021)

DOI: 10.1103/PhysRevB.103.075406

I. INTRODUCTION

Lattice vibration is of importance to understand the dynamical properties of solids. The crystal lattice is dynamically stable if the vibrational frequency is real over the entire Brillouin zone, while if a specific vibrational mode has an imaginary frequency, the crystal lattice is unstable against such a mode [1]. Due to the development of a first-principles approach such as density-functional theory (DFT) [2], the dynamical stability has been studied in a variety of materials [3–5]. For simple metals, fcc metals in the hcp structure and hcp metals in the fcc structure are dynamically stable, i.e., metastable state. However, fcc metals in the bcc structure and vice versa are, in general, dynamically unstable [1]. Also metastable phases have attracted significant interest in recent years due to their unconventional properties [6,7].

Recently, one of the authors studied the dynamical stability of two-dimensional (2D) layers of simple metals using the first-principles approach [8,9]. We have considered three types of 2D lattice structures: the hexagonal (HX), buckled honeycomb (BHC), and buckled square (BSQ) structures, as shown in Fig. 1 [9]. It has been proposed that (i) if the HX structure is dynamically stable, the fcc and/or hcp structures are also dynamically stable; (ii) if only the HX structure is dynamically stable, the bcc structure is dynamically stable; (iii) if only the BSQ structure is dynamically stable, the hcp structure is dynamically stable; and (iv) if the HX and BSQ structures are dynamically stable, the hcp or fcc structures are stable depending on the group in the periodic table. It is interesting to study the stability relationship between 2D and three-dimensional (3D) systems by using simpler models that enable us to derive the vibrational frequencies at some symmetry points analytically.

In this paper, we focus on the Lennard-Jones (LJ) crystals and investigate how the dynamical stabilities in the 2D and 3D structures (HX, BHC, and BSQ) and 3D structures (fcc, bcc, and hcp) are correlated with each other. We categorize the stability property into four groups (Fig. 2) and discuss the stability relationship between the LJ crystals and the elemental metals in the periodic table. We also provide analytical expressions for studying the dynamical stability of the HX, BSQ, and bcc LJ crystals.

Our goal in the present paper is not to describe the dynamical stability of realistic systems accurately but to reveal some aspects of them. This is accomplished by using a LJ potential that is simple and has adjustable parameters for the interatomic forces between atoms. The LJ potential is a central potential that depends on only the interatomic distance and can describe the dynamics of rare-gas solids [10]. For positive integer pairs \((m, n)\), the generalized LJ potential is given by

\[
\phi(R) = \frac{C_m}{R^m} - \frac{C_n}{R^n},
\]

with \(C_m\) and \(C_n\) being the positive values. The first and second terms in Eq. (1) describe the repulsive and attractive potentials between atoms. The inequality \(m > n\) must hold since an atom cannot penetrate into the volume of other atoms. It is known that the fcc lattice is dynamically stable for all \(m > n\), while the bcc lattice is unstable except for small \(m\) and \(n\) [11,12]. Modified LJ potentials taking the Friedel oscillations into account have been used to study the stability of alloys [13]. The Morse-type, Coulomb-type, and other nonmonotonic potentials that are also central potentials have been used to study the chemical bonds in alloys [14], the stability of Wigner crystals [15,16], and the pattern formation in condensed matter [17], respectively. For an accurate description beyond the central potential approximation, many-body corrections are required, as implemented in, for example, the embedded atom method [18,19] and DFT [2]. We expect that the investigation of the LJ potentials will provide a simple understanding of the dynamical stability of solids.
II. THEORY

A. Basic concepts

Throughout this paper, we use the term “atom” to indicate the LJ particle. The total potential energy for $N$-atom systems is defined by

$$V = \frac{1}{2} \sum_{i=1}^{N} \sum_{j(i \neq j)}^{N} \phi(R_{ij}),$$  

(2)

where $R_{ij}$ is the interatomic distance between atoms $i$ and $j$. The factor of $1/2$ accounts for the double counting of the summation.

Within the harmonic approximation [10], the lattice dynamics of solids is determined by

$$M \frac{d^2u_{\alpha}(s, I)}{dt^2} = -\sum_{\alpha', l'} D^{\alpha \alpha'}_{ss}(I, l')u_{\alpha'}(s', l'),$$  

(3)

with the particle mass $M$ and the $\alpha$ ($= x, y, z$) component of the displacement $u_{\alpha}(s, I)$ for the $s$th atom in a unit cell characterized by the lattice vector $I$. The force constant matrix is defined by

$$D^{\alpha \alpha'}_{ss}(I, I') = \left. \frac{\partial^2 V}{\partial R_{\alpha}(s, I) \partial R_{\alpha'}(s', I')} \right|_0,$$  

(4)

where the derivative is evaluated at the equilibrium atom positions $R_{\alpha}(s, I)$. Assuming the plane wave solution

$$u_{\alpha}(s, I) = \epsilon_{\alpha, s}(q) e^{\imath q \cdot R(s, I)} e^{-\imath \omega t},$$  

(5)

with the frequency $\omega$ and the $\alpha$ component of the polarization vector $\epsilon_{\alpha, s}(q)$ for the wave vector $q$, one obtains

$$\omega^2 \epsilon_{\alpha, s}(q) = \sum_{\alpha', l'} D^{\alpha \alpha'}_{ss}(q) \epsilon_{\alpha', s'}(q),$$  

(6)

where $\tilde{D}$ is the dynamical matrix given by

$$D^{\alpha \alpha'}_{ss}(q) = \frac{1}{M} \sum_{l} D^{\alpha \alpha'}_{ss}(0, l) e^{iq \cdot [R(s, l) - R(s, 0)]}.$$  

(7)

The acoustic sum rule, that is, $\sum_{\alpha, l} D^{\alpha \alpha'}_{ss}(0, l) = 0$, is imposed by considering the translational symmetry of the crystal. When there is only one atom in the unit cell, Eq. (7) is written as [10]

$$D^{\alpha \alpha'}_{ss}(q) = \frac{2}{M} \sum_{l} \left[ A(L) \delta_{\alpha \alpha'} + B(L)(\hat{I})_{\alpha \alpha'} \right] \times \sin^2 \left( \frac{q \cdot l}{2} \right),$$  

(8)

with $L = |l|$, $A(L) = \phi'(L)/L$, and $B(L) = \phi''(L) - \phi'(L)/L$, where the prime denotes the derivative with respect to $R$, $(\hat{I})_{\alpha \alpha'}$ is the dyadic, defined as $u_{\alpha}u_{\alpha'}/L^2$. The summation in Eq. (8) is taken over the lattice vectors except $l = 0$. If the eigenvalue $\lambda_j(q)$ of $\tilde{D}$ for $q$ and $j = 1, \ldots, 3n_a$ ($n_a$ is the number of atoms in a unit cell) is positive (negative), the $N$-atom system is dynamically stable (unstable) against the vibrational mode $(q, j)$.

B. LJ potential optimization

In order to determine the parameters of the LJ potential given by Eq. (1), we first consider the HX structure because the HX structure can be a building block for constructing other structures such as the fcc, hcp, and BHC structures. The primitive lattice vectors of the HX structure are given by

$$a_1 = (a, 0, 0), \quad a_2 = \left( -\frac{a}{2}, \frac{\sqrt{3}a}{2}, 0 \right), \quad a_3 = (0, 0, c),$$  

(9)

with $a$ being the lattice constant. The interlayer distance $c$ is taken to be much larger than $a$ in order to study the lattice dynamics of the isolated thin films. We set the total energy per atom $V/N$ and the lattice parameter $a$ to be $-E_0$ and $a_0$, respectively, providing the following simultaneous equations:

$$\begin{pmatrix} -E_0 \\ 0 \end{pmatrix} = \begin{pmatrix} J_m & -J_n \\ mJ_m & -nJ_n \end{pmatrix} \begin{pmatrix} C_m \\ C_n \end{pmatrix},$$  

(10)

where $J_m$ for an integer $m$ is defined as

$$J_m = \frac{1}{2} \sum_{j \neq i} R_{ij},$$  

(11)
TABLE I. $R_0$ in the LJ potential and the optimized values ($E$, $a$, and $\delta$) for the BHC and BSQ structures. $R_0$, $a$, and $\delta$ are in units of $a_0$, whereas $E$ is in units of $E_0$.

| Group | $R_0$ | $E_{BHC}$ | $a_{BHC}$ | $\delta_{BHC}$ | $E_{BSQ}$ | $a_{BSQ}$ | $\delta_{BSQ}$ |
|-------|-------|-----------|-----------|----------------|-----------|-----------|----------------|
| (12,6) in group A | 1.010 | $-1.656$ | 0.989 | 0.818 | $-1.503$ | 0.979 | 0.735 |
| (8,4) in group B | 1.060 | $-1.869$ | 0.963 | 0.870 | $-1.716$ | 0.946 | 0.831 |
| (6,3) in group C | 1.187 | $-2.129$ | 0.928 | 0.967 | $-1.988$ | 0.885 | 0.990 |
| (9,3) in group D | 1.099 | $-1.985$ | 0.948 | 0.899 | $-1.820$ | 0.923 | 0.866 |

As an example for each group, we study the (12,6), (8,4), (6,3), and (9,3) LJ crystals in the HX, BHC, BSQ, fcc, bcc, and hcp structures. The optimized parameters for these structures are listed in Tables I and II. $R_0$’s satisfying $\phi(R_0) = 0$ are also listed in Table I. Figure 3 shows the $R$ dependence of the (12, 6), (8, 4), (6, 3), and (9, 3) LJ potentials. For the case $(m, n) = (12, 6)$, the LJ potential takes a minimum at $R = R_0 \simeq a_0$ and decays to zero monotonically as $R$ increases, which will create the short-range interaction forces between atoms. As the values of $(m, n)$ decrease, the value of $R_0$ shifts to large $R$, as listed in Table I, and the minimum value of the LJ potential becomes shallow. The curvature around $R$ being the lattice parameter is important to understand the instability of the bcc and 2D structures, which will be discussed below.

B. Analytical discussion

The dispersion curves for the (12,6), (8,4), (6,3), and (9,3) LJ crystals are shown in Figs. 4, 5, 6, and 7, respectively. The vibrational frequency is expressed in units of $\omega_0 = \sqrt{E_0/(M a_0^2)}$. The imaginary frequency is represented as a negative value of $\omega$. As shown in Figs. 4(a)–7(a), the instability of the HX structure is attributed to the appearance of the imaginary frequencies of the out-of-plane (ZA) mode over the Brillouin zone. With Eq. (8), the frequency of the ZA mode for the HX structure is expressed as

$$\omega(q) = \sqrt{\frac{2}{M} \sum \phi(L)/L \sin^2 \left( \frac{q \cdot l}{2} \right)}.$$  

III. RESULTS AND DISCUSSION

A. Numerical results

The main results are summarized as follows: For any sets of $(m, n)$, the fcc and hcp structures are dynamically stable, which is consistent with previous studies [11,12]. However, the HX structure is unstable, which is due to the zero thickness of this system, as discussed below. The stability properties for the bcc, HHC, and BSQ structures are presented in Fig. 2. They are categorized into four groups: (A) The BHC and BSQ structures are dynamically stable (blue), (B) only the BHC structure is dynamically stable (green), (C) only the bcc structure is dynamically stable (red), and (D) no stable structures are found (orange).

FIG. 3. The $R$ dependence of the (12, 6), (8, 4), (6, 3), and (9, 3) LJ potentials.
where the summation is taken over the lattice sites having a magnitude of \( L = a_0, \sqrt{3}a_0, 2a_0, \ldots \). The dominant contribution is from sites with \( L = a_0 \), but \( \phi'(a_0) \) is always negative because the minimum of \( \phi(R) \) is located at \( R = R_0 > a_0 \), as listed in Table I. The second-largest contribution is from sites with \( L = \sqrt{3}a_0 \), but the size of \( \phi'(\sqrt{3}a_0)(>0) \) is not large enough to stabilize the ZA mode.

When buckling is assumed as in BHC and BSQ, the lattice parameter is shortened compared to the HX structure, resulting in lower total energy, as listed in Table I. The second-largest contribution is from sites \( L = \sqrt{3}a_0 \), so that the inequality in Eq. (15) is easily satisfied. For the case of \((m,n) = (6,3)\), the size of \( a_{BSQ} = 0.885a_0 \) is smaller than \( d_{12} = 1.171a_0 \approx R_0 \), leading to \( A(a_{BSQ}) < 0 \) (see Fig. 3). In addition, since the LJ potential is shallow, the magnitude of \( B(d_{12})(>0) \) is not large enough to cancel the negative \( A \) in the same brackets in Eq. (15).

This gives rise to the instability of the BSQ structure. This is due to the long-range nature of the \((6,3)\) LJ potential: The size of \( a_{BSQ} \) becomes small in order to increase the energy gain, whereas \( a_{BSQ} \) is shifted from \( R_0 \). Unfortunately, it was difficult to derive the stability condition analytically for the BHC structure because the off-diagonal elements in Eq. (7) are not zero.

The dynamical stability of the bcc structure shows the opposite tendency: When the long- and short-range LJ potentials are used, the bcc structure is dynamically stable and unstable, respectively. As shown in Figs. 4(e)–7(e), the bcc structure is dynamically stable for only the \((6,3)\) LJ crystal; otherwise it is unstable against the vibrational modes along the \( \Gamma-X \) direction. The lowest frequency at point \( N \) is expressed by \[ \omega_{N} = \sqrt{\frac{4[A(a_{1}) + A(a_{2})] + 2B(d_{12})}{M}}, \]

where in Eq. (8) the force constants up to the second NN sites, \( a_{1} = \sqrt{3}a_{bcc}/2 \) and \( a_{2} = a_{bcc} \) are considered. Since \( A(a_{1}) < 0 \), the positive value of \( B(a_{2}) \) must be large enough to overcome the negative contribution from \( A(a_{1}) \). When the set \((m,n) = (6,3)\) is used, the size of \( a_{bcc} \) is about 0.8a0, yielding \( a_{1} \approx 0.7a_{0} \) and \( a_{2} = 0.8a_{0} \). Since these are less than \( R_{0} = 1.187a_{0} \), the relation \( B(a_{2}) \gg |A(a_{1})| \) holds, so that the bcc structure becomes dynamically stable.

| \((m,n)\) in group | \(E_{\text{fcc}}\) | \(a_{\text{fcc}}\) | \(E_{\text{bcc}}\) | \(a_{\text{bcc}}\) | \(E_{\text{bsq}}\) | \(a_{\text{bsq}}\) |
|------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \((12,6)\) in A  | \(-2.546\)     | 1.387          | \(-2.435\)     | 1.110          | \(-2.546\)     | 0.981          |
| \((8,4)\) in B   | \(-4.840\)     | 1.274          | \(-4.775\)     | 1.015          | \(-4.839\)     | 0.900          |
| \((6,3)\) in C   | \(-16.961\)    | 1.011          | \(-16.870\)    | 0.804          | \(-16.963\)    | 0.715          |
| \((9,3)\) in D   | \(-10.070\)    | 1.186          | \(-9.943\)     | 0.945          | \(-10.069\)    | 0.838          |

FIG. 4. The dispersion curves of the (12,6) LJ crystals for (a) HX, (b) BHC, (c) BSQ, (d) fcc, (e) bcc, and (f) hcp structures.
C. Relationship to the stability of elemental metals

We discuss the stability relationship between the LJ crystals and the elemental metals in the periodic table. In a previous study [9], it was shown that most transition metals in the BHC and BSQ structures are dynamically stable, while those in the HX structure are unstable. In this respect, most transition metals are classified as group A in Fig. 2. This classification is related to the fact that they have a close-packed (fcc or hcp) structure for their ground state. Interestingly, the overall shapes of the dispersion curves in the (12,6) LJ crystals in the HX, BHC, and BSQ structures are quite similar to that in 2D Ni, Pd, and Pt (see the Supplemental Material (SM) [22], including Fig. 20 from Ref. [9]).

hcp Co may be classified as group B because only the BHC structure is dynamically stable (see the SM [22], including Figs. 11, 12, and 21 from Ref. [9]). Recent DFT and empirical potential calculations have shown that alkali metals (Li, Na, and K) in the fcc, bcc, and hcp structures are quite similar to that in 2D Ni, Pd, and Pt (see the Supplemental Material (SM) [22], including Fig. 20 from Ref. [9]).

We have studied the lattice dynamics of 2D and 3D LJ crystals by diagonalizing the dynamical matrix numerically and analytically. For all \((m, n)\), the HX structure is unstable due to the zero thickness. The buckling is important for obtaining dynamically stable 2D crystals: The HX and/or BSQ structures are dynamically stable if the interaction between the LJ particles is described by the short-range potential. We have categorized the stability property into four groups shown in Fig. 2 and shown that the stability property of the LJ crystals with short-range potential \((m + n \geq 17\) and \(n \geq 6)\) is similar to that of transition metals in the periodic table. In addition, by studying the discrepancy between the LJ model and DFT calculations with regard to the dynamical stability and identify the interesting properties characteristic of the elemental metals. The LJ model calculations do not follow property (ii) derived from DFT [9], where if only the BHC structure is dynamically stable, then the bcc structure is dynamically stable. The latter property has been observed in the alkali metals (Li, Na, and K), the group 6 metals (Cr, Mo, and W), and ferromagnetic Fe [9]. We consider that the discrepancy between the LJ model and DFT results may be attributed to the peculiarity of these elements. For the alkali metals [24], the pairwise potential shows a Friedel-like oscillation that is never expressed by the standard LJ potential. For the group 6 metals except Cr, high-buckled and low-buckled BHC structures are present, and the former and the latter are dynamically unstable and stable, respectively [9]. Within the LJ model, it is difficult to describe such metastability in detail. The stability of bcc Fe is due to the magnetic effect [1], which is not included in the LJ model.

IV. CONCLUSION

We have studied the lattice dynamics of 2D and 3D LJ crystals by diagonalizing the dynamical matrix numerically and analytically. For all \((m, n)\), the HX structure is unstable due to the zero thickness. The buckling is important for obtaining dynamically stable 2D crystals: The HX and/or BSQ structures are dynamically stable if the interaction between the LJ particles is described by the short-range potential. We have categorized the stability property into four groups shown in Fig. 2 and shown that the stability property of the LJ crystals with short-range potential \((m + n \geq 17\) and \(n \geq 6)\) is similar to that of transition metals in the periodic table. In addition, by studying the discrepancy between the LJ model and DFT [9], we have shown how the LJ model fails to describe the stability property of elemental metals and, conversely, identified the peculiarity of some metals.

APPENDIX: DERIVATION OF EQUATION (15)

A straightforward calculation of the dynamical matrix at point \(X\) yields a 6 \(\times\) 6 matrix of \(D_{\alpha\beta}^{ss} \equiv [q = (\pi/\alpha_{BSQ}, 0, 0)]\). By considering up to the second NN sites, the matrix elements are expressed as follows: For \(s = s'\),

\[
\tilde{D}_{\alpha\beta}^{ss} = 4[A + B(\alpha_{BSQ}) + aB(d_{12})].
\]  (A1)
\[ \tilde{D}^{xy}_{zz} = 4[\tilde{A} + \alpha B(d_{12})], \quad (A2) \]
\[ \tilde{D}^{zz}_{xx} = 4[\tilde{A} + \beta B(d_{12})], \quad (A3) \]
and for \( s \neq s' \),
\[ D_{12}^{zz} = D_{12}^{ss} = -4iB(d_{12})\sqrt{\alpha \beta}, \quad (A4) \]
\[ D_{21}^{zz} = D_{21}^{ss} = 4iB(d_{12})\sqrt{\alpha \beta}, \quad (A5) \]
and the other elements are zero. The three eigenvalues (doubly degenerate) are obtained as
\[ \omega_1^2 = \frac{1}{2M}\left[-\sqrt{(x-y)^2 + 4z^2} + x + y\right], \quad (A6) \]
\[ \omega_2^2 = \frac{1}{2M}\left[\sqrt{(x-y)^2 + 4z^2} + x + y\right], \quad (A7) \]
with \( x = D_{12}^{ss}, \ y = \tilde{D}^{xy}_{zz}, \) and \( z = 4B(d_{12})\sqrt{\alpha \beta}. \) The condition \( \omega_1^2 > 0 \) is equivalent to Eq. (15).

[1] G. Grimvall, B. Magyari-Köpe, V. Ozoliņš, and K. A. Persson, Lattice instabilities in metallic elements, Rev. Mod. Phys. 84, 945 (2012).
[2] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140, A1133 (1965).
[3] K. Parlinski, Z. Q. Li, and Y. Kawazoe, First-Principles Determination of the Soft Mode in Cubic ZrO₂, Phys. Rev. Lett. 78, 4063 (1997).
[4] S. Baroni, S. Gironcoli, A. D. Corso, and P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, Rev. Mod. Phys. 73, 515 (2001).
[5] A. Togo and I. Tanaka, First principles phonon calculations in materials science, Scr. Mater. 108, 1 (2015).
[6] X. Huang, S. Li, Y. Huang, S. Wu, X. Zhou, S. Li, C. L. Gan, F. Boey, C. A. Mirkin, and H. Zhang, Synthesis of hexagonal close-packed gold nanostructures, Nat. Commun. 2, 292 (2011).
[7] S. Schönecker, X. Li, M. Richter, and L. Vitos, Lattice dynamics and metastability of fcc metals in the hcp structure and the crucial role of spin-orbit coupling in platinum, Phys. Rev. B 97, 224305 (2018).
[8] S. Ono, Two-dimensional square lattice polonium stabilized by the spin-orbit coupling, Sci. Rep. 10, 11810 (2020).
[9] S. Ono, Dynamical stability of two-dimensional metals in the periodic table, Phys. Rev. B 102, 165424 (2020).
[10] N. W. Ashcroft, N. D. Mermin, and D. Wei, Solid State Physics, revised ed. (Cengage, Boston, 2016).
[11] M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, Oxford, 1954).
[12] D. C. Wallace and J. L. Patrick, Stability of crystal lattices, Phys. Rev. 137, A152 (1965).
[13] M. Mihalković and C. L. Henley, Empirical oscillating potentials for alloys from ab initio fits and the prediction of quasicrystal-related structures in the Al-Cu-Sc system, Phys. Rev. B 85, 092102 (2012).
[14] O. Alsalmi, M. Sanati, R. C. Albers, T. Lookman, and A. Saxena, First-principles study of phase stability of bcc XZn (X = Cu, Ag, and Au) alloys, Phys. Rev. Mater. 2, 113601 (2018).
[15] G. Goldoni and F. M. Peeters, Stability, dynamical properties, and melting of a classical bilayer Wigner crystal, Phys. Rev. B 53, 4591 (1996).
[16] I. V. Schweigert, V. A. Schweigert, and F. M. Peeters, Melting of the Classical Bilayer Wigner Crystal: Influence of Lattice Symmetry, Phys. Rev. Lett. 82, 5293 (1999).
[17] H. J. Zhao, V. R. Misko and F. M. Peeters, Analysis of pattern formation in systems with competing range interactions, New J. Phys. 14, 063032 (2012).
[18] M. W. Finnis and J. E. Sinclair, A simple empirical N-body potential for transition metals, Philos. Mag. A 50, 45 (1984).
[19] S. M. Foiles, M. I. Baskes, and M. S. Daw, Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys, Phys. Rev. B 33, 7983 (1986).
[20] S. Ono, Lattice dynamics for isochorically heated metals: A model study, J. Appl. Phys. 126, 075113 (2019).
[21] S. Ono and D. Kobayashi, Phonon softening in sodium with a stepwise electron distribution, J. Appl. Phys. 127, 165105 (2020).
[22] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.103.075406 for the phonon dispersion curves of elemental metals, extracted from Ref. [9].
[23] A. Takahashi, A. Seko, and I. Tanaka, Linearized machine-learning interatomic potentials for non-magnetic elemental metals: Limitation of pairwise descriptors and trend of predictive power, J. Chem. Phys. 148, 234106 (2018).
[24] A. Nichol and G. J. Ackland, Property trends in simple metals: An empirical potential approach, Phys. Rev. B 93, 184101 (2016).
[25] O. Hellman, I. A. Abrikosov, and S. I. Simak, Lattice dynamics of anharmonic solids from first principles, Phys. Rev. B 84, 180301(R) (2011).