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Nearly metastable rhombohedral phases of bcc metals

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The energy $E(c/a)$ for a bcc element stretched along its [001] axis (the Bain path) has a minimum at $c/a=1$, a maximum at $c/a=\sqrt{2}$, and an elastically unstable local minimum at $c/a>\sqrt{2}$. An alternative path connecting the bcc and fcc structures is the rhombohedral lattice. The primitive lattice has $R\bar{3}m$ symmetry, with the angle α changing from 109.4° (bcc), to 90° (simple cubic), to 60° (fcc). We study this path for the non-magnetic bcc transition metals (V, Nb, Mo, Ta, and W) using both all-electron linearized augmented plane wave and projector augmented wave VASP codes. Except for Ta, the energy $E(\alpha)$ has a local maximum at $\alpha=60°$, with local minima near 55° and 70°, the latter having lower energy, suggesting the possibility of a metastable rhombohedral state for these materials. We first examine the elastic stability of the 70° minimum structure, and determine that only W is elastically stable in this structure, with the smallest eigenvalue of the elastic tensor at 4 GPa. We then consider the possibility that tungsten is actually metastable in this structure by looking at its vibrational and third-order elastic stability.

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I. INTRODUCTION

Consider a periodic crystal with one atom in a rhombohedral unit cell. For a fixed rhombohedral angle α, find the minimum energy of the crystal as a function of unit cell volume. As a function of α, this curve must have several extrema: (a) at $\alpha=60°$, corresponding to a face-centered cubic (fcc) structure, (b) at $\alpha=90°$, corresponding to a simple cubic (sc) structure, and (c) at $\alpha=109.471°$, corresponding to a body-centered cubic (bcc) structure. Given our physical intuition that the fcc and bcc structures are close in energy for most elements, we would naively expect that if an element has a bcc ground state, then $E(\text{bcc})<E(\text{fcc})<E(\text{sc})$, where $E(\text{bcc})$ is the global minimum, $E(\text{sc})$ is a local maximum, and $E(\text{fcc})$ is a local minimum. Previous calculations[1] show that this fcc structure has the elastic constant $C_{11}-C_{12}<0$, indicating instability with respect to a tetragonal distortion. However, the expectation that the fcc structure is a local minimum of the rhombohedral structure would require that C_{44} be positive for the fcc lattice.

This turns out not to be the case. Wang, Šob, and co-workers[2,3] have shown that C_{44} is negative for fcc vanadium, niobium, molybdenum, and tungsten. We have performed similar calculations, as in Fig. 1 for tungsten, which plots the energy versus rhombohedral angle. The fcc angle, $\alpha=60°$, is a local maximum, and there are two local minima at $\alpha\approx57.5°$ and $\alpha\approx66.4°$. This rhombohedral structure is the same type found in α-Hg,[4] where $\alpha=70.5°$, so we will refer to it by the α-Hg *Strukturbericht*[5] designation $A10$.

Reference 1 previously considered a similar situation for tetragonal strains for the fcc and bcc transition and noble metals. There, symmetry requires the existence of a local minimum in the total energy of the crystal as a function of tetragonal strain. When the local minimum was then tested for stability, it was found that the minimum was always unstable, meaning that the transition and noble metals do not have free-standing metastable tetragonal phases at zero temperature and pressure.

We can now address similar questions for the $A10$ structure described above. Specifically, we first (Sec. II) evaluate the energy of the five non-magnetic bcc transition elements (V, Nb, Mo, Ta, and W) as a function of rhombohedral angle. For those elements (all except Ta) which show a minimum at $\alpha\neq60°$ we then (Sec. III) compute the elastic constants of the equilibrium $A10$ rhombohedral structure. Most of the elements (all except W) are unstable with respect to elastic deformation. The surviving element (W) is tested for vibrational stability (Sec. IV), and shown to have no imaginary phonon frequencies within the harmonic approximation. Finally, we show (Sec. V) that for tungsten there is an early breakdown of Hooke's law for the $A10$ phase, so that none of the elements exhibit rhombohedral metastability. Section VI concludes by considering possible cases where the $A10$ phase might be grown epitaxially.

II. STRAIN ENERGY

We consider the nonmagnetic transition metals with body-centered cubic ground states V, Nb, Mo, Ta, and W, computing the energy of each structure using an all-electron general-potential linearized augmented plane wave (LAPW) code,[6] including local orbitals[7] to represent the (3s,3p) semicore

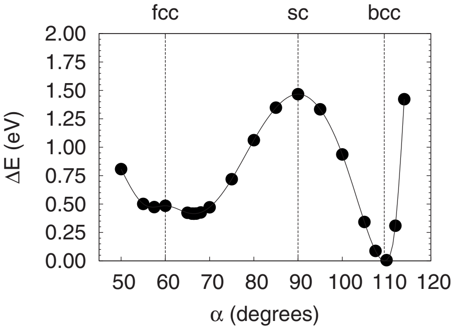


FIG. 1. First-principles total energy of tungsten (per atom) as a function of the rhombohedral angle, minimizing the total energy as a function of volume at each point.

TABLE I. Structural parameters and energy relative to the fcc structure for the bcc, fcc, and $A10$ (rhombohedral) structures. V is the volume/atom of the minimum energy structure, α is the rhombohedral angle, and a and c are the lattice constants of the corresponding hexagonal representation. ΔE is the energy difference (meV/atom) with respect to the fcc phase. Negative energies for the $A10$ phase indicate possible metastable structures.

Element	Structure	V (Å)	α	a (Å)	c (Å)	ΔE
V	bcc	12.532	109.471			−283
	fcc	12.984	60.000			0
	rhomb.	12.793	68.994	2.81	5.62	−28
Nb	bcc	17.114	109.471			−366
	fcc	17.727	60.000			0
	rhomb.	17.514	68.755	3.11	6.27	−89
Mo	bcc	15.074	109.471			−430
	fcc	15.260	60.000			0
	rhomb.	15.435	67.615	2.96	6.11	−53
Ta	bcc	17.129	109.471			−292
	fcc	17.687	60.000			0
	rhomb.	17.687	60.000			0
W	bcc	15.490	109.471			−485
	fcc	15.747	60.000			0
	rhomb.	15.892	66.433	2.96	6.27	−70

orbitals in vanadium, the $(4s,4p)$ orbitals in niobium and molybdenum, the $(4f,5s,5p)$ orbitals in tantalum, and the $(5s,5p)$ orbitals in tungsten. All computations use the standard Kohn-Sham[8] formulation of density functional theory[9] and the parametrization of the local density approximation in Ref. 10. We carefully checked the convergence of the energy as a function of (a) plane-wave cutoff, setting $RK_{\mathrm{max}}=8.5$ and (b) k-point sampling,[11] using meshes with up to 1513 points in the irreducible Brillouin zone for structures with $\alpha \approx 60°$ and a Fermi broadening scheme with a broadening temperature of 5 mRy. Our estimated error due to k-point summation is less than 0.1 mRy/atom for all systems. We also checked several of the calculations using the Vienna Ab-initio Simulation Package[12–14] (VASP) and the projector augmented wave (PAW) formalism,[15,16] finding results in close agreement the all-electron LAPW method.

Table I reproduces the calculations of Ref. 3, showing the structural data for the bcc, fcc, and $A10$ (rhombohedral) phases, as well as the energy of the bcc and $A10$ phases relative to the fcc structure. Note that, as in Ref. 3, tantalum is stable with respect to a rhombohedral distortion of the fcc lattice. Since we have previously shown[1] that $C_{11}-C_{12}$ is negative in this case, we eliminate tantalum from our search for new metastable states.

III. ELASTIC STABILITY

TABLE II. Finite strains used to determine linear combinations of elastic constants in the $A10$ structures described in Table I, using the methods of Refs. 17 and 18 with the quadratic expansion (1). For a given elastic constant, all unlisted strain parameters are set to zero.

Elastic constant	Strains
$C_{11}+C_{12}$	$e_1=e_2$
C_{33}	e_3
$C_{11}+C_{12}+2C_{33}-4C_{13}$	$e_1=e_2=(1+e_3)^{-1/2}-1$
$C_{11}-C_{12}$	$e_2=-e_1/(1+e_1)$
C_{44}	$e_3=1/4e_4^2$
$C_{11}-C_{12}+2C_{44}+4C_{14}$	$e_6=e_5,\ e_1=1/2e_5^2$

V, Nb, Mo, and W all have a lower energy in the $A10$ structure with $\alpha \approx 70°$ than in the fcc structure. We have not, of course, shown that these states are metastable. To check that, we first determine the elastic behavior of these materials in the rhombohedral phase, using the finite strain method for determining elastic constants.[17,18] The $A10$ structure has space group symmetry $R\bar{3}m$ and so has six independent elastic constants.[19] We calculate the elastic constants by computing the total energy as a function of the elastic strain constants e_i,[20,21] fitting this to the quadratic form

$$E = E_0 + V_0\left[\begin{array}{cc} & 1/2C_{11}(e_1^2+e_2^2) \\ + & C_{12}e_1e_2 \\ + & 1/2C_{33}e_3^2 \\ + & C_{13}(e_1+e_2)e_3 \\ + & C_{14}(e_1-e_2)e_4 \\ + & 1/2C_{44}(e_4^2+e_5^2) \\ + & C_{14}e_5e_6 \\ + & 1/4(C_{11}-C_{12})e_6^2 \end{array}\right] + O[e_i^3], \qquad (1)$$

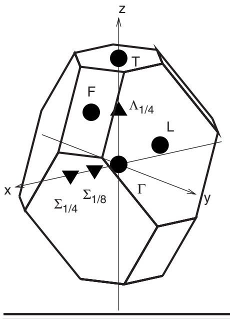
and determining linear combinations of the C_{ij} using the strains described in Table II. The resulting elastic constants are given in Table III.

The Born criterion[22] requires that all of the eigenvalues of the tensor implied by Eq. (1) be positive. From Table III we immediately see that both vanadium and niobium have $C_{44} < 0$, violating the Born criterion. While all of the diagonal elastic constants for molybdenum are positive, the smallest eigenvalue of the elastic tensor is negative. Therefore in the

TABLE III. Elastic constants (in GPa) for the $A10$ structures of Table I, using the finite strains in Table II and the quadratic expansion (1). C_{min} is the linear combination of elastic constants which gives the smallest eigenvalue of the elastic tensor implied by Eq. (1).

Element	C_{11}	C_{12}	C_{13}	C_{33}	C_{14}	C_{44}	C_{min}
V	235	203	139	279	10	−60	−62
Nb	221	195	146	322	−2	−22	−22
Mo	376	163	214	493	52	15	−9
W	414	215	233	561	−46	27	4.5

TABLE IV. Computed phonon frequencies for $A10$ tungsten (Table I), calculated as described in the text. Frequencies are in inverse wave numbers (cm^{-1}). The k points used are shown in the figure.

	Symmetry	Frequencies
	T	124 124 217
	L	83 89 216
	F	128 148 214
	Σ (1/8)	60 69 126
	Σ (1/4)	67 138 187
	Λ (1/4)	63 63 157

$A10$ structure vanadium, niobium, and molybdenum are all elastically unstable. The remaining element in the table, tungsten, has a positive definite elastic tensor, and so may be metastable in the $A10$ state.

IV. VIBRATIONAL STABILITY OF $A10$ TUNGSTEN

For complete metastability, a crystal must be stable against small vibrations of any atom, i.e., there can be no imaginary phonon frequencies. For $A10$ tungsten we compute frequencies via the frozen phonon approximation,[23] using the FROZSL program[24] to generate supercells, computing the change in energy versus amplitude by LAPW calculations, and determining the phonon frequency assuming harmonic response.

We make a limited sample of the Brillouin zone at the points shown in Table IV, which also shows the phonon frequencies for the different polarizations at each k point. The phonon frequencies for tungsten are all positive definite. This is a rather small collection of k points, and is certainly not exhaustive. However, since the elastic tensor is positive definite, as we saw in the previous section, we know that the long-wavelength phonons are real,[21] and it is unlikely that there are any other "soft" phonon modes in the crystal. We therefore conclude that, based on the harmonic approximation, $A10$ tungsten should be metastable at zero temperature.

V. NONLINEAR STRAINS

Though we have shown that $A10$ tungsten is harmonically metastable, the low value of the smallest elastic tensor eigenvalue, 4.5 GPa, is worrisome, since typically elastic constant calculations have numerical errors of this order. Thus it may be that this elastic constant is zero, or even slightly negative. To test this, we look at the eigenvectors of the elastic matrix described by Eq. (1). The eigenvector associated with the smallest eigenvalue, 4.5 GPa, can be roughly approximated by the elastic strain

$$e_1 = -e_2 = 1/4 e_4,$$

$$e_3 = -(8 - 3e_4 - e_4^2)/(4 + e_4)^2,$$

and

$$e_5 = e_6 = 0, \tag{2}$$

where the value of e_3 is chosen to conserve the unit cell volume for arbitrary values of e_4. The elastic response of this strain should yield the energy

$$E(e_4) = E_0 + V[1/4(C_{11} - C_{12}) + C_{14} + C_{44}]e_4^2 + O[e_4^3], \tag{3}$$

where $1/4(C_{11}-C_{12})+C_{14}+C_{44} \approx 4.5$ GPa. Our computed $E(e_4)$ for $|e_4| \leq 1/10$ is shown in Fig. 2.

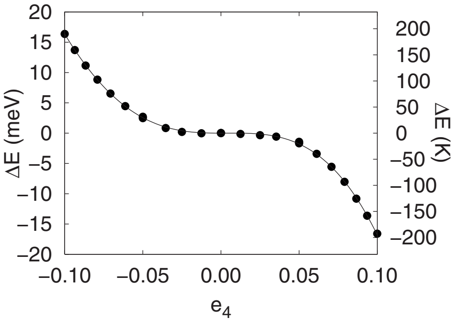


FIG. 2. Energy (3) per atom of rhombohedral tungsten as a function of the strain given in Eq. (2).

For very small strains ($e_4 < 0.01$), the energy $\Delta E = E(e_4) - E(0)$ is very flat, and the elastic constant is indeed very close to zero. For larger positive strains, however, the energy begins to decrease. We conclude that the $A10$ tungsten structure with parameters given in Table I is, in fact, unstable with respect to the cubic and higher terms in Eq. (1), and that there is at best a very small region where the elastic relation-

TABLE V. Room-temperature equilibrium nearest-neighbor distances for the close-packed planes of several fcc and hcp elements, and the mismatch with the $A10$ tungsten nearest-neighbor distance of 2.96 Å. We show both the mismatch with the experimental lattice constant[25] and the LDA lattice constant.

Element	Experiment		LDA	
	R_{NN}	Mismatch	R_{NN}	Mismatch
		fcc elements		
Al	2.86	−3.4%	2.81[a]	−4.9%
Ag	2.89	−2.4%	2.84[a]	−4.0%
Au	2.88	−2.7%	2.87[b]	−2.9%
		hcp elements		
Ti	2.95	−0.3%	2.87[b]	−2.9%
Cd	2.98	0.7%	2.91[c]	−1.7%

[a] Reference 26.
[b] Reference 27.
[c] Computed using the VASP code (Refs. 12–14) within the PAW (Refs. 15 and 16).

ship (3) holds. We are therefore left with the conclusion that none of the non-magnetic bcc transition metals has a stable $A10$ phase, even though Table I shows that a small rhombohedral distortion from the fcc structure actually lowers the energy of the system.

VI. CONCLUSION: EPITAXIAL GROWTH?

Even though we have shown that the free standing rhombohedral ($A10$) structures do not exist, it may be possible to create it by epitaxy, if a suitable substrate can be found. As seen in Fig. 2, the energy of $A10$ tungsten does not change appreciably for strains $e_4 < 0.05$, so small lattice mismatches can be easily tolerated. Growing (0001) planes of rhombohedral tungsten requires a close packed base of (111) fcc planes or (0001) hcp planes matching the nearest-neighbor distance of 2.96 Å (from Table I). Table V lists candidate elements for such a substrate, showing close-packed nearest neighbor distances obtained from experiment[25] and first-principles LDA calculations.[26,27] Comparing to experiment, we note that titanium is a close match, having a 0.3% smaller nearest-neighbor distance than our $A10$ tungsten structure, and cadmium is a close second, with a nearest-neighbor distance that is 0.7% larger. Comparing to theory, cadmium is by far the best choice, with a nearest-neighbor mismatch of −1.7%. We therefore suggest that experimentalists who wish to look for $A10$ tungsten consider titanium and cadmium surfaces for the substrate. The search for this phase may be complicated its large energy (485 meV) above the bcc phase and the presence of the $A15$ tungsten phase, which is only 97 meV/atom above the bcc phase.

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