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Γ -point lattice free energy estimates from $O(1)$ force calculations

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We present a new method for estimating the vibrational free energy of crystal (and molecular) structures employing only a single force calculation, for a particularly displaced configuration, in addition to the calculation of the ground state configuration. This displacement vector is the sum of the phonon eigenvectors obtained from a fast—relative to, e.g., density-functional theory (DFT)—Hessian calculation using interatomic potentials. These potentials are based here on effective charges obtained from a DFT calculation of the ground state electronic charge density but could also be based on other, e.g., empiric approaches. © 2008 American Institute of Physics.

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I. INTRODUCTION

At finite temperatures, the stability of a crystalline system is not only determined by the ground state energy but by the free energy. For a perfect crystal, the phononic contributions to the entropy are most important. In addition to minimizing the potential energy to locate the ground state configuration, the calculation of free energies is important to estimate phase stabilities of the system. The ability to quickly assess the free energy of a given crystal structure is particularly important in the investigation of phase stabilities or decomposition temperatures of theoretically predicted materials or structures. The approach to approximate free energy calculation presented here will be of particular value to predictive screening studies, where quick free energy estimates are essential to cover wide ranges of possible structural input parameters for exploring trends in thermodynamic properties.

According to the Hellmann–Feynman theorem,^{1,2} the forces acting on the ionic cores, i.e., first order energy derivatives, can be calculated within classical electrostatics from the ground state charge density, since the electronic eigenenergies only change in second order with first order wave function variations. For the calculation of the Hessian matrix of the energy, i.e., second order derivatives, charge density changes have to be evaluated. These can be obtained within density functional perturbation theory³ or from finite force differences of displaced configurations. By the former approach, the phonon frequencies can be calculated at a given k -point in the Brillouin zone with the computational complexity of an iterative ground state charge density calculation using density-functional theory⁴ (DFT). For nonzero k -points, the latter approach requires enlarged supercells to resolve interatomic couplings between the periodic images. Furthermore, charge densities for $O(N)$ displaced configurations have to be calculated, where N is the number of atoms

in the unit cell. The computational effort can be significantly reduced for both approaches by taking crystal symmetries into account.

We present a method that obtains phonon frequencies using finite force differences, where the frequencies are extrapolated from the forces due to a single displacement, independent of the number of atoms. A decoupling of displaced planes of atoms due to the periodic boundary conditions is not possible within this approach. Therefore, only the Γ -point contribution to the free energy can be calculated, which is a good approximation for sufficiently large systems. Within linear response or density functional perturbation theory, the computational effort for the calculation of the Γ -point frequencies scales as the effort for a single ground state charge density calculation. The displacement approach presented here can be of interest, since no perturbations according to the single degrees of freedom are necessary but all degrees of freedom are taken into account by one displacement, irrespective of the system size. Moreover, the method presented here only employs the classical ionic degrees of freedom and the corresponding forces, making this approach generally applicable when linear response calculations are unavailable.

II. Γ -POINT PHONON FREQUENCIES

In a harmonic approximation, the phononic contribution to the free energy is given as

$$F_{\text{vib}}(T) = rk_B T \int_0^\infty d\omega g(\omega) \ln \left[2 \sinh \left(\frac{\hbar\omega}{2k_B T} \right) \right], \quad (1)$$

where $g(\omega)$ is the normalized phonon density of states, r is the number of degrees of freedom in the unit cell, and k_B is Boltzmann's constant. The contribution of the Γ -point to Eq. (1) is

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$$F_{\text{vib}}^{\Gamma}(T) = k_B T \sum_{i=1}^{3N} \ln \left[2 \sinh \left(\frac{\hbar \omega_i}{2k_B T} \right) \right], \quad (2)$$

where N is the number of atoms in the unit cell and ω_i are the phonon frequencies. The prime denotes that the three zero frequencies corresponding to translational invariance are left out. In the zero temperature limit, Eq. (2) becomes a sum over the phonon frequencies, while for high temperatures $k_B T \gg \max(\hbar \omega_i)$, Eq. (2) approaches the logarithm of the product of the phonon frequencies:

$$F_{\text{vib}}^{\Gamma}(T \gg \max(\hbar \omega_i)/k_B) \rightarrow k_B T \ln \left(\frac{\prod_i' \hbar \omega_i}{(k_B T)^{3N-3}} \right), \quad (3)$$

where the prime again denotes that the zero frequencies due to the translational invariance are left out.

The frequencies of a system of coupled oscillators are the square roots of the eigenvalues of the generalized eigenvalue problem

$$\underline{H}\underline{v} = \omega^2 \underline{M}\underline{v}, \quad (4)$$

where \underline{H} is the Hessian matrix and \underline{v} is an eigenvector. $M_{i,j} = m_{[i/3]} \delta_{i,j}$ is a mass matrix, with the atomic masses m_k . Equation (4) can be easily converted to the eigenvalue problem

$$\tilde{\underline{H}}\tilde{\underline{v}} = \omega^2 \tilde{\underline{v}}, \quad (5)$$

yielding the same eigenvalues ω^2 as Eq. (4). $\tilde{\underline{H}}$ is a mass-scaled Hessian matrix:

$$\tilde{\underline{H}} = \underline{L}\underline{H}\underline{L}, \quad (6)$$

with

$$L_{i,j} = \frac{1}{\sqrt{m_{[i/3]}}} \delta_{i,j}. \quad (7)$$

In the following, we will use Eq. (5) to calculate the vibrational eigenfrequencies of the system.

III. METHOD

The main idea of this method is that the eigenvalues of the Hessian matrix can be estimated from $O(1)$ force calculations, if rather rough approximations to the eigenvectors are available. For a given configuration (optimized within, e.g., DFT), a model Hamiltonian is constructed, such that it yields an energetic minimum for the given atomic coordinates. With this computationally inexpensive representation of the system, the Hessian matrix is approximated. From the sum of the eigenvectors \underline{u}_i of this approximate Hessian, a displacement vector \underline{w} is constructed:

$$\underline{w} := \sum_i \underline{u}_i. \quad (8)$$

The Hessian \underline{H} of the more accurate Hamiltonian (here, DFT) is projected onto this displacement vector to extract the Hessian eigenvalues h_i :

$$h_i \approx \underline{u}_i^T \underline{H} \underline{w}. \quad (9)$$

The Hessian-vector product is approximated by the forces acting on a displaced configuration:

$$\underline{H}\underline{w} \approx \varepsilon^{-1} [\underline{\nabla} E(\underline{r}_0 + \varepsilon \underline{w}) - \underline{\nabla} E(\underline{r}_0)], \quad (10)$$

where \underline{r}_0 are the ground state coordinates and ε is used to scale the displacement for the finite difference. The gradient of the ground state configuration $\underline{\nabla} E(\underline{r}_0)$ might be neglected, if the configuration is well relaxed.

For the calculation of the vibrational eigenfrequencies, the Hessian matrix has to be mass scaled according to Eq. (6). This can either be performed for a Hessian matrix constructed from the approximate eigenpairs (h_i, \underline{u}_i) or by mass scaling the displacement and the calculated forces by a multiplication of both vectors with the matrix \underline{L} [Eq. (7)]. For the latter way of obtaining the mass-scaled Hessian, the eigenvalues are obtained using approximate eigenvectors of Eq. (5). We have found the former approach of the mass scaling of the constructed Hessian to generally give more accurate results. Especially for systems with large mass differences, the accuracy of the finite force difference obtained from the mass-scaled displacement can be reduced.

We construct the approximate set of Hessian eigenvectors using interatomic potentials. We construct these potentials from the ground state charge density. We assume the energy of the system to be locally described by the Coulomb interaction of effective point charges at the atomic positions. The forces on the point charges are calculated using Ewald summation.⁵ We use a Bader charge density analysis⁶ as implemented in Refs. 7 and 8 to attribute valence electron charge density to the ionic cores. We assume the attributed charges to be effective point charges at the corresponding atomic coordinates. We optimize the effective charges by using nonlinear least squares fitting⁹ to minimize the forces on the ground state configuration (only modifying the effective charges but not the atomic coordinates). We constrain the sum of negative and positive charges to be constant, respectively, to avoid the trivial solution of zero charges. For systems containing coordinates that are completely fixed by symmetry, the corresponding forces are always zero and therefore no fitting is necessary. Using these interatomic potentials, we calculate approximate Hessian eigenpairs.

Whereas these eigenvalues are generally not useful, the eigenvectors \underline{u}_i reflect symmetries and coordination, and a projection of an accurate Hessian onto these vectors can give frequencies in reasonable ranges. Generally, the interatomic potential representation of the system might be unstable, i.e., there are negative curvatures due to these potentials. However, we still find the geometric information contained in the eigenvectors to be useful by considering the absolute value of the right-hand side of Eq. (9) when extracting the eigenvalues. Since the vectors \underline{u}_i are only approximate eigenvectors, which are linear combinations of the eigenvectors of an accurate Hessian matrix, the phonon frequencies are mixed and degeneracies are generally not resolved. In the special case of complex compounds with a broad range of phonon

frequencies, it is possible to reduce the frequency mixing for the lowest eigenfrequencies by linear extrapolation (see Sec. V A for an example).

For low temperatures, compared to the lowest Γ -point phonon energies, the free energy calculated from the Hessian matrix constructed from the forces due to the displacement as outlined above is generally a good estimate, because the free energy is basically a sum of the phonon energies, and thus less sensitive to errors in the eigenmode vectors than single phonon energies.

For temperatures higher than the highest phonon energies, the free energy calculated from the approximate frequencies generally will not be a good estimate, since the free energy converges to the logarithm of the product of eigenfrequencies [see Eq. (3)]. Based on the single displacement (8), we estimate the change of a $3N$ -dimensional volume after the linear transformation given by the Hessian matrix. This provides an estimate of the determinant of the Hessian matrix, which equals the product of its eigenvalues h_i . We estimate this product by

$$\prod_i h_i \approx \prod_j (\underline{x}_j^T \underline{H} \underline{w}) / \left(\sum_k \underline{x}_k^T \underline{u}_k \right), \quad (11)$$

again using Eq. (10) to approximate $\underline{H} \underline{w}$. The \underline{x}_j are the basis vectors of the canonical real space basis of the atomic coordinates. Equation (11) is exact for vibrationally decoupled atomic coordinates and can generally be interpreted as an estimate of how the volume spanned by the canonical basis vectors \underline{x}_j is scaled by the Hessian matrix. To obtain the product of eigenfrequencies, Eq. (11) has to be mass scaled. Since the determinant of a product of matrices equals the product of the determinants of the matrices, the scaling can simply be performed by a division with the product of the atomic masses.

In the following, we provide examples of the application of the method to the calculation of free energies.

IV. ELECTRONIC STRUCTURE CALCULATION

The energy gradients were calculated within DFT (Ref. 4) using two different programs to test the general applicability and implementation of the approach. The software package DACAPO (Ref. 10) was used for the K_2NaAlH_6 and GaAs examples and VASP (Ref. 11) for the remaining crystal structures, using plane wave basis sets with cutoff energies of 350–400 eV and the Perdew–Wang-91 exchange-correlation functional^{12,13} for all calculations. DACAPO uses ultrasoft pseudopotentials¹⁴ for a description of the ionic cores, while for VASP projector-augmented wave¹⁵ potentials¹⁶ were used. The electronic Brillouin zones were sampled with k -point spacings of $\sim 0.1 \text{ \AA}^{-1}$.

To assess the accuracy of the free energy estimates, we perform reference calculations using $3N$ displacements for diagonalization of the full Hessian matrices.

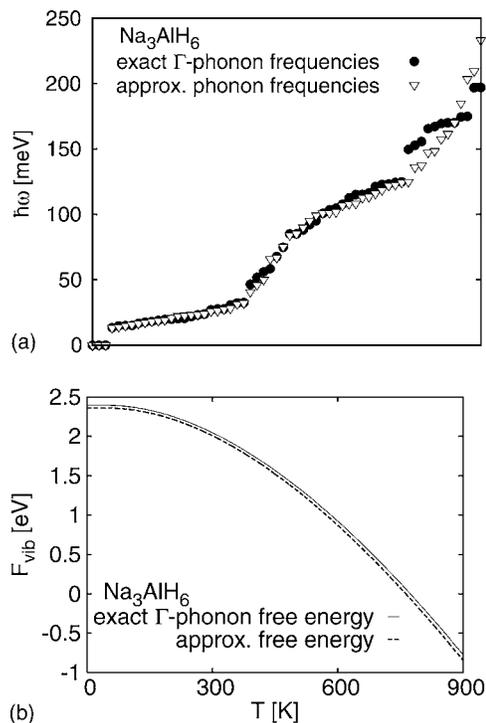


FIG. 1. Comparison of Γ -point phonon frequency spectra (a) and lattice free energies (b) calculated for Na_3AlH_6 both from $3N$ displacements and the $O(1)$ method presented here, respectively. To improve the quality of the lowest approximate phonon frequencies, the five lowest nonzero frequencies were generated from a linear extrapolation of the ten next higher frequencies.

V. EXAMPLES

In this section, representative results for the free energy calculation method are presented for different classes of materials, covering both the low and high phonon frequency ranges.

A. Na_3AlH_6 and K_2NaAlH_6

As a first example, we consider two complex metal aluminum hexahydrides^{17–19} of interest as reversible hydrogen storage materials,^{20–25} where cation alloying is possible, rendering them interesting for screening studies.

The phonon spectrum of the complex metal hydride Na_3AlH_6 (space group $P2_1/n$) (Ref. 26) contains relatively high energetic librational and bond-stretching (in this case Al–H bonds) modes, which are typical for the phonon spectrum of this kind of material. A distinct feature is the high frequency band of bond-stretching modes around 170 meV [see Fig. 1(a)]. While degeneracies are not resolved in the single-displacement frequencies, the correct range of phonon energies is covered, interpolating the “exact” spectrum. Only a small fraction of the spectrum lies below typical values of $k_B T$, and therefore the approximated free energy is in good agreement with the result based on $3N$ displacements [see Fig. 1(b)], since the free energy approaches the arithmetic average of the phonon energies for temperatures low compared to the high phonon energies.

One of the important thermodynamic properties that can be calculated based on the lattice free energies is the decomposition temperature of a compound by comparing to the

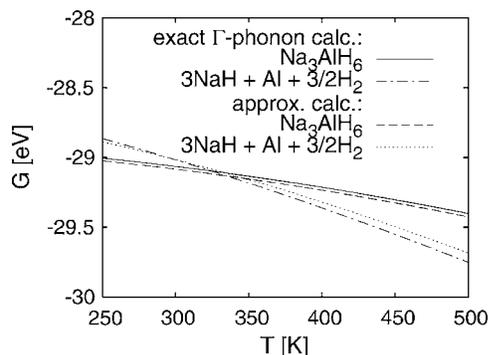
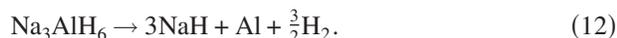


FIG. 2. Gibbs free energies for Na_3AlH_6 and its decomposition products calculated both by diagonalization of the full Hessian and the $O(1)$ method.

energies of the constituents. For known materials, these energies can either often be obtained from tabulated data or be calculated. As an example, we estimate the decomposition temperature of Na_3AlH_6 . Figure 2 shows the Gibbs free energies (pV terms for solid phases have been neglected) for Na_3AlH_6 and its decomposition products in the reaction



The Gibbs free energy for Al has been generated from data in Ref. 27; data for H_2 have been taken from Ref. 28. The free energies of Na_3AlH_6 and NaH have been calculated both using 1 and $3N$ displacements. The agreement between the two approaches is good, yielding a decomposition temperature of ~ 350 K. Ke and Tanaka²⁸ have previously calculated a decomposition temperature of 390 K for Na_3AlH_6 . Considering that the latter value is based on a quasiharmonic approximation and that the phonon dispersion has been taken into account, our quick estimate of the decomposition temperature yields a satisfactory result. Experimentally,²⁹ a value of 423 K has been obtained for the decomposition temperature.

A stable binary cation alloy is K_2NaAlH_6 (space group $Fm\bar{3}m$),³⁰ with larger atomic mass differences than Na_3AlH_6 . As a test case for alloyed systems, we have estimated the free energy of this compound using the $O(1)$ method presented here. For this compound, the bond-stretching band lies at 160 meV [see Fig. 3(a)]. The corresponding degeneracy is not resolved at all in the extrapolated spectrum. Since low temperature free energies basically depend on the average phonon frequency, the lattice free energy approximation still is quite good [see Fig. 3(b)].

B. GaAs

We continue with tests for systems that do not show high frequency modes due to the molecular bonding in the crystal. As a model semiconductor, we have considered GaAs, which crystallizes in the zinc blende structure (space group $F\bar{4}3m$).³¹ The optical Γ -point frequencies are separated by ~ 18 meV from the acoustic frequencies [see Fig. 4(a)]. The frequencies obtained from the $O(1)$ method do not show this gap; optical and acoustic modes are mixed. The average error in the six lowest optical frequencies is about 15% with a corresponding error of $\sim 40\%$ in the eigenvectors. The error

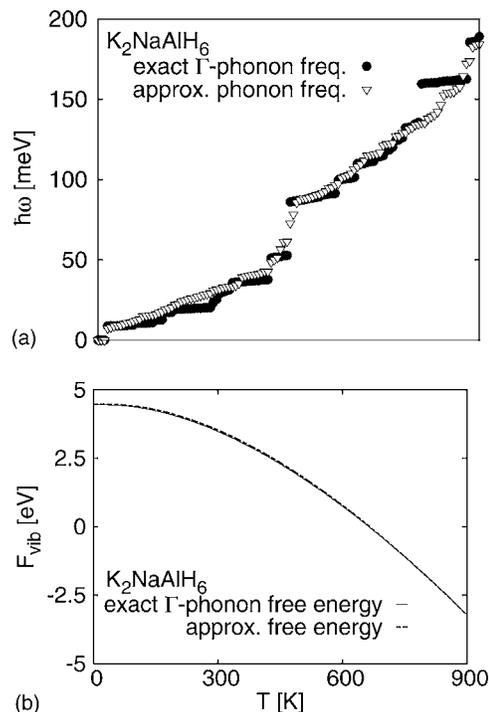


FIG. 3. Comparison of Γ -point phonon frequency spectra (a) and lattice free energies (b) calculated for K_2NaAlH_6 both with 1 and $3N$ displacements, respectively.

in the higher frequencies is smaller: $\sim 3\%$. The maximal phonon frequencies are relatively low, only about 30 meV, which is of the same magnitude as $k_B T$ at room temperature. Therefore, the free energy calculated using the approximate frequencies obtained from the $O(1)$ method is not a good approximation for temperatures $T > 0$ [see Fig. 4(b)]. Alter-

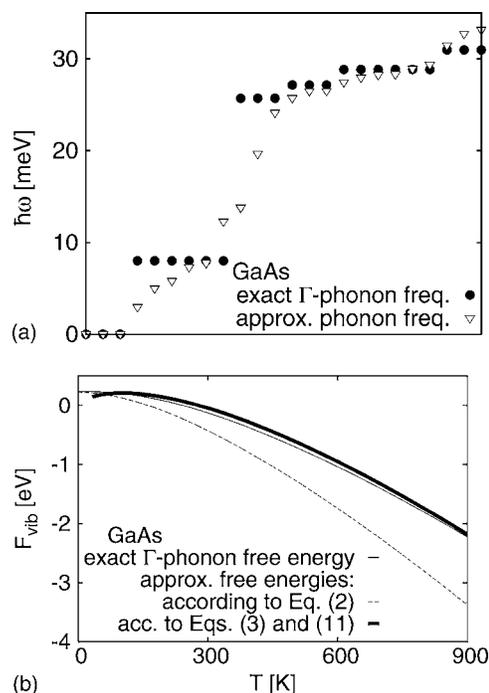


FIG. 4. Comparison of Γ -point phonon frequency spectra (a) and lattice free energies (b) calculated for GaAs both with 1 and $3N$ displacements, respectively.

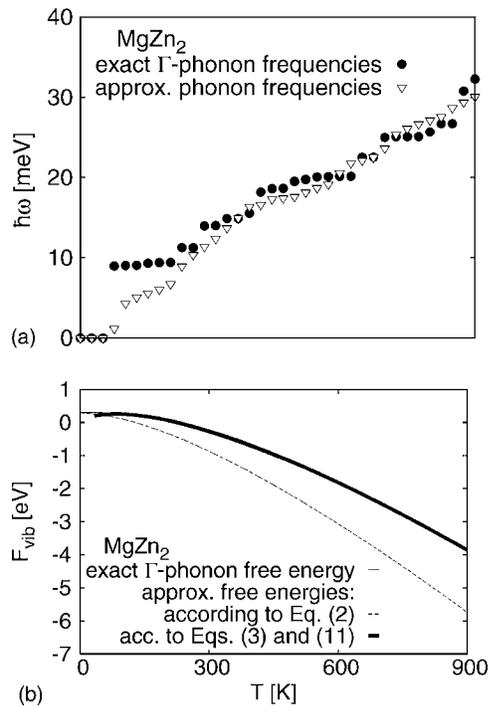


FIG. 5. Comparison of Γ -point phonon frequency spectra (a) and lattice free energies (b) calculated for MgZn_2 both with 1 and $3N$ displacements, respectively.

natively, the product of the phonon frequencies is directly approximated using Eq. (11) from the forces due to the single displacement, instead of projecting the forces onto the approximate eigenvectors to extract the frequencies. The high temperature free energy approximation according to Eq. (3) using this product yields relatively good results (even for temperatures below $k_B T = 30$ meV).

C. MgZn_2

Finally, we apply our method to a simple metallic alloy. We have considered the hexagonal η -phase of MgZn_2 (space group $P6_3/mmc$),³² which is the reference C14 Laves phase material. Similar to the case of GaAs, the highest phonon energies are around 30 meV due to the absence of “molecularlike” modes [see Fig. 5(a)]. Also here, the free energy calculated from the approximated phonon frequencies is only a good approximation for $T \rightarrow 0$. Using the direct approximation of the product of the phonon frequencies [Eq. (11)] together with the high temperature approximation, Eq. (3), which basically depends on the geometric mean value of the frequencies, the corresponding approximated free energy is in good agreement with the “exactly” calculated free energy for temperatures higher than about 50 K [see Fig. 5(b)].

The average error in the frequencies obtained using the $O(1)$ method for the four example cases considered here is about 10% with a corresponding error of 30% in the eigenvectors. The errors in the modes could be reduced using better potentials for the Hessian eigenvector approximation. An advantage of the simple point charge model used here is that it can be optimized to yield an energetic minimum for given atomic coordinates, i.e., the ground state configuration obtained using, e.g., DFT. A possibility to improve the

interatomic potentials could be the inclusion of the forces due to the special displacement calculated using DFT as additional constraints into a reoptimization or extension of the model potentials.

VI. CONCLUSION

We have developed a method for a fast approximation of lattice free energies. This approach can be very useful for quick estimates of decomposition temperatures of new or theoretically proposed compounds. These fast, rough estimates are very important for screening studies of, e.g., alloy stability at finite temperatures. It is, however, in general, not expected to be accurate enough for a reliable determination of phase transition temperatures based on an energetic comparison of different phases lying very close in energy, since degeneracies in the phonon spectrum, determining the peak heights in the phonon density of states, are not resolved within this approach.

Free energies can be extrapolated from the forces due to a single atomic displacement for low and high temperatures compared to the phonon energies, rendering this approach suitable both for complexes with molecular bonds and high phonon energies and semiconductors and metals.

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- ¹H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937).
- ²R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
- ³S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987).
- ⁴P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ⁵P. Ewald, *Ann. Phys.* **64**, 253 (1921).
- ⁶R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford University Press, Oxford, 1990).
- ⁷G. Henkelman, A. Arnaldsson, and H. Jónsson, *Comput. Mater. Sci.* **36**, 254 (2006).
- ⁸E. Sanville, S. D. Kenny, R. Smith, and G. Henkelman, *J. Comput. Chem.* **28**, 899 (2007).
- ⁹Minpack, University of Chicago (1999).
- ¹⁰B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
- ¹¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹²J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ¹³J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **48**, 4978(E) (1993).
- ¹⁴D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ¹⁵P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ¹⁶G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁷J. Graetz, Y. Lee, J. J. Reilly, S. Park, and T. Vogt, *Phys. Rev. B* **71**, 184115 (2005).
- ¹⁸O. M. Løvvik, O. Swang, and S. M. Opalka, *J. Mater. Res.* **20**, 3199 (2005).
- ¹⁹H. B. Y. Nakamura, A. Fossdal, and B. Hauback, *J. Alloys Compd.* **416**, 274 (2006).
- ²⁰B. Bogdanović and M. Schwickardi, *J. Alloys Compd.* **253–254**, 1 (1997).
- ²¹S. Li, P. Jena, and R. Ahuja, *Phys. Rev. B* **73**, 214107 (2006).

- ²²J. Voss, Q. Shi, H. Jacobsen, M. Zamponi, K. Lefmann, and T. Vegge, *J. Phys. Chem. B* **111**, 3886 (2007).
- ²³A. Peles, J. A. Alford, Z. Ma, L. Yang, and M. Y. Chou, *Phys. Rev. B* **70**, 165105 (2004).
- ²⁴M. E. Arroyo y de Dompablo and G. Ceder, *J. Alloys Compd.* **364**, 6 (2004).
- ²⁵P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg, *Phys. Rev. B* **71**, 092103 (2005).
- ²⁶V. Subrtova, *Collect. Czech. Chem. Commun.* **31**, 4455 (1966).
- ²⁷P. D. Desai, *Int. J. Thermophys.* **8**, 621 (1987).
- ²⁸X. Ke and I. Tanaka, *Phys. Rev. B* **71**, 024117 (2005).
- ²⁹K. J. Gross, S. Guthrie, S. Takara, and G. Thomas, *J. Alloys Compd.* **297**, 270 (2000).
- ³⁰M. H. Sorby, H. W. Brinks, A. Fossdal, K. Thorshaug, and B. C. Hauback, *J. Alloys Compd.* **415**, 284 (2006).
- ³¹S. Adachi, *J. Appl. Phys.* **58**, R1 (1985).
- ³²Y. Komura and K. Tokunaga, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **36**, 1548 (1980).