PHASE TRANSITIONS AND STABILITY
OF GROUP IV BCC METALS

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Born stability criteria were employed in the framework of extended generalised exponential potential to calculate the theoretical strength and range of stability of a perfect uniaxially stressed crystal lattice of group IV bcc metals: titanium, zirconium, and hafnium. The analysis depicts two ranges of stability, a bcc phase and a body centered tetragonal phase. The computed value of theoretical strength and strain of bcc Ti, Zr and Hf agree satisfactorily with the experimental limits. The second-order elastic constants C_{11} and C_{12} were also computed.

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1. Introduction

The phase transitions in high-temperature superconductors (HTS) as well as in metals of bcc and fcc configuration have assumed interesting and significant dimensions in the theoretical and experimental fields. It has been established by Abrikosov et al. [1] that the twinning in high-temperature superconductors is due to the phase transition from the tetragonal to orthorhombic structure and the twinning planes usually form periodic structure with the distance [2] between twinning planes in the range 200–2000 Å. Also, there are many strong evidences [3–12] that the elastic and lattice dynamical properties of high-temperature superconductors are considerably affected by phase transitions from tetragonal to orthorhombic structure. Encouraged by these studies, we have been motivated to undertake the study of elastic behaviour during phase transitions initially from cubic to tetragonal structure and the stability of the metals of bcc origin. The study can later be extended for phase transitions from tetragonal to orthorhombic structure.

Many authors [13] have estimated the theoretical or ideal strength of perfect crystals using a variety of theoretical models. In fact, ideal strength means the theoretical upper limit to the maximum applied stress of a particular nature on a perfect specimen of the material before it becomes mechanically unstable [14]. Since a perfect crystal lattice is homogeneous throughout, it cannot become mechanically unstable till the system lowers its total energy by spontaneously undergoing uniform deformations, usually called twinning or nucleation [1, 15].

Taylor [16] and Wassermann [17] have shown that the strength of crystals may be increased many times when their size is made sufficiently small. Further, the problem of determining the ideal strength of a perfect crystal is of fundamental importance because it is thought that the strength of some metallic whiskers or fine filaments approach the theoretical limit. In addition, the problem of calculating the theoretical strength of perfect crystals is relevant to our understanding of many phenomena occurring in solid state physics such as deformation of whiskers, martensitic transformation, efficiency of grinding processes and mechanical properties of small structures such as metallized integrated circuit structures.

Because of numerous applications of the problem of theoretical strength of solids and widespread interest in whiskers and their impact on modern theory of solids, many workers [18] have studied this problem of theoretical strength both for undeformed and deformed crystal lattices with various modes of deformations and with various forms of interactions between the atoms. Recently, Singh [19] has computed theoretical strength of noble metals in [100] direction by using a pseudopotential approach and has made a rigorous estimation of binding energy. Needless to say our present knowledge of interatomic interactions in solids is still handicapped by many constraints and therefore an accurate quantitative calculation of the theoretical strength for most of the solids is hardly tractable. Even though, by using pseudopotential models or more simplified model potentials, it has been attempted to gain semiquantitative information about the theoretical strength and range of stability for some crystalline solids [19, 20].

The purpose of the present communication is to apply Born stability criteria [1] using the extended generalised exponential potential (EGEP) to the problem involving any kind of lattice deformation, that is, either homogeneous expansion or contraction and interpret the results of detailed numerical computations carried out for bcc titanium (Ti), zirconium (Zr) and hafnium (Hf). The theoretical strength and range of stability of bcc metals namely V, Nb and Ta of group VA of periodic table have recently been computed [20] successfully in the framework of present potential. The presently computed values of theoretical strength and strain for bcc Ti, Zr and Hf agree reasonably well with the experimental limits.

2. Theory

2.1. Extended generalised exponential potential

The extended generalised exponential potential representing the true and realistic nature of the repulsive as well as the attractive components of the interactions coupling the i-th and j-th atoms separated by a distance r_{ij} assumes the form

$$\Phi_m(r_{ij}) = [D/(m-1)][e^{-m\alpha(r_{ij}-r_0)}/(\alpha r_{ij})^n - m(\alpha r_{ij})^n e^{-\alpha(r_{ij}-r_0)}], \qquad (1)$$

where m and n are the parameters which take care of electronic exchange and correlation effects and the three-body forces such as volume forces in an alternative and simpler form, respectively. D and α are parameters with dimensions of energy and $(distance)^{-1}$ respectively, such that D is depth parameter and stands for dissociation energy of the pair and α, the width parameter, is a measure of the hardness of the potential. Finally, r_0 stands for the equilibrium separation parameter.

The details concerning the evaluation of the parameters of the potential are discussed in our earlier paper [21]. The input data for bcc metals studied and their computed potential parameters are given in Table I and Table II, respectively.

TABLE I

Input data for bcc metals.

Metal	Semi-lattice constant $[\times 10^{-10}$ m]	Bulk modulus $[\times 10^{11}$ N/m$^2]$
Ti	1.664	1.180
Zr	1.812	0.870
Hf	1.805	1.123

TABLE II

Computed potential parameters for bcc metals.

Met.	n	m	αa_0	$\alpha \times 10^{10}$ m^{-1}	β	$D \times 10^{-21}$ J	$r_0 \times 10^{-10}$ m
Ti	1	2.0	1.87350	1.125901	465.7123	1.257433	5.456577
Zr	1	1.5	1.78080	0.982781	4878.8660	0.110512	8.641461
Hf	2	1.5	2.04445	1.132659	1761365.0000	0.000083	12.697200

2.2. Theoretical considerations

The necessary and sufficient conditions for a lattice to be in stable equilibrium, as has been discussed in considerable detail by Milstein [18], under the effect of uniaxial stress in [100] direction in terms of Born stability criteria take the form

$$B_{11} > 0, \quad B_{22} > 0, \quad B_{12} > 0, \quad B_{23} > 0, \tag{2}$$

$$AA = B_{22} - B_{23} > 0, \tag{3}$$

$$BB = B_{11}(B_{22} + B_{23}) - 2(B_{12})^2 > 0. \tag{4}$$

The moduli B_{ij}, internal energy (E) per unit cell and the stress acting normal to the face of the unit cell in the direction a_1 are represented by the following equations:

$$B_{ij} = \left[\frac{\partial^2 E}{\partial a_i \partial a_j} \right], \tag{5}$$

$$E = (1/2)n' \sum_{l_1 l_2 l_3} \phi(r), \tag{6}$$

$$\sigma = \frac{1}{a_2 a_3} \left[\frac{\partial E}{\partial a_1} \right], \tag{7}$$

where i and j have their values ranging from 1 to 6 and n' is the number of atoms per unit cell. Also a_1, a_2 and a_3 refer to semi-lattice constants and a_4, a_5 and a_6 are the angles between a_2 and a_3, a_3 and a_1; a_1 and a_2, respectively, and for a tetragonal crystal lattice

$$a_2 = a_3 \quad \text{and} \quad a_4 = a_5 = a_6 = \pi/2, \tag{8}$$

$$r = \left[l_1^2 a_1^2 + (l_2^2 + l_3^2) a_2^2 \right]^{1/2}. \tag{9}$$

The other details concerning the formulation of theoretical strength and its computation are given in our recent paper [20].

3. Results and discussion

A close review of the literature reveals that a variety of metallic whiskers have exhibited maximum stresses in the range of about 0.17×10^{10} N/m^2 (for Ag) to about 1.31×10^{10} N/m^2 (for Fe) with a corresponding strains estimated to be about 3% to 5% [22–24].

The instability in compression and in tension for the bcc lattice results from the violation of the conditions defined by Eq. (3) and Eq. (4), respectively.

The body centred tetragonal (bct) lattice fails in compression by violating the condition defined by Eq. (4) as a result of its inability to support an additional compressive load, while in tension by violating the condition $B_{23} > 0$ wherein the angle a_4 (the angle between a_2 and a_3) deviates from 90°.

We now discuss below our findings for bcc metallic crystals in the framework of extended generalised exponential potential, concerning the moduli B_{ij}, applied stress and internal energy.

3.1. Titanium

Figure 1 shows the variation of $AA = B_{22} - B_{23}$ and $BB = B_{11}(B_{22} + B_{23}) - 2B_{12}^2$ as a function of semi-lattice constant a_1 for Ti. Figure 2 shows the variation of applied stress and internal energy of Ti as a function of semi-lattice constant a_1. It follows from Figs. 1 and 2 that bcc lattice of Ti becomes unstable at a theoretical tensile stress of 0.3445×10^9 N/m^2 and a corresponding strain of 1.8% when $BB < 0$ and in compression, the bcc lattice of Ti becomes unstable at an applied stress of -0.5222×10^9 N/m^2 with a strain of 1.6% when $AA < 0$ for $n = 1$, $m = 2$ and $\alpha a_0 = 1.8735$. Thus the range of stability of Ti is from $a_1 = 1.637376$ Å, $a_2 = 1.676791$ Å, to $a_1 = 1.693952$ Å, $a_2 = 1.649544$ Å.

Again it follows from Figs. 1 and 2 that the theoretical strength of bct phase of Ti is 1.956×10^{10} N/m^2 in tension when $B_{23} < 0$ at $a_1 = 2.3296$ Å, $a_2 = 1.424506$ Å resulting into a peak in BB at this value of a_1 and -0.39×10^{10} N/m^2 in compression when Eq. (4) is violated; the corresponding strains are 9.8% in tension and -5.88% in compression. The bct phase of Ti is stable within the range
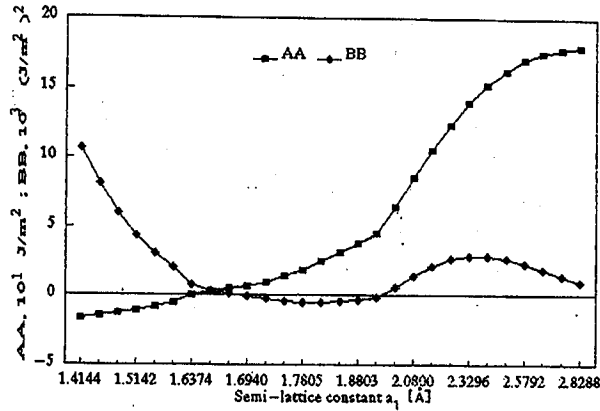
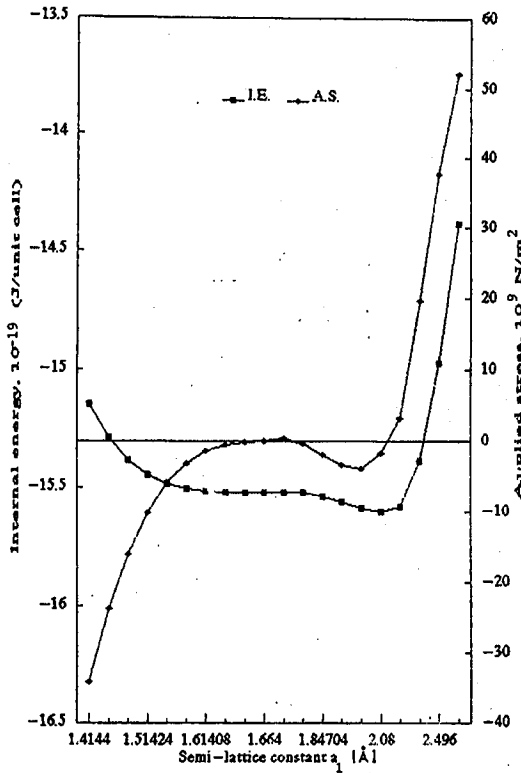Fig. 1. Variation of AA and BB as a function of semi-lattice constant for Ti.

Fig. 2. Variation of internal energy and applied stress as a function of semi-lattice constant for Ti.

of semi-lattice constants $a_1 = 1.9968$ Å, $a_2 = 1.512215$ Å to $a_1 = 2.3296$ Å, $a_2 = 1.424506$ Å.

3.2. Zirconium

Figure 3 shows the variation of $AA = B_{22} - B_{23}$ and $BB = B_{11}(B_{22} + B_{23})$ $-2B_{12}^2$ as a function of semi-lattice constant a_1 for Zr. Figure 4 shows the variation of applied stress and internal energy of Zr as a function of semi-lattice constant a_1. Figures 3 and 4 show that bcc lattice of Zr becomes unstable at a theoretical tensile stress of 0.9421×10^9 N/m^2 and a corresponding strain of 3.9% when $BB < 0$ and in compression, the bcc lattice of Zr becomes unstable at an applied stress of -1.9086×10^9 N/m^2 with a strain of 3.4% when $AA < 0$ for $n = 1$, $m = 1.5$ and $\alpha a_0 = 1.7808$. Thus the range of stability of Zr is from $a_1 = 1.750392$ Å, $a_2 = 1.840167$ Å to $a_1 = 1.882668$ Å, $a_2 = 1.779211$ Å.
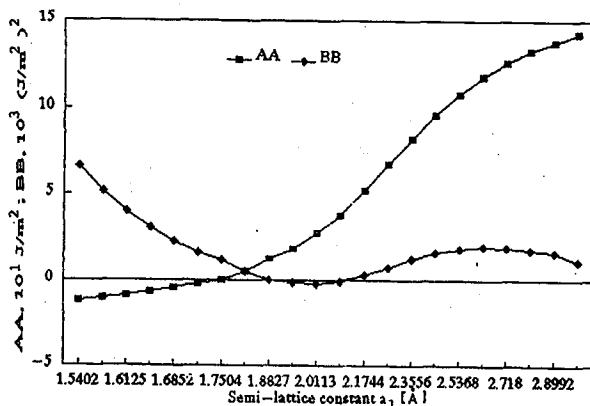

Fig. 3.   Variation of AA and BB as a function of semi-lattice constant for Zr.

Figures 3 and 4 depict that the theoretical strength of bct phase of Zr is 2.074×10^{10} N/m^2 in tension when $B_{23} < 0$ at $a_1 = 2.6274$ Å, $a_2 = 1.541015$ Å resulting into a peak in BB at this value of a_1 and -0.112×10^{10} N/m^2 in compression when Eq. (4) is violated; the corresponding strains are 16.89% in tension and –3.23% in compression. The bct phase of Zr is stable within the range of semi-lattice constants $a_1 = 2.1744$ Å, $a_2 = 1.651645$ Å to $a_1 = 2.6274$ Å, $a_2 = 1.541015$ Å.

3.3. Hafnium

Figure 5 shows the variation of $AA = B_{22} - B_{23}$ and $BB = B_{11}(B_{22} + B_{23})$ $- 2B_{12}^2$ as a function of semi-lattice constant a_1 for bcc Hf. Figure 6 shows the variation of applied stress and internal energy of bcc Hf as a function of semi-lattice constant a_1. It follows from Figs. 5 and 6 that bcc lattice of Hf becomes unstable at a theoretical tensile stress of 0.4078×10^9 N/m^2 and a corresponding strain of 1.98% when $BB < 0$ and in compression, the bcc lattice of Hf becomes unstable at an applied stress of -0.6418×10^9 N/m^2 with a strain of 1.82% when $AA < 0$ for $n = 2$, $m = 1.5$ and $\alpha a_0 = 2.04445$. Thus the range of stability of bcc Hf is from $a_1 = 1.772149$ Å, $a_2 = 1.620701$ Å to $a_1 = 1.840739$ Å, $a_2 = 1.787827$ Å.
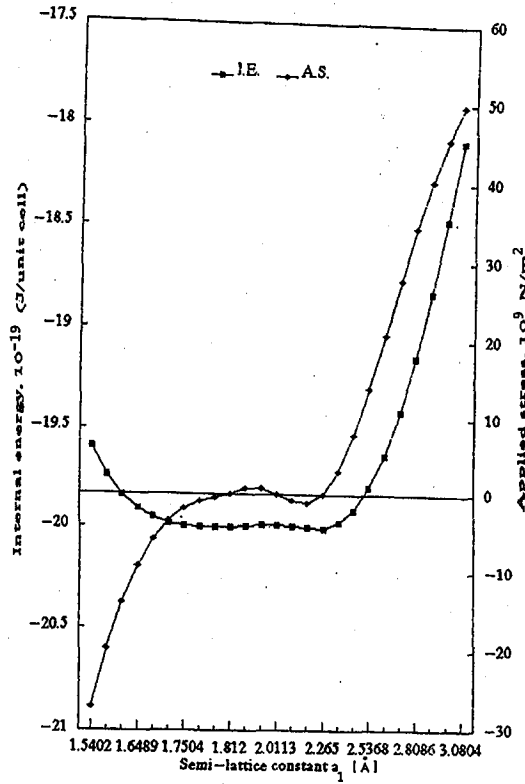
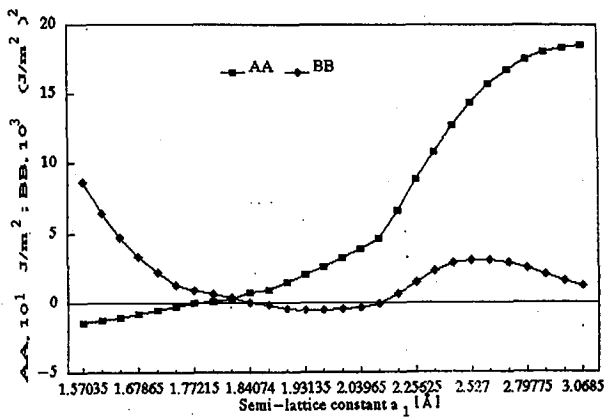Fig. 4. Variation of internal energy and applied stress as a function of semi-lattice constant for Zr.

Fig. 5. Variation of AA and BB as a function of semi-lattice constant for Hf.

Again it follows from Figs. 5 and 6 that the theoretical strength of bct phase of Hf is 1.858×10^{10} N/m^2 in tension when $B_{23} < 0$ at $a_1 = 2.527$ Å, $a_2 =$
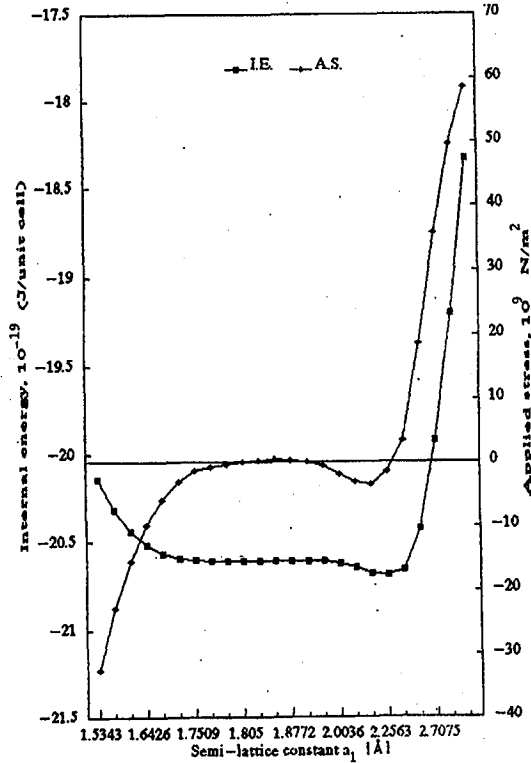
Fig. 6. Variation of internal energy and applied stress as a function of semi-lattice constant for Hf.

1.545943 Å resulting into a peak in BB at this value of a_1 and -0.349×10^{10} N/m^2 in compression when Eq. (4) is violated; the corresponding strains are 9.8% in tension and -5.88% in compression. The bct phase of Hf is stable within the range of semi-lattice constants $a_1 = 2.166$ Å, $a_2 = 1.640438$ Å to $a_1 = 2.527$ Å, $a_2 = 1.545943$ Å.

4. Conclusions

The following main conclusions emerge on the basis of our investigations carried out for bcc metals under study of group IV:

(i) The variation of internal energy defined by Eq. (6) with semi-lattice constant a_1 for the bcc metals under study shows *two distinct minima*: one for bcc phase (where stress σ_1 becomes negative) and the other for bct phase (where stress $\sigma_1 = 0$). It is to be noted that the internal energy minimum (IEM) of the bct phase is considerably lower than that of the bcc phase. The unstressed ($\sigma_1 = 0$) bct phase possesses the semi-lattice constant $a_1 = b_1^o$ and $a_2 = b_2^o$ corresponding to the minimum of internal energy. The values of semi-lattice constants a_1, a_2 and the corresponding values of the energy minima for the bcc and bct phases of the metals studied are given in Table III.

TABLE III

Internal energy minima (IEM) and stress.

(a) bcc phase				
Metal	a_1 [Å]	a_2 [Å]	Minima position [10^{-19} J/unit cell]	Stress [10^9 N/m^2]
Ti	1.78048	1.608335	−15.522	−0.373
Zr	2.04756	1.704053	−19.992	−0.336
Hf	1.93135	1.744075	−20.608	−0.434
(b) bct phase				
Metal	$a_1 = b_1^o$ [Å]	$a_2 = b_2^o$ [Å]	Minima position [10^{-19} J/unit cell]	Stress [10^9 N/m^2]
Ti	2.121600	1.470275	−15.605	0.0
Zr	2.246880	1.627884	−20.007	0.0
Hf	2.301375	1.595221	−20.705	0.0

(ii) It follows from the analysis of our results mentioned in Sec. 3 for the metals studied that the range of stability of the bct phase is considerably greater than that of the bcc phase.

TABLE IV

Computed values of C_{11} and C_{12} for bcc phase in 10^{11} N/m^2.

Metal	C_{11}	C_{12}	Remark
Ti	1.2369	1.1484	At equilibrium
	1.1044	1.1453	At failure in tension
	1.3926	1.1499	At failure in compression
Expt.	1.34	1.10	[25]
Zr	0.9613	0.8228	At equilibrium
	0.7535	0.8127	At failure in tension
	1.2610	0.8239	At failure in compression
Expt.	0.97	0.82	[26]
Hf	1.1841	1.0904	At equilibrium
	1.0470	1.0855	At failure in tension
	1.3552	1.0912	At failure in compression
Expt.	1.31	1.03	[27]

(iii) The second-order elastic constants (Table IV) C_{11} and C_{12} are calculated, similarly as by Milstein [18], at the stress-free equilibrium values of semi-lattice constant and at failure in tension and compression values of semi-lattice con-

stant. It is observed that in general computed values of elastic constants (C_{11} and C_{12}) decrease in tension and increase in compression as a result of phase transitions.

Acknowledgments

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