Temperature-driven $\alpha$-to-$\beta$ phase transformation in Ti, Zr and Hf from first-principles theory combined with lattice dynamics

P. Souvatzis$^{(a)}$, S. Arapan$^{1,2}$, O. Eriksson$^1$ and M. I. Katsnelson$^3$

$^1$ Department of Physics and Astronomy, Division of Materials Theory Uppsala University
Box 516, SE-751210, Uppsala, Sweden, EU
$^2$ Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova
Academiei 3/3, MD-2028 Chişinău, Moldova
$^3$ Radboud University Nijmegen, Institute for Molecules and Materials - NL-6525 AJ Nijmegen, The Netherlands, EU

received 30 September 2011; accepted in final form 9 November 2011
published online 14 December 2011

PACS 64.70.kd – Metals and alloys
PACS 63.20.kg – Phonon-phonon interactions
PACS 63.20.Ry – Anharmonic lattice modes

Abstract – Lattice dynamical methods used to predict phase transformations in crystals typically deal with harmonic phonon spectra and are therefore not applicable in important situations where one of the competing crystal structures is unstable in the harmonic approximation, such as the bcc structure involved in the hcp-to-bcc martensitic phase transformation in Ti, Zr and Hf. Here we present an expression for the free energy that does not suffer from such shortcomings, and we show by self-consistent $ab\text{ initio}$ lattice dynamical calculations (SCAILD), that the critical temperature for the hcp-to-bcc phase transformation in Ti, Zr and Hf, can be effectively calculated from the free-energy difference between the two phases. This opens up the possibility to study quantitatively, from first-principles theory; temperature-induced phase transitions.

Copyright © EPLA, 2011

Introduction. – Martensitic phase transformations are common, both in alloys frequently used in industry, such as shape memory alloys [1], and in the the elemental group 3 to 4 transition metals [2], not to mention martensitic transformation in iron and iron-based alloys, a crucial phenomenon for metallurgy [3]. Thus there exists a substantial interest both from an industrial, applied and an academic point of view to develop accurate and effective methods to understand and even predict martensitic phase transformations.

The hcp-to-bcc (or $\alpha$-to-$\beta$) transition in Ti, Zr and Hf is a martensitic phase transformation that has been thoroughly investigated both from an experimental [2,4] and a theoretical [5–8] perspective. Recently Hennig et al. [5] developed and used a classical potential of the modified embedded atom method (MEAM) [9] to accurately reproduce the phase boundary between the hcp and bcc structure in Ti. However, there is up to this date a lack of first-principles theoretical studies made of the martensitic hcp-to-bcc phase transformation in Ti, Zr and Hf. The problem is that anharmonic effects in lattice dynamics [10] are of crucial importance for finite-temperature structural phase transitions, and their quantitative first-principle treatment is a real challenge.

A straightforward calculation using DFT molecular dynamics (DFT-MD) [11] should in principle be able to reproduce the bcc-to-hcp phase transformation in Ti and similar materials, since DFT-MD implicitly include anharmonic effects. However, DFT-MD is a computationally very demanding task which makes its use problematic. Instead we will here exploit the method of self-consistent $ab\text{ initio}$ lattice dynamical calculations (SCAILD) [12]. Here, we further develop this method in order to be able to calculate thermodynamic properties, such as structural free-energy difference (before we were restricted by the calculations of temperature-dependent phonon frequencies only [12–16]). The SCAILD scheme is a constrained sampling method, in that it only samples the lattice dynamical phase space along the normal mode directions of commensurate phonons, and only at atomic displacements corresponding to the mean square atomic deviations dictated by thermodynamics [12,13]. Furthermore,

$^{(a)}$E-mail: petros.souvatzis@fysik.uu.se
in the SCAILD scheme thermal equilibrium is set \textit{a priori} [12,13], instead of reached \textit{a posteriori}, as in DFT-MD. Hence, by virtue of not being forced to establish thermal equilibrium and due to the limited phase space sampling, SCAILD calculations are much faster and, thus, much more practical than the corresponding DFT-MD calculations.

We propose here a new expression of the free energy of the SCAILD scheme, and we show that from the atomic configurations and the phonon density of states produced by the SCAILD calculations, an accurate measure of the free energy for the different phases can be obtained.

Method. – In order to properly describe temperature-driven phase transformations in general, one must include the interaction between phonons [10]. As a result, phonon frequencies turn out to be temperature dependent which we explore numerically in this study by means of the SCAILD method [12–16].

The SCAILD method is based on the calculation of Hellman-Feynman forces of atoms in a supercell. The method can be viewed as an extension of the frozen phonon method [17], in which all phonons with wave vectors \( \mathbf{q} \) commensurate with the supercell are excited together in the same cell by displacing atoms situated at the undistorted positions \( \mathbf{R} + \mathbf{b}_\sigma \), according to \( \mathbf{R} + \mathbf{b}_\sigma \rightarrow \mathbf{R} + \mathbf{b}_\sigma + \mathbf{U}_{\mathbf{R} \sigma} \), where the displacements are given by

\[
\mathbf{U}_{\mathbf{R} \sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}, \sigma} A^{\mathbf{q}}_{\mathbf{R} \sigma} \epsilon^{\mathbf{q}}_{\mathbf{R} \sigma} e^{i \mathbf{q} \cdot (\mathbf{R} + \mathbf{b}_\sigma)}. \tag{1}
\]

Here \( \mathbf{R} \) represent the \( N \) Bravais lattice sites of the supercell, \( \mathbf{b}_\sigma \) the position of atom \( \sigma \) relative to this site, \( \epsilon^{\mathbf{q}}_{\mathbf{R} \sigma} \) are the phonon eigenvectors corresponding to the phonon mode, \( s \), and the mode amplitude \( A^{\mathbf{q}}_{\mathbf{R} \sigma} \) is calculated from the different phonon frequencies \( \omega_{\mathbf{q}s} \) through

\[
A^{\mathbf{q}}_{\mathbf{q}s} = \pm \sqrt{\frac{\hbar}{M_s \omega_{\mathbf{q}s}} \left( \frac{1}{2} + n_{\mathbf{q}s} \right)}, \tag{2}
\]

where \( n_{\mathbf{q}s} = n\left(\frac{\omega_{\mathbf{q}s}}{2 k_B T}\right) \), with \( n(x) = 1/(e^x - 1) \), are the phonon occupational numbers, \( M_s \) the atomic masses and \( T \) is the temperature of the system. Thus, due to the anharmonic nature of the force constants, and through the Bose-Einstein occupational factors, \( n_{\mathbf{q}s} \), appearing in the mode amplitudes \( A_{\mathbf{q}s} \), the temperature dependence is introduced to the renormalized phonon frequencies. The phonon frequencies, \( \omega_{\mathbf{q}s} \), are obtained through projecting the Fourier-transformed atomic forces, \( \mathbf{F}_{\mathbf{q}s} \) along the eigenvectors, \( \epsilon^{\mathbf{q}}_{\mathbf{R} \sigma} \), of the phonon modes [12].

Since in the SCAILD scheme, the atomic displacements present in the calculation of the forces, are the results of superpositions of all the commensurate phonon modes (as opposed to displacing the atoms along one single mode, which would correspond to the frozen phonon method), the interaction between different lattice vibrations are taken into account\(^1\) and the phonon frequencies are thus renormalized by the very same interaction. For more details on the SCAILD method we refer to refs. [12–14]. It should be mentioned that we do not consider here the phonon decay processes (see, e.g., ref. [18] and references therein).

The free energy as a function of volume, \( V \), and temperature for the bcc and hcp structures can be calculated through the expression

\[
F(T, V) = U_0(V) + F_{ph}(V, T) + F_{el}(V, T), \tag{3}
\]

where \( U_0 \) is the static ground-state energy of the respective structures at \( T = 0 \) K (i.e. without any phonons excited and temperature excitations of electronic states ), \( F_{ph} \) is the free energy of the phonons and \( F_{el} \) is the free energy of the electrons. The temperature dependent parts of the free energy can be found as

\[
F_{ph}(V, T) + F_{el}(V, T) = \frac{1}{N_I} \sum_{\{\mathbf{U}_R\}} \Delta F^\ast\left(\{\mathbf{U}_R\}, V, T\right),
\]

\[
+ \frac{3}{2} k_B T - T S_{ph}(V, T). \tag{4}
\]

Here \( \Delta F^\ast \) is the change in free energy relative to the ground-state energy \( U_0 \), caused by the phonon-induced atomic displacements described by eq. (1), and thermal excitations of the electronic states. Here it should be noted that included in the term \( \Delta F^\ast \) is also the free energy of the electrons \( F_{el} \). The sum on the right-hand part of eq. (4) is over the \( N_I \) number of different atomic configurations, \( \{\mathbf{U}_R\} \), generated throughout the SCAILD self-consistent run. Since \( \Delta F^\ast \) are calculated at atomic configurations accommodating the different frozen phonon superposition of eq. (1), \( \Delta F^\ast \) not only contains the finite-temperature contribution to the electronic free energy for a given atomic configuration, but also, the potential energy provided by the frozen lattice waves, i.e. the potential energy of the phonons at a particular phonon superposition [19]. The phonon kinetic energy is given by \( 3 k_B T/2 \) per atom which means that atomic motion is considered as classical; typically, temperatures of structural phase transformations are higher than the Debye temperature, thus, this approximation is well justified.

In practice, the sum of the finite-temperature electron free energy and phonon potential energy, \( \Delta F^\ast \), was obtained by calculating the total free energy of the corresponding atomic configuration, \( \{\mathbf{U}_R\} \), using a Fermi-Dirac temperature smearing of the Kohn-Sham occupational numbers [20], and then subtracting the static potential energy \( U_0 \) (here \( U_0 \) is calculated with the tetrahedron method to provide a good reference to the temperature excited electronic states). The number of atomic configurations, \( N_I \), used for each volume and temperature was typically 400.

Another problem is how to calculate the phonon entropy. We will assume that it depends on the phonon occupation numbers \( n_{\mathbf{q}s} \) in the same way as for

---

\(^1\)See eq. (16), p. 890 and the appendix of ref. [13].
noninteracting bosons:

\[ S_{ph} = k_B \sum_{q_s} \left[ (1 + n_{q_s}) \ln (1 + n_{q_s}) - n_{q_s} \ln n_{q_s} \right]. \]  

(5)

This is the only entropy expression consistent with eq. (2), which can be proved in the exact same manner as was done for fermions in the Landau theory of a normal Fermi liquid [21]. Thus the SCAILD scheme, together with a free energy defined through eqs. (4) and (5), constitutes nothing but a theory of a “normal Bose liquid”. Expression (5) can be written in terms of the phonon density of states, \( g(\omega) \), produced by a converged SCAILD calculation, and is given by

\[ TS_{ph}(V,T) = \int_0^\infty d\omega g(\omega,V,T) \hbar \omega \left( n \left( \frac{\hbar \omega}{k_B T} \right) - k_B T \hbar \omega \ln \left( 1 - e^{-\frac{\hbar \omega}{k_B T}} \right) \right). \]  

(6)

Here the phonon frequencies used to calculate the phonon density of states, \( g(\omega) \), are the normal mode configurational mean values

\[ \langle \hbar \omega_{q_s} \rangle = \frac{1}{N_f} \sum_{\{U_{nm}\}} \frac{\delta E_{tot}(\{U_{nm}\},V,T)}{\delta n_{q_s}}. \]  

(7)

It should be stressed that the partitioning of the free energy through eqs. (3), (4) and (6) has been chosen to maximize both the accuracy of the phonon potential energy, which in the form of eq. (4) take into account anharmonicity up to infinite order, and the phonon entropy, which in the form given by eq. (6) is accurate to leading order in anharmonic perturbation theory [22].

The phonon density of states and the corresponding free energies for the hcp and bcc structures were calculated at up to five different temperatures, and at each temperature, SCAILD calculations were performed at up to five different volumes.

As regards the other computational details of the force calculation we used the VASP package [20], within the generalized gradient approximation (GGA). The projector augmented-wave (PAW) potentials required energy cutoffs of 232 eV. The Ti(4s,3d), Zr(4s,4p,5s,4d) and Hf(6s,5d) levels were treated as valence electrons. The \( k \)-point mesh was a \( 5 \times 5 \times 5 \) Monkhorst-Pack grid in the bcc phase calculations. In the hcp phase calculations \( 6 \times 6 \times 6 \) gamma centered mesh was used. In order to include the electron entropy in the calculations, Fermi-Dirac temperature smearing were applied to the Kohn-Sham occupation numbers. The bcc and hcp supercells used were obtained by increasing the bcc primitive cell 4 times and the hcp primitive cell 3 times, along the respective bcc and hcp primitive lattice vectors. The sizes of the supercells where chosen such that to ensure a sufficient decay of the interatomic force constant within the supercell, permitting a proper sampling of the lattice dynamical phase space [23]. For the calculations of the static potential energy, \( U_0 \) in eq. (3), the all-electron full-potential linearized augmented-plane wave (FP-LAPW) package ELK [24] was used within the GGA approximation. This was found necessary to ensure a high accuracy of the zero temperature part of the bcc-hcp energy difference. An energy cutoff of 270 eV together with a \( 24 \times 24 \times 24 \) \( k \)-point mesh and a \( 24 \times 24 \times 15 \) \( k \)-point mesh were used for the bcc and hcp structures, respectively, in these calculations the Methfessel-Paxton integration scheme was used.

Fig. 1: (Color online) In (a), (c) and (e) the calculated free energy of the bcc and hcp phase, in Ti, Zr and Hf, respectively. In (b), (d) and (f) the calculated free-energy difference, \( \Delta F = F_{hcp} - F_{bcc} \), in Ti, Zr and Hf, respectively.
with a 0.2 eV smearing of the Kohn-Sham eigenvalues. It should be noted that the electronic smearing used in the calculations of the static energy, $U_0$, was only introduced in order to achieve faster convergence of the energy with respect to the number of $k$-points, and not introduced on physical grounds, as in the case of the Fermi-Dirac temperature smearing employed in the calculations of $\Delta F^*$. To gauge the error introduced by the utilized 0.2 eV smearing, additional calculations were performed with the same $k$-point mesh but with the much more accurate linear tetrahedron scheme [25]. The energies obtained with the less accurate smearing scheme differed only with $\sim 0.3$ meV, which is two orders of magnitude smaller than the energy of the zero point motion or the electronic entropy at $T = 1100$ K.

Results. – For each temperature the free energy obtained through eq. (4) was fitted to a first-order polynomial in $V$. Then by using these first-order fits together with eq. (3), the total free energy at each temperature was obtained through minimization with respect to volume. In fig. 1(a), (c) and (e), the minimized free energy at each temperature is displayed for the bcc and hcp structure in Ti, Zr and Hf, respectively. In fig. 1(b), (d) and (f) the free-energy difference between the structures is displayed for Ti, Zr and Hf, respectively. Due to the computational intensity involved in the free-energy calculations, only in the case of Ti the free energy was calculated for 5 temperatures, whereas in the case of Zr and Hf, the calculations were limited to two temperatures.

The temperature-driven hcp-to-bcc phase transformation in Ti can be seen to occur at $T \sim 1100$ K, which is reasonably close to the experimentally observed phase transition temperature of 1155 K [26], whereas in Zr and Hf, the transition is predicted to occur at $T \sim 920$ K and $T \sim 1660$ K, respectively. The theoretical estimates of the transition temperature in Zr and Hf, with their respective experimental data of 1135 K and 2015 K [2], do not correspond to experimental data as well as in the case of Ti, however, given that these transition temperatures were achieved by means of interpolating the free-energy difference on a twice as sparse temperature mesh as compared with the temperature mesh employed in the Ti free-energy calculations, and that first-principles calculations (at $T = 0$), with current exchange and correlations functionals, have a problem in resolving energy differences between different crystallographic phases better than $\sim 10$ meV/atom, one may not expect from any first-principles–based theory, like the SCAILD method used here, to reproduce temperature-induced phase transitions with an accuracy better than a few hundred kelvin.

It should be noted here that the presently used free-energy expression differs significantly from the previously used expression from quasi-harmonic theory (e.g. used in ref. [13]) in that it takes into account the anharmonic contributions to the lattice dynamical potential energy without projecting it down on a quasi-harmonic description as in ref. [13]. In fact, using the old free-energy expression together with the first-principles interatomic forces calculated in this work, results in the hcp phase in Ti being $> 90$ meV lower in free energy compared to the free energy of the bcc phase throughout the entire temperature interval 800 K $< T < 1200$ K.

It may also be of interest to mention the importance of the different energy contributions appearing in the present calculations. Here the static potential energy, $U_0$, of the hcp phase was in the order of $\sim 100$ meV lower than the corresponding energy in the bcc phase. The most important contribution to the decrease of the free-energy difference between the two phases at elevated temperatures was the phonon-related free energy, where the bcc phase free energies were of the order $\sim 100$ meV lower compared to the corresponding energies in the hcp phase. The electronic free-energy contribution related to the thermal excitations was one order of magnitude smaller compared to the corresponding phonon contribution.

Fig. 2: The calculated phonon dispersions for Ti in the bcc and hcp phases, here displayed as full drawn curves. In (a) the phonon dispersion for Ti in the bcc phase calculated at the finite temperature $T = 1293$ K, here displayed together with experimental data [26] obtained at the same temperature (down-pointing triangles). In (b) the phonon dispersion of hcp Ti calculated at $T = 0$ K, here displayed together with experimental data [27] measured at $T = 295$ K (filled black circles). In (c) the calculated phonon dispersion for hcp Ti at $T = 1000$ K, here displayed together with experimental data [27] measured at $T = 1054$ K (up-pointing triangles).
Furthermore, to show that the phonon part of the calculation is comparable to experimental data, we here also show in fig. 2, as an example, the calculated Ti phonon dispersions for three representative cases. Apart from the complete absence of imaginary modes in the phonon dispersion of the Ti bcc structure, see fig. 2(a), one of the more striking temperature effects can be seen by studying the low- and high-temperature phonon dispersions of the Ti hcp phase, shown in fig. 2(b), (c). Here the hardening of the high-frequency mode between the \( \Gamma \) and \( A \) high-symmetry points, as well as between the \( \Gamma \) and \( M \) symmetry points, is captured, resulting in an increased splitting between the longitudinal and transverse optic modes, not only along the [001] direction, but also along the [100] direction close to the \( \Gamma \) point, as the temperature is increased to 1000 K, which is also the observation made in experiment.

**Conclusion.** – In summary, we introduce here an expression for the free energy which is applicable also for highly anharmonic crystals. The free-energy expression can readily be interfaced with lattice dynamic methods, for instance the SCAILD technique, and we show that the temperature-induced hcp \( \rightarrow \) bcc transition of Ti, Zr and Hf can be reproduced by theory. Theory puts the transition temperature in Ti, Zr and Hf to 1100 K, 920 K and 1660 K, respectively.

***

We would like to thank the Swedish National Infrastructure for Computing (SNIC) for the allocation of computational time at NSC, HPC2N and C3SE that made this work possible. Support from VR, ERC (grant 247062 - ASD), the KAW foundation and ESSENCE is acknowledged.

REFERENCES

[1] Otsuka K. and Wayman C. M. (Editors), *Shape Memory Materials* (Cambridge University Press, Cambridge) 1998.

[2] Petry W., *Phase Transitions*, 31 (1991) 119.

[3] Cahn R. W. and Haasen P. (Editors), *Physical Metallurgy* (North Holland, Amsterdam) 1996.

[4] Fisher E. S. and Renken C. J., *Phys. Rev.*, 135 (1964) A482.

[5] Hennig R. G., Lenosky T. J., Trinkle D. R., Rudin S. P. and Wilkins J. W., *Phys. Rev. B*, 78 (2008) 054121.

[6] Chureeart J. and Pinsook U., *J. Sci. Res. Chula. Univ.*, 31 (2006) 27.

[7] Persson K., Ekman M. and Ozolinš V., *Phys. Rev. B*, 61 (2000) 11221.

[8] Moroni E. G., Grimvall G. and Jarlbo T., *Phys. Rev. Lett.*, 76 (1996) 2758.

[9] Lenosky T. J., Sadigh B., Alonso E., Bulatov V. V., de La Rubia T. D., Kim J., Voter A. F. and Kress J. D., *Model. Simul. Mater. Sci. Eng.*, 8 (2000) 825.

[10] Katsnelson M. I., *Encyclopedia of Condensed Matter Physics*, edited by Bassani G. F., Liedl G. L. and Wyder P. (Elsevier, Amsterdam) 2005, p. 77.

[11] Car R. and Parrinello M., *Phys. Rev. Lett.*, 55 (1985) 2471.

[12] Souvatzis P., Eriksson O., Katsnelson M. I. and Rudin S. P., *Phys. Rev. Lett.*, 100 (2008) 095901.

[13] Souvatzis P., Eriksson O., Katsnelson M. I. and Rudin S. P., *Comput. Mater. Sci.*, 44 (2009) 888.

[14] Souvatzis P. and Rudin S. P., *Phys. Rev. B*, 78 (2008) 184304.

[15] Souvatzis P., Björckm T., Eriksson O., Andersson P., Katsnelson M. I. and Rudin S. P., *J. Phys.: Condens. Matter*, 21 (2009) 175402.

[16] Luo W., Johansson B., Eriksson O., Arapian S., Souvatzis P., Katsnelson M. I. and Ahuja R., *Proc. Natl. Acad. Sci. U.S.A.*, 107 (2010) 9962.

[17] Harmon B. N., Weber W. and Hamann D. R., *Phys. Rev. B*, 25 (1982) 1109.

[18] Katsnelson M. I., Trefilov A. V., Khlopkin M. N. and Khromov K. Yu., *Philos. Mag. B*, 81 (2001) 1893.

[19] Arapan S., PhD Thesis (Uppsala University, Uppsala) 2008.

[20] Kresse G. and Furthmuller J., *Phys. Rev. B*, 54 (1996) 11169.

[21] Landau L. D., *Zh. Eksp. Teor. Fiz.*, 30 (1956) 1058.

[22] Cochran W. and Cowley R. A., *Handbook der Physik* (Springer-Verlag, Berlin) 1967.

[23] Souvatzis P., Delin A. and Eriksson O., *Phys. Rev. B*, 73 (2006) 054110.

[24] The ELK code can be found at the web address: http://elk.sourceforge.net/.

[25] Jepsen O. and Andersen O. K., *Solid State Commun.*, 9 (1971) 1763.

[26] Petry W., Heiming A., Trampenau J., Alba M., Herzig C., Schober H. R. and Vogl G., *Phys. Rev. B*, 43 (1991) 10933.

[27] Stassis C., Arch D., Harmon B. N. and Wakabayashi N., *Phys. Rev. B*, 19 (1979) 181.