

# Entropy driven stabilization of energetically unstable crystal structures explained from first principles theory

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Conventional methods to calculate the thermodynamics of crystals evaluate the harmonic phonon spectra and therefore do not work in frequent and important situations where the crystal structure is unstable in the harmonic approximation, such as the body-centered cubic (bcc) crystal structure when it appears as a high-temperature phase of many metals. A method for calculating temperature dependent phonon spectra self consistently from first principles has been developed to address this issue. The method combines concepts from Born's inter-atomic self-consistent phonon approach with first principles calculations of accurate inter-atomic forces in a super-cell. The method has been tested on the high temperature bcc phase of Ti, Zr and Hf, as representative examples, and is found to reproduce the observed high temperature phonon frequencies with good accuracy.

Many elements, alloys, and compounds appear in crystal structures which should not be energetically stable. The inter-atomic interactions places these systems at energy saddle points on the potential surface for atomic positions corresponding to the lattice sites of these structures rather than minima for statically stable structures. The body centered cubic (bcc) structure prevails as the simplest and best known example. Although a stable structure at low temperatures for several elements in the Periodic Table, bcc becomes unstable in the harmonic approximation [1, 2, 3] for the group IVB elements, for the rare-earth elements, for the actinides, and for several alkaline-earth elements. Nevertheless, at elevated temperatures the bcc structure emerges as the stable crystal structure for all these elements. Zener considered this enigma long ago and proposed a possible explanation: the large vibrational entropy of the bcc crystal structure makes it thermodynamically favourable at finite temperatures [5]. Also, Grimvall *et al* [4] pointed out the importance of electronic entropy in the stabilization of the bcc crystal structure of the group IVB elements Ti and Zr.

So far no satisfactory, quantitative explanation has been presented for this situation. Density functional theory (DFT) [6] forms the basis of contemporary microscopic solid state theory and allows, in principle, to calculate different properties of crystals completely *ab initio*, without any fitting parameters. In particular, phonon spectra in the harmonic approximation can be efficiently evaluated in this way [7]. However, for the bcc phases mentioned above the phonon spectra in the harmonic approximation reveal imaginary phonon frequencies of e.g. Zr [8, 9] for some wave-vectors, which shows that the bcc phase is from a lattice dynamics point of view unstable (hence these elements are energetically unstable, and are referred to as dynamically unstable in the bcc phase). A straightforward calculation using DFT molecular dynamics (MD) [10] should in principle be able to reproduce the stability of the bcc phase for the above discussed el-

ements, since MD implicitly include temperature effects. However, MD suffers from the fact that obtaining reliable free energies implies a computationally very demanding task, which in many cases make these types of calculations intractable.

We propose here a solution to this problem, which builds on a self-consistent *ab initio* lattice dynamics (SCAILD) approach. In this paper we describe the essential aspects of our method and apply it to the problem of stability of the bcc phase for the group IVB elements. Although several aspects of our proposed theory have not been considered before we note that it conceptually has similarities with the self-consistent phonon approach by Born [11], and that several other self-consistent methods [12, 13] have been developed in the past. We will show that the SCAILD theory gives phonon spectra of the bcc phase of Ti, Zr and Hf which are in agreement with observations [15, 16, 17]. Although we will in the rest of this manuscript focus on the group IV elements, we point out here that what we provide is a general scheme which can be used for any element and compound.

Self consistent phonon calculations are a natural extension of the theory of the harmonic lattice, and we initiate our methodological description by first presenting the most important features of this theory. The Hamiltonian

$$\mathcal{H}_h = \sum_{\mathbf{R}} \frac{\mathbf{P}_{\mathbf{R}}^2}{2M} + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \mathbf{U}_{\mathbf{R}} \bar{\bar{\Phi}}(\mathbf{R} - \mathbf{R}') \mathbf{U}_{\mathbf{R}'}, \quad (1)$$

describes a harmonic lattice where  $\mathbf{R}$  are the equilibrium lattice positions of the atoms,  $\mathbf{U}_{\mathbf{R}}$  the displacements of the atoms,  $\mathbf{P}_{\mathbf{R}}$  the momentum of the atoms,  $M$  the atomic mass and  $\bar{\bar{\Phi}}$  the inter-atomic force constant matrices (Here the vectors  $\mathbf{R}$  refer to the positions of a Bravais lattice). Diagonalizing the dynamical matrix

$$\bar{\bar{D}}(\mathbf{k}) = \frac{1}{M} \sum_{\mathbf{R}} \bar{\bar{\Phi}}(\mathbf{R}) e^{-i\mathbf{k}\mathbf{R}}. \quad (2)$$

for each wave vector  $\mathbf{k}$  in the first Brillouin zone one finds the eigenvalues  $\omega_{\mathbf{k}s}$  and eigenvectors  $\epsilon_{\mathbf{k}s}$  of different phonon modes (longitudinal or transverse) labeled by the symbol  $s$ ,  $N$  being the number of atoms. Introducing the canonical phonon coordinates  $\mathbf{U}_{\mathbf{R}}$  and  $\mathbf{P}_{\mathbf{R}}$

$$\mathbf{U}_{\mathbf{R}} = \frac{1}{\sqrt{MN}} \sum_{\mathbf{k},s} Q_{\mathbf{k}s} \epsilon_{\mathbf{k}s} e^{i\mathbf{k}\mathbf{R}} \quad (3)$$

$$\mathbf{P}_{\mathbf{R}} = \frac{1}{\sqrt{MN}} \sum_{\mathbf{k},s} P_{\mathbf{k}s} \epsilon_{\mathbf{k}s} e^{i\mathbf{k}\mathbf{R}}. \quad (4)$$

allows a separation of the original Hamiltonian of the crystal into the Hamiltonians of  $3N$  independent harmonic oscillators.

The thermodynamic average of the operators  $Q_{\mathbf{k}s}^\dagger Q_{\mathbf{k}s}$  determines the mean-square atomic displacements and is given by

$$\langle Q_{\mathbf{k}s}^\dagger Q_{\mathbf{k}s} \rangle = \frac{\hbar}{\omega_{\mathbf{k}s}} \left[ \frac{1}{2} + n \left( \frac{\hbar \omega_{\mathbf{k}s}}{k_B T} \right) \right], \quad (5)$$

where  $n(x) = 1/(e^x - 1)$  is the Planck function. In the classical limit, i.e for sufficiently high temperatures, the operators  $(1/\sqrt{M})Q_{\mathbf{k}s}$  are replaced by real numbers,

$$A_{\mathbf{k}s} \equiv \pm \sqrt{\frac{\langle Q_{\mathbf{k}s}^\dagger Q_{\mathbf{k}s} \rangle}{M}}. \quad (6)$$

Calculating the gradient of the potential energy in Eqn. 1 with respect to the atomic displacements gives the restoring force

$$\mathbf{F}_{\mathbf{R}} = - \sum_{\mathbf{R}'} \bar{\Phi}(\mathbf{R} - \mathbf{R}') \mathbf{U}_{\mathbf{R}'}. \quad (7)$$

Fourier transforming Eqn. 7 and substituting  $\mathbf{U}_{\mathbf{R}}$  with the expression in Eqn. 3 gives

$$\mathbf{F}_{\mathbf{k}} = - \sum_s M \omega_{\mathbf{k}s}^2 A_{\mathbf{k}s} \epsilon_{\mathbf{k}s}. \quad (8)$$

Finally, using the orthogonality of the eigenvectors  $\epsilon_{\mathbf{k}s}$  the phonon frequencies can be expressed as

$$\omega_{\mathbf{k}s} = \left[ - \frac{1}{M} \frac{\epsilon_{\mathbf{k}s} \mathbf{F}_{\mathbf{k}}}{A_{\mathbf{k}s}} \right]^{1/2}. \quad (9)$$

The equations discussed so far can be solved for dynamically stable materials, where each atom is located in a minimum of the function  $U_{\mathbf{R}}$ . It is important to note that this does not have to correspond to a global total energy minimum of the lattice, a local minimum suffices. For dynamically unstable materials  $U_{\mathbf{R}}$  does not have a minimum at the lattice sites of the crystal structure. In this situation the equations discussed so far can not be used straight forwardly since they result in imaginary phonon frequencies. This represents a situation where the lattice under consideration spontaneously

shifts atomic planes and/or atomic positions so that a new crystal structure lowers the total energy. We demonstrate the problem at hand by comparing in Fig.1 the calculated (zero temperature) phonon spectra of the bcc phase of the group IVB elements with experimental data obtained at elevated temperatures. At these temperatures the group IVB elements are observed to be stable in the bcc crystal structure, and the measured phonon frequencies are naturally positive for all lattice vectors. Fig.1 shows that calculations using a static bcc lattice result in a dynamically unstable situation with imaginary phonon frequencies. It should be noted that the failure describing the bcc phase of the group IVB elements using harmonic lattice theory (Fig.1, right column) is not caused by any obvious error in the energy functional used, and are likely not to be improved even if an exact functional for a static lattice were found.

In order to properly describe the high temperature phase of the group IVB elements one must include the interaction between phonons [18]. As a result, phonon frequencies turn out to be temperature dependent which we explore numerically in this study. However, we neglect the phonon damping due to decay processes of phonons (see, e.g., Ref. [19] and Refs. therein), another anharmonic effect. In the present calculations thermal expansion effects have not been taken into account, all calculations have been performed at constant volume. Furthermore, the thermal excitations of the electronic subsystem has not been considered in the present calculations of the phonon frequencies.

The method used to calculate temperature dependent phonons presented in this paper considers a supercell containing a number of atoms which are allowed to deviate from the lattice positions stipulated by the crystal structure. The deviations are calculated as a function of temperature, by solving equations 3 to 9 self consistently. The deviation of the atomic positions away from the ideal lattice points provides an extra entropy to the system and the stabilization of the bcc structure for the group IVB elements as a function of increasing temperature may as we will see below be found.

As regards the calculational details of the force calculation we used the VASP package [14], within the generalized gradient approximation (GGA). The PAW potentials used required energy cutoffs of 197 eV for Ti, 175 eV for Zr, and 243 eV for Hf. The k-point mesh was a 6x6x6 Monkhorst-Pack grid, and the supercell used was obtained by increasing the bcc primitive cell 4 times along the 3 primitive lattice vectors.

In practice our calculations are done by first calculating a starting guess for the phonon dispersions by means of a standard supercell calculation, see e.g Ref. 20. The phonon frequencies corresponding to k-vectors commensurate with the supercell are then used to calculate the atomic displacements through Eqns. 3-6. Here it should be noted that the signs of the amplitudes  $A_{\mathbf{k}s}$  (see

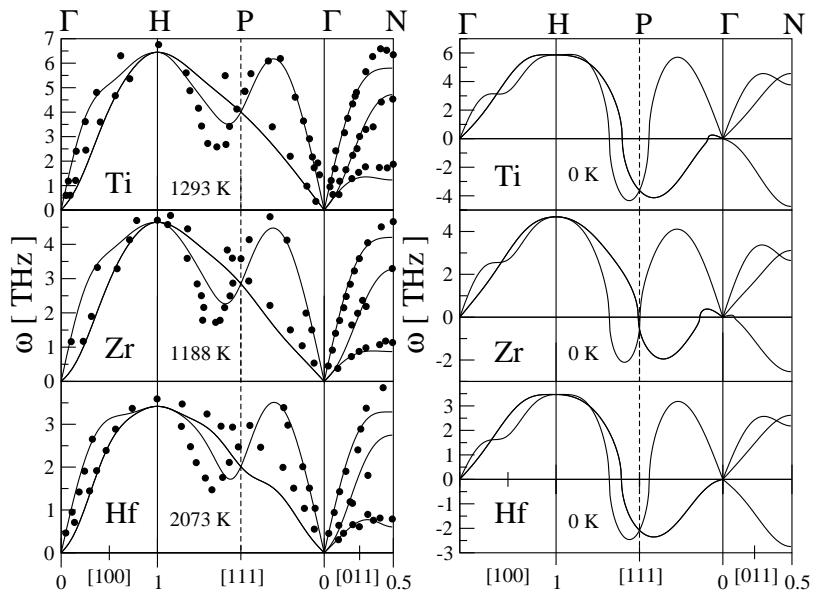


FIG. 1: The phonon dispersions of the group IVB metals. The solid lines are the first principles self consistent phonon calculations. In the left column the finite temperature calculations, and in the right column the  $T = 0$  K calculations. The filled circles are the experimental data of Ref. [15, 16, 17].

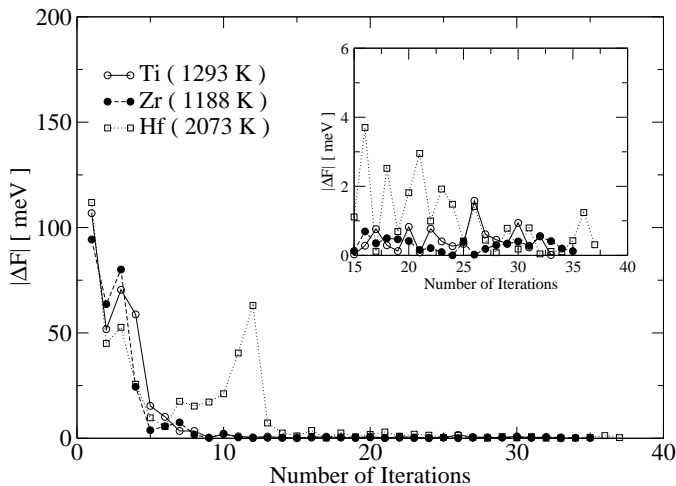


FIG. 2: The change in free energy between two consecutive iterations, here plotted as a function of the number of iterations. The inset in the figure shows the same plots but at a smaller energy scale.

Eqn.6), should be chosen randomly, with equal probabilities for + and -. This is an approximation to the procedure in which  $\mathcal{A}_{\mathbf{k}_s}$  is sampled continuously to obtain the correct mean square deviations of the modes. This approximation however conserves correctly the property that the displacements in Eqn. 3 are  $\mathbf{R}$ -dependent. Furthermore, it should be noted that the eigenvectors  $\epsilon_{\mathbf{k}_s}$  calculated in the initial calculation are not updated throughout the rest of the procedure. This however does not

introduce any extra approximation, it merely guarantees that the longitudinal and transverse modes are fixed to the modes of the bcc lattice. Starting from the equilibrium geometry used in the initial supercell calculation, the atoms are displaced according to Eq. 3, and the forces on these displaced atoms are calculated. From the Fourier transform of the atomic forces a new set of frequencies are calculated through Eqn (9). To retain the correct symmetry of the calculated phonon dispersion the symmetries of the different  $\mathbf{k}$ -vectors are restored by

$$\Omega_{\mathbf{k}_s}^2 = \frac{1}{m_{\mathbf{k}}} \sum_{S \in \mathcal{S}(\mathbf{k})} \omega_{S^{-1}\mathbf{k}_s}^2, \quad (10)$$

where  $\mathcal{S}(\mathbf{k})$  is the symmetry group of the wave vector  $\mathbf{k}$ , and  $m_{\mathbf{k}}$  the number of elements of the group. From the different iterations frequency distributions of the modes are obtained, and a new set of frequencies are supplied by the mean frequencies of these distributions,

$$\omega_{\mathbf{k}_s}^2(N) = \frac{1}{N} \sum_{i=1}^N \Omega_{\mathbf{k}_s}^2(i), \quad (11)$$

where  $\Omega_{\mathbf{k}_s}(i)$ ,  $i = 1, \dots, N$  are the symmetry restored frequencies from all iterations. The new set of frequencies calculated in (11) determine a new set of displacements used to calculate a new set of forces. Philosophically our approach is similar to Born's self consistent phonon theory, with the main difference being that we consider a direct force calculation from a super cell with Hellman-Feynman forces calculated from density functional theory.

Figure 1 shows the calculated phonon dispersions together with the experimental data of Ref. [15, 16, 17] for the bcc phase of the group IVB metals at temperatures 1293 K, 1188 K, and 2073 K for Ti, Zr, and Hf, respectively. The finite temperature calculations predict the stability of the bcc phase of all group IVB metals by promoting the frequencies of the phonons along the  $\Gamma$  to  $N$  symmetry line and around the  $P$  symmetry point from imaginary to real. The finite temperature calculations of phonons result in an overall quantitative agreement with experimental values. Smaller deviations are observed around the P and H point of the Brillouin-zone, most likely due to finite size effects of the supercell used in the calculations.

From the self consistent phonon spectrum the free energy is approximated from the density of states of the phonons  $g(\omega)$  through the expression

$$F(T) = \int_0^\infty d\omega g(\omega) \left[ \frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\hbar\omega/k_B T}) \right], \quad (12)$$

which has been shown by Cochran *et al.* [21] to give an entropy correct to leading order in anharmonic perturbation theory. Figure 2 shows the convergence of free energy for the three elements considered in this work. In all calculations presented here the self consistent cycle was terminated when the difference in the approximate free energy of the lattice between two consecutive iterations was less than 1 meV. Convergence in the free energy with such accuracy is very encouraging and opens up the possibility to investigate temperature induced phase stability for a very large set of materials, since the accuracy needed to e.g. resolve crystallographic energy differences is of the order of a few meV or more. This prediction has also been tested by using inter-atomic forces calculated with the embedded atom potentials of Ref. 22, 23. The free energy difference between the hcp and bcc structures where calculated as functions of temperature for Ti and Zr. Here the theoretically predicted hcp to bcc transition temperatures where within  $\sim 400$  K of the corresponding experimental temperatures.

In summary, a quantitative theory successfully explains the long lasting question concerning thermal, entropy driven stabilization of dynamically unstable materials. Application to the group IVB elements reproduces the measured phonon spectrum of these elements at elevated temperatures with good accuracy. We note that the presented method reproduces observed high temperature phonon spectra with good accuracy and that the method when used at low, but non-zero temperatures, results in imaginary frequencies for e.g. bcc Ti. This shows that at low temperatures this element is unstable in the bcc phase, in agreement with observations. Other systems where one can expect success of this method are the bcc phase of f-electron materials as well as, the high pressure phase of Fe, and many of the ferroelectrics. The

approach has advantages over traditional methods such as MD simulations in that complications associated with metallic materials are avoided and, most importantly, that a much smaller set of atoms are needed.

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