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Landau free energy for a bcc-hcp reconstructive phase transformation

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We study the bcc-hcp phase transition in Ti and Zr with the use of first-principles calculations. We have determined the complete energy surface from the bcc to hcp structure. The results are used to find an appropriate Landau free energy density for describing this transformation. The proposed Landau free energy density has two relevant order parameters: shear and shuffle. Through first-principles calculations, we show that the bcc structure is unstable with respect to the shuffle of atoms (TA_1 N-point phonon) rather than the shear. Therefore, we reduce the two order parameter Landau free energy to an effective one order parameter (shuffle) potential, which is a reasonable approximation. In general, the effective Landau free energy is a triple-well potential. From the phonon dispersion data and the change in entropy at the transition temperature we find the free energy coefficients for Ti and Zr.

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I. INTRODUCTION

The bcc-hcp transformation, together with the bcc-fcc transformation, are the most commonly encountered types of reconstructive transformations in crystals of elements. They are found in about twenty elements, such as Sc, Y, Ti, Zr, Hf, Fe, and Tl as well as in their alloys. There is no group-subgroup relationship between the space groups of the two crystal phases in these transformations. The mechanism generally assumed for the bcc-hcp transformation is the so-called Burgers mechanism[1] that first established the crystallographic relationship between the bcc and hcp structures:

$$(110)_{\mathrm{bcc}} \| (0001)_{\mathrm{hcp}} \quad \text{and} \quad [\bar{1}11]_{\mathrm{bcc}} \| [\bar{2}110]_{\mathrm{hcp}}.$$

This transformation can be achieved by the superposition of two lattice distortions: (i) The transverse $TA_1 1/2(110)$ (i.e., N-point) phonon with $[\bar{1}10]$ polarization, which displaces neighboring (110) planes in $[\bar{1}10]$ direction. An amplitude of $\delta = a\sqrt{2}/12$ (where a is the bcc lattice constant) is required to achieve the correct stacking sequence of the hcp phase. We refer to this type of displacement as *shuffle*, i.e., atoms move by a fraction of the lattice constant.[2,3] (ii) Two equivalent long wavelength shears, such as the $(1\bar{1}\bar{2})$ $[\bar{1}11]$ and $(\bar{1}12)[1\bar{1}\bar{1}]$, squeeze the bcc octahedron into a regular hcp one, thereby changing the angle from 109.47° to 120° (or equivalently, 70.53° to 60°) in the basal plane. The corresponding shear modulus is approximately given by the initial slope of the transverse $TA_1[\xi\xi 2\xi]$ phonon branch with (approximately) $[11\bar{1}]$ polarization.

This transformation mechanism has been described by Lindgard and Mouritsen[2] (LM) in terms of a Landau free-energy (LFE) expansion with respect to two order parameters (OP's), representing shuffles and shears. By eliminating the shear through a minimization they obtained an effective triple-well LFE (ϕ^6 model) in terms of a single primary OP (shuffle), which is in agreement with other approaches[3] for finding the appropriate Landau free-energy for this type of transformation.

This model was experimentally confirmed for Ti,[4] Zr,[5] and Hf.[6] In these cases a low lying TA_1 N-point mode was found that (for Ti and Zr) clearly shows (albeit only partial) softening; however, no (or negligibly small) softening of the elastic constant associated with the $[111]/[11\bar{1}]$ TA_1 phonon branch was observed for Ti and Zr, respectively.[4,5] Because partial softening is sufficient[7] for first order displacive transformations, the bcc-hcp transformation may be considered an improper ferroelastic transformation.

In the Landau theory of phase transitions the free energy is a function that must be invariant under the symmetry group of the high-temperature (parent) phase. Because of a group-subgroup relationship between the high and low temperature phases, the free energy is also invariant under the symmetry group of the low-temperature (product) phase. Therefore in the absence of group-subgroup relationships, which is the case for reconstructive phase transformations such as bcc to hcp, an explanation of the LFE of the system in terms of the symmetry of only one phase entails a more careful examination.

An alternative is to consider a LFE with two (or more) relevant order parameters as studied by Lindgard and Mouritsen.[2] Although the effective Landau free-energy density of LM is in agreement with other one-dimensional models, there has been no serious attempt to prove the validity of the two order-parameter LFE density. In particular, LM considered only the lowest possible coupling term between the order parameters and the importance of higher order coupling terms was neglected.

In this work we attempt to investigate the validity of the Lindgard-Mouritsen Landau free-energy density by using a first-principles method. We will show that the higher-order coupling terms are necessary for improving the fit between the LFE and first-principles calculations. By minimizing the new improved LFE density with respect to the shear order parameter we can still obtain an effective LFE in terms of the shuffle order parameter.

The paper is organized as follows. In the next section we briefly present the first-principles results. In Sec. III we first add higher order shuffle-shear coupling terms, obtain an effective free energy in the shuffle OP, and then determine coefficients of the Landau-Ginzburg free energy for titanium and zirconium based on electronic structure calculations and experimental data. Finally we summarize our findings in Sec. IV.

II. FIRST-PRINCIPLES CALCULATIONS

We have used a full-potential linear muffin-tin orbital technique[8,9] in the calculations reported here. The calculations were scalar relativistic (i.e., the Darwin term and relativistic corrections to the kinetic energy were included but not spin-orbit term) and employed no shape approximation to the charge density or potential. The electron core was treated fully relativistically and recalculated in each iteration. The base geometry was a muffin-tin geometry with nonoverlapping muffin-tin spheres; the basis function, charge density and potential were expanded in a spherical harmonic series within the muffin tins and in Fourier series in the interstitial region. The basis set was comprised of augmented linear muffin-tin orbitals.[10,11] The tails of the basis functions (the extension of the bases outside their parent spheres) were either Hankel or Neuman functions with nonzero kinetic energy. Four different tails were used in these calculations. Spherical-harmonic expansions were carried out up to $l=8$ for the bases, charge density, and potential. For sampling the Brillouin zone we used the special **k**-point method,[12,13] 1008 **k** points for a unit cell with 2 atoms. For calculating the ground-state energies, in addition to using the special **k**-point technique, in order to speed up the convergence of the **k**-point sampling we associated each calculated eigenvalue with a Gaussian function having a width of about 5 mRy. Finally, the calculations used a gradient-corrected functional, i.e., generalized gradient approximation (GGA), for exchange and correlation terms.[14] A very preliminary account of these results was reported earlier.[15]

TABLE I. Comparison between calculated and experimental (Refs. 4 and 5) equilibrium bcc lattice parameters and bulk moduli for different elements at zero temperature.

bcc structure	Lattice constant (calc. Å)	Lattice constant (expt. Å)	Bulk modulus (calc. GPa)	Bulk modulus (expt. GPa)
Ti	3.244	3.263	110.6	118.0
Zr	3.568	3.574	90.4	96.7

The lattice constants used in our first-principles calculations correspond to the theoretical equilibrium values. Calculated theoretical bcc lattice constants for Ti and Zr are 3.244 and 3.568 Å. Temperature-dependent lattice parameters of bcc-Ti,[4] $a(T)=3.308[1+1.555\times10^{-5}(T(\mathrm{K})-1155)]$, and bcc-Zr,[5] $a(T)=3.574+3.37\times10^{-5}T(\mathrm{K})$ Å, give lattice constants equal to 3.263 and 3.574 Å, respectively at $T=0$ K, where our first-principles calculations are valid. Comparison between the experimental and theoretical lattice constants and bulk modulus are shown in Table I.

To obtain the bcc-hcp phase transformation path, we calculated the total energy of the crystal as a function of the TA_1 N-point phonon atomic displacements (shuffle) and the angle of the shear motion, for 121 different points in the shuffle-shear plane. The complete energy surfaces for the bcc to hcp structure are shown in Fig. 1. The contour plot of the calculated total energies is shown in Fig. 2. The darker area indicates regions with lower energies. In our calculations hcp energy is not a global minimum, since the volume of the different structures were kept constant during the calculations. The energy-surface results show that the bcc structure is completely stable with respect to a pure shear transformation. However, frozen-phonon calculations for evaluating the frequency of the TA_1 N-point phonon predict that this mode is unstable for small displacements and the bcc structure therefore has a tendency toward the hcp phase transformation for both Ti and Zr. Instability of the N-point phonon in the case of Zr is also confirmed by other first-principles methods.[16]

III. LANDAU FREE ENERGY DENSITY

A. Higher-order coupling terms

The LFE for the bcc-hcp phase transformation suggested by Lindgard and Mouritsen[2] has two scalar order parameters: η (shuffle) and ε (shear),

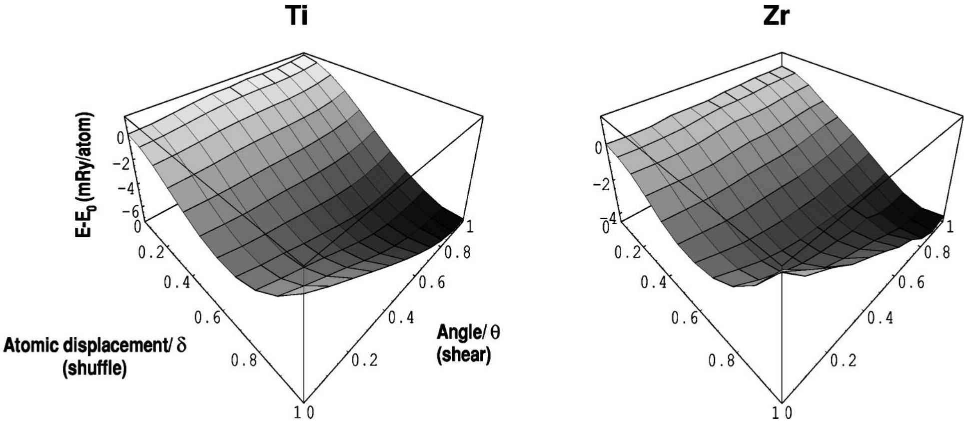

FIG. 1. Energy surfaces for Ti and Zr. E_0 corresponds to the bcc structure of each element. Units of atomic displacement and angle are $\delta=a\sqrt{2}/12$ and $\theta=10.53°$, respectively.

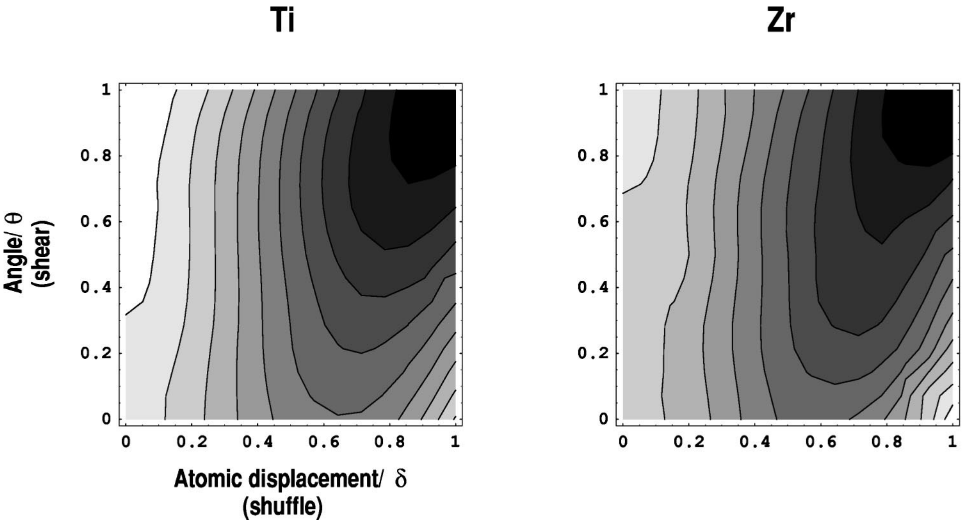

FIG. 2. Energy contour plot for Ti and Zr. Regions with lower energy are darker. Units of atomic displacement and angle are $\delta = a\sqrt{2}/12$ and $\theta = 10.53°$, respectively.

$$F_{\mathrm{LM}} = \frac{A}{2}\eta^2 + \frac{B}{4}\eta^4 + \frac{C}{6}\eta^6 + \frac{A_1}{2}\varepsilon^2 + \frac{B_1}{4}\varepsilon^4 + C_1\varepsilon\eta^2. \quad (1)$$

The C_1 term couples the uniform strain (shear) with two internal strains (shuffle). The anharmonic terms are not expected to vary rapidly with temperature near T_M (the transition temperature). In an attempt to investigate the validity of the LFE, we have tried to fit the first-principles results to the LFE given by Eq. (1). The basic idea of the fit is to take the LM free energy, and try to find a least-squares fit to the first-principles data. The results of these fits are shown in Fig. 3. These fits show that the LFE density proposed by Lindgard and Mouritsen,[2] Eq. (1), is not a good fit to the first-principles results and it overestimates the stability region of the bcc and hcp structures. In particular, for the beginning and the end of the transformation this LFE tends to minimize the effects of the shuffle OP. Therefore, reducing the LFE to an effective free energy may also be questionable. To find a better fit to the first-principles results we modified the LFE density by (i) considering the effect of linear combinations of higher-order coupling terms and (ii) eliminating higher order terms in shear (e.g., ε^4, ε^6, and the symmetry allowed coupling term $\eta^2\varepsilon^4$). The latter is easily justified from the results of first-principles calculations. Figure 1 shows that the energy of structures varies fairly smoothly with shearing of atoms. Therefore higher order shear terms, ε^4 and ε^6, as well as $\eta^2\varepsilon^4$ are not necessary. Our experience with different terms showed that to achieve a better fit it is best to use a LFE density consisting of two order parameters given by

$$F_L = \frac{A}{2}\eta^2 + \frac{B}{4}\eta^4 + \frac{C}{6}\eta^6 + \frac{A_1}{2}\varepsilon^2 + (C_1\eta^2 + C_2\eta^4)\varepsilon + \left(\frac{C_3}{2}\eta^2 + \frac{C_4}{2}\eta^4\right)\varepsilon^2. \quad (2)$$

The F_L is a two-variable polynomial of sixth order. Presence of the higher-order terms (more than six) did not modify the results, and their effects were therefore ignored. Figure 4 depicts the results of the fit of Eq. (2) to the data.

The goodness of fit is measured by the quantity $\kappa^2 = \Sigma_i(E_i - F_i)^2$, where E_i is the electronic structure energy of ith data point, and F_i is the value obtained from the fit. The best fit is the one which minimizes κ^2. Table II shows the comparison between the LM and modified Landau free en-

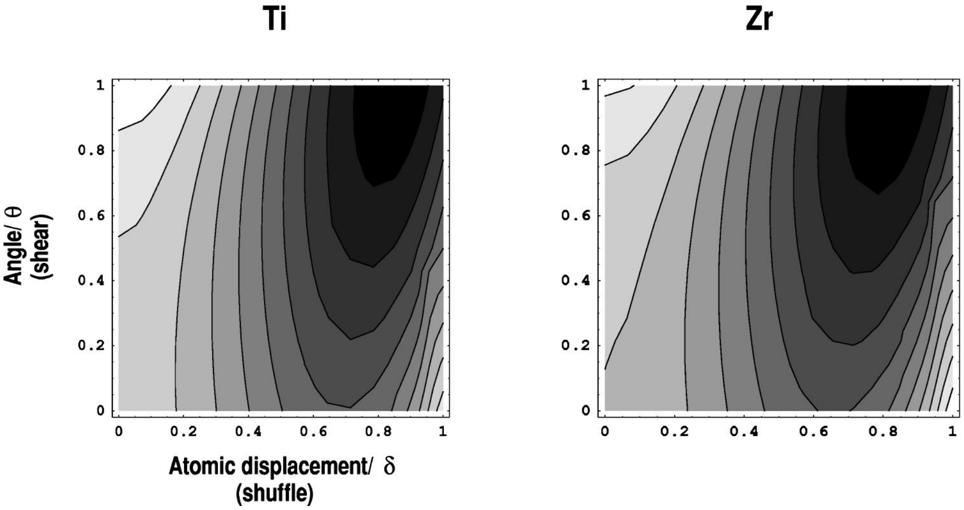

FIG. 3. Energy contour plot of the Lindgard-Mouritsen LFE fitted to first-principles calculations. Regions with lower energy are darker. Units of atomic displacement and angle are $\delta = a\sqrt{2}/12$ and $\theta = 10.53°$, respectively.

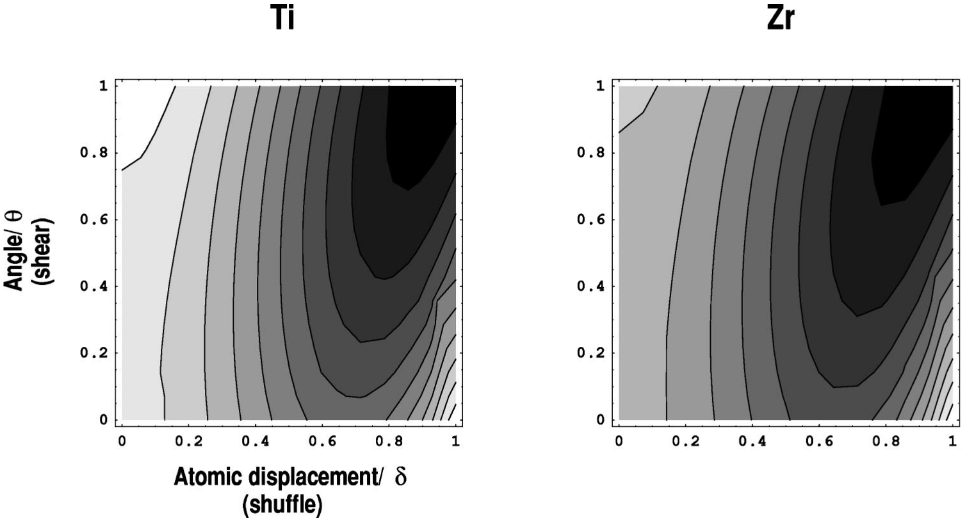

FIG. 4. Energy contour-plot fit of the modified LFE fitted to first-principles calculations. Regions with lower energy are darker. Units of atomic displacement and angle are $\delta = a\sqrt{2}/12$ and $\theta = 10.53°$, respectively.

ergies. Calculated κ^2 values confirmed that our modified LFE is a better fit to the first-principles data. In Fig. 5 the goodness of fit between electronic structure and fitted free energies (LM and modified) is shown. For a perfect fit one expects to see a plane (for $E-F=0$) and any deviation from this plane shows the region and extent of misfit between electronic structure and free energies. A comparison of fitted contour plots (Figs. 2, 3, and 4) and Fig. 5 confirms our previous assertion that the LM free energy overestimates stability of the bcc, hcp (and intermediate) structures, and the modified free energy [Eq. (2)] improves the fit in all of the shear-shuffle regions for Ti and Zr. In a separate approach we investigated the effect of the ε^4 term on LM and modified Landau free energies. For the LM free energy the fit to electronic structure calculations improved without the ε^4 term. With the ε^4 term the fit to the modified free energy did not improve and we found the value of the calculated coefficient to be very small. This further corroborates our omission of terms of the fourth order in shear in Eq. (2). Table III lists the coefficients of the modified free energy obtained by a fit to electronic structure data.

It is possible to use a simple mechanical analog to understand Fig. 4. If we consider the modified Landau free energy (F_L) as a classical ''potential,'' then the bcc-hcp phase transformation can be interpreted as the motion of a particle in this classical potential. Figure 6 shows a plot of gradient field of energy obtained from the first-principles calculations (Fig. 2). The length of the arrows represents the magnitude of the vector at that point, and the direction of the arrow represents the direction of the field at that point. These vector fields provide some understanding of the most probable path chosen by the system to transform from the bcc phase to hcp one (at zero temperature). According to Hamilton's principle the correct path of motion of a particle can be found from a variation of the action integral. In other words by solving equations obtained from equilibrium conditions, $\partial F_L/\partial\varepsilon = 0$ and $\partial F_L/\partial\eta = 0$, one can find the actual path of the phase transformation.

TABLE II. Goodness of fit, $\kappa^2 = \Sigma_i (E_i - F_i)^2$, for Ti and Zr.

LFE	κ^2 (Ti)	κ^2 (Zr)
LM	44.2	23.7
Modified	16.2	6.2

The energy surfaces of Ti and Zr show an instability of the bcc structure with respect to the shuffle OP. Therefore, to reduce the LFE from two order parameters to an effective LFE in terms of one order parameter, we can minimize the LFE with respect to the shear order parameter (ε)

$$\frac{\partial F_L}{\partial \varepsilon} = (C_1\eta^2 + C_2\eta^4) + (A_1 + C_3\eta^2 + C_4\eta^4)\varepsilon = 0. \quad (3)$$

In a first approximation, if we expand ε in terms of the shuffle OP (η), we obtain

$$\varepsilon \approx -\frac{C_1}{A_1}\eta^2 + \left(-\frac{C_2}{A_1} + \frac{C_1 C_3}{A_1^2}\right)\eta^4 + O(\eta^6). \quad (4)$$

Equation (4) suggests that the lowest free-energy path between the bcc-hcp structures occurs in the shuffle (η)-shear (ε) plane along a valley with a minimum and a saddle point along the path. By replacing the value obtained for ε [Eq. (4)] in Eq. (2) one can obtain an effective LFE

$$F_{\text{eff}} = \frac{A}{2}\eta^2 + \frac{B^*}{4}\eta^4 + \frac{C^*}{6}\eta^6, \quad (5)$$

where

$$B^* = B - \frac{2C_1^2}{A_1}, \quad C^* = \frac{C}{6} - \frac{C_1 C_2}{A_1} + \frac{C_1^2 C_3}{2A_1^2}. \quad (6)$$

For $B^* < 0$ and $C^* > 0$ this effective LFE describes a first-order phase transformation if the harmonic coefficient A has a positive temperature coefficient. The effective LFE describes the different stages of the phase transformation for different values of coefficients.[17,18]

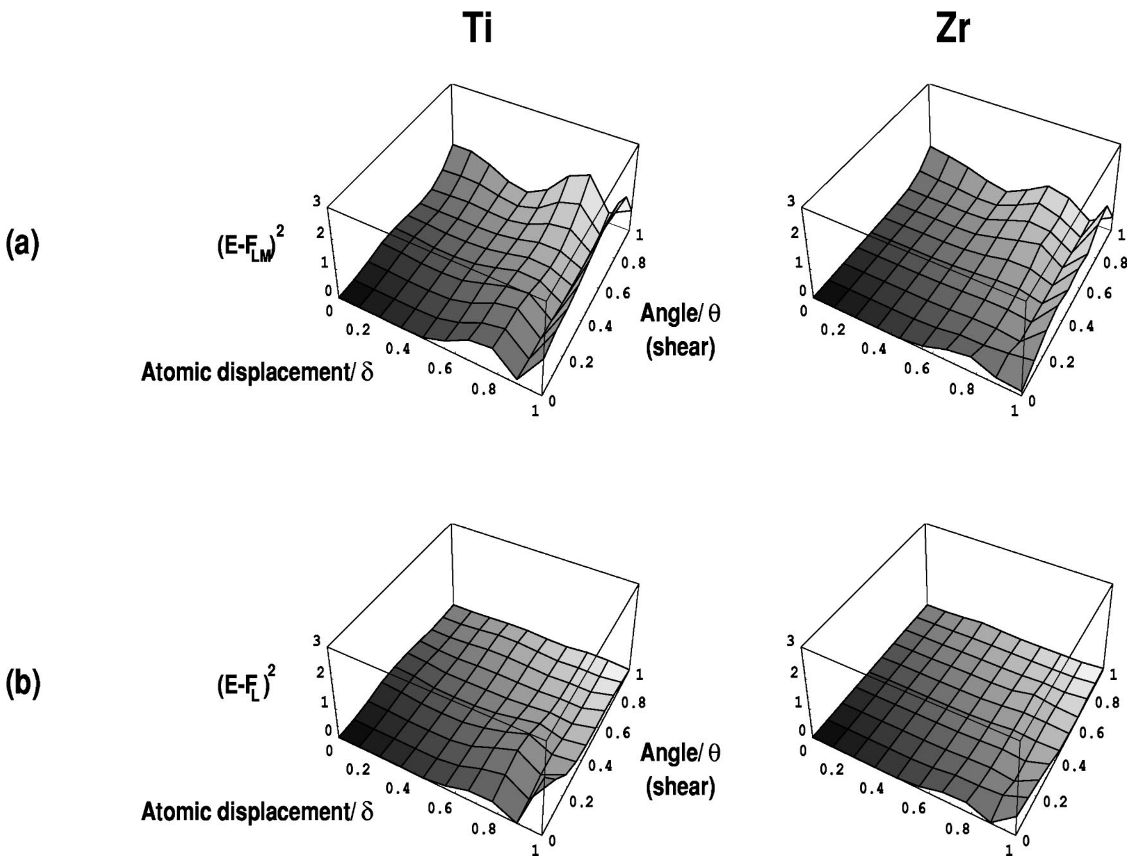

FIG. 5. Goodness of fit for LM free energy (a) and modified free energy (b) for Ti and Zr.

B. Effective Landau free energy parameters

One advantage of the reduction of the LFE [Eq. (2)] to an effective one order parameter is that the LFE coefficients can be found by using experimental data such as the change of entropy at the transition temperature and the phonon dispersion of the high-temperature bcc phase. In this way we include the effect of vibrational entropy in free energy which is absent in first-principles calculations. In the Landau theory of phase transitions, the coefficient of the second-order term is usually assumed to be temperature dependent.[19] Near the transition temperature this dependency is assumed to be linear. Therefore one can rewrite the effective LFE as

$$F_{\text{eff}}=\frac{A_0(T-T_0)}{2}\,\eta^2+\frac{B^*}{4}\,\eta^4+\frac{C^*}{6}\,\eta^6, \tag{7}$$

where T_0 is the temperature at which complete phonon softening would occur. However, since the bcc-hcp transformation is first order, the softening of the phonon (soft mode) is not complete, and the phase transition occurs at a temperature T_M higher than T_0. By minimizing the effective LFE at the transition temperature one can find the values of the order parameters and a relation between the LFE coefficients and transition temperature T_M:

$$\eta=0, \quad \eta=\pm\sqrt{\frac{3|B^*|}{4C^*}}; \quad \frac{C^*A_0(T_M-T_0)}{B^{*2}}=\frac{3}{16}. \tag{8}$$

At the transition temperature the effective LFE has three degenerate minima and the two different phases (bcc and hcp) coexist. The zero order parameter value refers to the high-temperature bcc structure and the two nonzero order parameter values correspond to the (two degenerate) hcp structures, since Eq. (4) allows shuffle order parameters with different signs related to the same shear order parameter. Also, the entropy change of the system at the transition temperature is given by

TABLE III. Landau free energy density [Eq. (2)] coefficients for Ti and Zr.

Element	A $\left(\frac{\text{J}}{\text{m}^5}\right)$ $\times 10^{30}$	B $\left(\frac{\text{J}}{\text{m}^7}\right)$ $\times 10^{51}$	C $\left(\frac{\text{J}}{\text{m}^9}\right)$ $\times 10^{64}$	A_1 $\left(\frac{\text{J}}{\text{m}^3\text{rad}^2}\right)$ $\times 10^{9}$	C_1 $\left(\frac{\text{J}}{\text{m}^5\text{rad}}\right)$ $\times 10^{30}$	C_2 $\left(\frac{\text{J}}{\text{m}^7\text{rad}}\right)$ $\times 10^{50}$	C_3 $\left(\frac{\text{J}}{\text{m}^5\text{rad}^2}\right)$ $\times 10^{31}$	C_4 $\left(\frac{\text{J}}{\text{m}^7\text{rad}^2}\right)$ $\times 10^{52}$
Ti	−2.9	4.3	4.7	8.1	−5.3	−6.4	4.7	−2.0
Zr	−1.2	1.7	1.4	3.1	−2.0	−5.2	2.4	−8.5

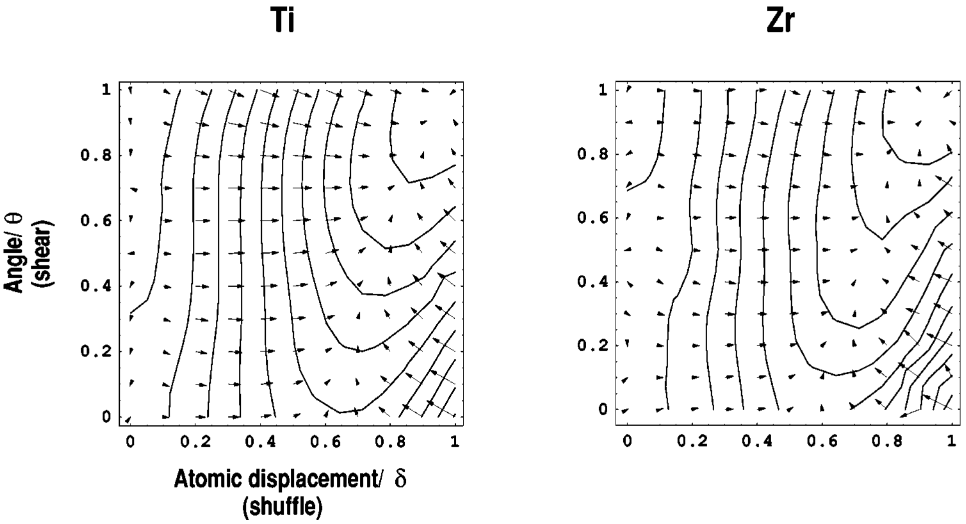

FIG. 6. Energy contour plot of first-principles calculations and gradient of energy field. The length and direction of arrows represent magnitude and direction of the field at that point, respectively.

$$\triangle S=-\frac{3A_0|B^*|}{8C^*}. \tag{9}$$

To identify other coefficients we need the phonon dispersion data of the material measured for at least two different temperatures. The phonon dispersion relation in the linearized form (small wave vectors or long wavelength limit) is related to the Ginzburg-Landau parameters. When the wave vector k differs slightly from TA_1 N-point wave vector (k_N); the phonon dispersion relation is given by[20,21]

$$\rho_0\omega^2=A_0(T-T_0)+G|k_N-k|^2, \tag{10}$$

where ρ_0 is the mass density of the material and G is the coefficient of the shuffle gradient, $(\nabla\eta)^2$, i.e., the Ginzburg term.

The phonon dispersion data and value of the entropy changes for Ti and Zr give us enough information to calculate the free energy coefficients for these elements. Corresponding effective LFE density parameters are shown in Table IV. It is interesting to mention that complete phonon softening would occur at a finite temperature (T_0). In other words the bcc structure of Ti and Zr is unstable at $T=0$ K, which confirms the results of our frozen-phonon calculations.

Note that if we calculate the values of B^* and C^* using Table III and Eq. (6) we find $B^*=-2.6\times10^{51}$, $C^*=9.6\times10^{72}$ for Ti and $B^*=-1.0\times10^{51}$, $C^*=4.8\times10^{72}$ for Zr. Clearly, these are different from the values given in Table IV. However, this is not surprising given the difference between experimental data and first-principles calculations. In addition to our approximation in Eq. (4), the effect of vibrational entropy as well as possible (weak) temperature dependence of B^* and C^* may account for this discrepancy.

IV. CONCLUSION

We have presented a LFE density that explains the bcc-hcp phase transformation in Ti and Zr. Using first-principles calculations we have shown that the static bcc structure is unstable with respect to a shuffling of the atoms, but that (as shown in[22] for Zr) at high temperatures it is mechanically stabilized by anharmonic phonon-phonon interactions, and thermodynamically stabilized by its larger vibrational entropy relative to the hcp phase. We showed that the effect of higher-order coupling terms between order parameters is very important. In an attempt to simplify the LFE density, we have eliminated the shear order parameter by minimizing the LFE with respect to this order parameter.

By calculating the free energy density coefficients from the phonon dispersion data and the change of entropy at the transition temperature we find theoretical values for the LFE parameters. If we augment the effective LFE [Eq. (7)] with a shuffle gradient $G(\nabla\eta)^2/2$ term, we can employ the above parameter values for calculating the domain wall (between bcc-hcp and the the two hcp variants) energy and width for these elements.[15,17,18,21] The gradient coefficient G can be determined either from the phonon dispersion data (near the N-point) or from a direct observation of the domain wall width using high-resolution electron microscopy (HREM).

Because the space group of the hcp structure ($P6_3/mmc$) is not a subgroup of the space group of the bcc structure ($Im\overline{3}m$), and because the [112] TA_1 mode in the long wave length limit is not a pure mode,[23] numerical application to a specific material would require extension of the present (simplified) model, i.e., it would have to be based on the full LFE for the six-component primary OP pertaining to the TA_1 N-point mode,[24] and it would have to include coupling terms between the primary OP and all six components of the strain tensor, and (probably) also higher-order terms in the elastic energy.[25] Indeed, preliminary results on the full LFE based on a six-component shuffle OP and strain[24] indicate that it reduces to Eq. (2) in the appropriate limit.

TABLE IV. Effective Landau free energy density [Eq. (5)] parameters for Ti and Zr.

Element	T_0 (K)	A_0 (J/m^{5}K)	B^* (J/m^7)	C^* (J/m^9)
Ti	484.4	6.3×10^{26}	-1.7×10^{51}	1.2×10^{72}
Zr	357.5	1.1×10^{26}	-1.1×10^{51}	7.1×10^{71}

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