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Phases of vanadium under pressure investigated from first principles

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Abstract

The existence and stability under pressure of three phases of vanadium are calculated from first principles. The phases are one body-centered cubic (bcc) and two rhombohedral phases (rh^u and rh^l), which have greater and lower α values than the primitive bcc rhombohedral cell. The bcc phase is shown in two ways to become unstable at 0.65 Mbar, in agreement with an observed phase transition, but in disagreement with previous higher estimates. The rh phases exist when the bcc phase is unstable, but the bcc phase stabilizes again at 3 Mbar, and the rh phases disappear. At 1.15 Mbar the rh^u phase becomes and remains unstable and the rh^l phase becomes the ground state up to 3 Mbar, where the rh^l phase disappears and the bcc phase takes over. The theory gives four phase transitions among the phases over the pressure range from 0 to 3 Mbar; two of them are bcc to rh^u—a low pressure (0.3 Mbar) thermodynamic transition found from Gibbs free energies being equal (not observed) and a higher pressure (0.65 Mbar) instability transition when the bcc phase becomes unstable (observed).

1. Introduction

In a recent paper on vanadium Ding *et al* [1] found with the diamond-anvil-cell a phase transition from body-centered cubic (bcc) structure to rhombohedral (rh) structure at pressure 0.63 Mbar. The angle α of the rh phase increased rapidly from the angle $\alpha^{\text{bcc}} = 109.47^\circ$ of the primitive bcc cell as the pressure increased and the bcc phase vanished. Ding *et al* interpreted this phase transition as a second-order transition in which the phase breaks symmetry and changes continuously into new rh phase.

In a paper by Landa *et al* [2] the shear elastic constant c_{44} of bcc vanadium is evaluated from first principles as a function of pressure. The function $c_{44}(p)$ is shown to go negative at about 2 Mbar and positive again at 3 Mbar. This calculation confirmed a weakness in the angular forces of the bcc lattice that could account for the phase transition. However the 2 Mbar pressure for the instability of bcc vanadium found in the calculation was considerably greater than the observed transition pressure, which suggested that the pressure correction, which makes substantial reduction in $C'(p) = (c_{11} - c_{12})/2$ and $c_{44}(p)$, as has been shown for bcc Fe [3], had been omitted. Recalculation of $c_{44}(p)$ using a procedure that includes the pressure correction [3], found $c_{44}(p)$ went negative at 0.65 Mbar, in good agreement with experiment and indicating that [2] had omitted the pressure correction.

Then a paper by Lee *et al* [4] made a detailed study of the phases of vanadium and their stability under pressure. Lee *et al* showed that there is a second rh phase (rh^l) with $\alpha < \alpha^{\text{bcc}}$ along with the rh phase (rh^u) with $\alpha > \alpha^{\text{bcc}}$. Lee *et al* also found that vanadium made a transition from bcc to rh^u and then at a higher p made a transition from rh^u to rh^l, and finally vanadium made a transition from rh^l back to bcc structure. However the instability in bcc vanadium occurred at 1.2 Mbar, which was still higher than experiment.

A recalculation of the phases of vanadium and their stability under pressure by a different procedure than was used in [4] confirmed the instability of bcc vanadium at 0.65 Mbar—in addition to the vanishing of $c_{44}(p)$ at that pressure; also all the critical pressures at which rh phases appeared and at which they became ground states were shifted downward in the recalculation.

Features of our procedure include: locating equilibrium states of vanadium in rh structure from minima in $E(\alpha)$ at constant volume; using the minimum E values of each phase to find a separate equation of state for each phase, bcc, rh^u, rh^l; constructing Gibbs free energy functions $G(p)$ for each phase and using the crossings of these $G(p)$ curves to find the pressures of the thermodynamic phase transitions bcc \rightarrow rh^u and rh^l \rightarrow bcc. We distinguish between *absolute instability* of an equilibrium state under pressure when the Gibbs free energy G is not a minimum for all strains and *relative stability* when a

second phase is about to have a lower G at that pressure. The first $\text{bcc} \rightarrow \text{rh}^{\text{u}}$ transition is a case of relative instability and is thermodynamically permitted, but may be hindered by energy barriers; the second transition is a case of absolute instability and is driven by the instability. Determination of absolute instability is made in every equilibrium state by a calculation that shows G is not a minimum, which uses all the elastic constants c_{ij} , $i, j = 1-6$.

Section 2 gives details of the computation of band energies, equilibrium states, equations of state, Gibbs free energies of three phases and their stabilities.

Section 3 describes results on the stability of the three phases and the critical pressures of existence and of thermodynamic transitions between phases in figures and a table.

Section 4 discusses and compares two procedures for finding equilibrium states under pressure, points out a possible source of error in the calculations in [4], and explains the description of the observed phase transition as an instability transition.

2. Computational details

The total internal energy is calculated using the WIEN2k_07 package [5], which is an implementation of the full-potential augmented-plane-wave plus local orbital (APW + lo) method together with the Perdew–Burke–Ernzerhof generalized-gradient-approximation (PBE-GGA). The APW + lo method expands the Kohn–Sham orbitals in atomiclike orbitals inside the atomic spheres and plane waves in the interstitial region. A plane-wave cutoff $R_{\text{MT}}K_{\text{max}} = 7$, $R_{\text{MT}} = 1.6$ au, $G_{\text{max}} = 14$, mixer = 0.05 and 1000 k -points in the irreducible Brillouin zone were used in all the band calculations. The k -space integration was done by the modified tetrahedron method. Tests with larger basis sets and different Brillouin zone samplings yielded only very small changes in the results. The convergence criterion on the energies is set at 1×10^{-3} mRyd (10^{-6} Ryd).

The total internal energy calculations of rh structure use a one-atom unit cell which is formed by lattice vectors $(\vec{a}, \vec{b}, \vec{c})$ with $a = b = c$ and $\alpha = \beta = \gamma$. The one-atom bcc unit cell is a special case of the 1-atom rh unit cell with $a = \frac{\sqrt{3}}{2}a_0$, $\alpha = \alpha^{\text{bcc}} = 109.47^\circ$, where a_0 is the lattice constant of the conventional cubic 2-atom bcc cell. The volume of the rh unit cell is given by

$$V = a^3(1 - \cos \alpha)\sqrt{1 + 2 \cos \alpha}. \quad (1)$$

The equilibrium states of vanadium are found at each volume from minima $E_{\text{m}}(V_i)$ in $E(\alpha)$ at constant volumes V_i , $i = 1-48$. The functions $E_{\text{m}}^{\text{ph}}(V_i)$ for each phase can then be differentiated to find the equation of state for each phase

$$p^{\text{ph}}(V) = -dE_{\text{m}}^{\text{ph}}/dV, \quad (2)$$

where $\text{ph} = \text{rh}^{\text{u}}, \text{bcc}, \text{rh}^{\text{l}}$. Then the Gibbs free energy of each phase can be obtained at p from

$$G^{\text{ph}}(p^{\text{ph}}(V)) = E_{\text{m}}^{\text{ph}}(V) + p^{\text{ph}}(V)V. \quad (3)$$

We also make use of $\alpha_{\text{m}}^{\text{ph}}$ the α values at each minimum of $E(\alpha)$ at V and of the curvature $(d^2E/d\alpha^2)_{\text{m}}$ at each minimum of E . The change of sign of the curvatures will be used to find the instability pressures. The $\alpha_{\text{m}}^{\text{ph}}$ values at each $V^{\text{ph}}(p)$ will describe the rh structure as a function of p .

The shear elastic constant $c_{44}(p)$ of bcc vanadium is calculated using two different methods.

Method 1 was our original calculation method as shown in [3]; it uses a conventional 2-atom bcc unit cell to calculate the Gibbs free energy G as a function of pressure. The second derivatives of G with respect to the strains at the equilibrium state give the elastic constants c_{ij} .

$$c_{ij} = \frac{1}{V_0} \left(\frac{\partial^2 G}{\partial \varepsilon_i \partial \varepsilon_j} \right)_{\text{eq}}, \quad (4)$$

where V_0 is the equilibrium volume. Then, as shown in [3], no pressure correction is required.

Method 2 also uses a conventional 2-atom bcc unit cell to calculate the total internal energy as a function of volume. Then c_{44} is obtained from the second derivative of the total internal energy with respect to δ , which is calculated using the strain matrix [6]

$$\varepsilon = \begin{pmatrix} 0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \delta^2/(1 - \delta^2) \end{pmatrix}, \quad (5)$$

with the corresponding strain energy

$$E(\delta) = E(0) + 2c_{44}V\delta^2 + O(\delta^4). \quad (6)$$

Method 2 also includes the pressure corrections because of the δ^2 term for ε_3 .

Finally we test each phase for stability by an MNP (minimum path) program which is the program in [7] generalized to handle cells of no symmetry that evaluates the 21 elastic constants c_{ij} . The c_{ij} , $i, j = 1-6$ form a 6×6 symmetric matrix whose eigenvalues determine stability, a negative eigenvalue means instability [8], hence the unstable equilibrium states can be identified.

3. Results

In figure 1 the basic calculation of total energy as a function of one structural parameter α at constant volume ($E(\alpha)$ at volume V) is shown for selected V_i , $i = 1-48$. The minima $E_{\text{m}}^{\text{ph}}(\alpha_{\text{m}})$ are the energies of equilibrium states at those V_i ; examples of one, two and three minima are shown, and $\text{ph} = \text{rh}^{\text{u}}, \text{bcc}, \text{rh}^{\text{l}}$ gives the corresponding phase. The phases come into existence or vanish as V_i changes and minima appear and disappear.

To find the pressure at each minimum, the energy value at the minimum of each phase $E_{\text{m}}^{\text{ph}}(V_i)$ (data not shown) is differentiated as in (2) to give the three equations of state (EOS) $p^{\text{ph}}(V)$. The EOS of the three phases are shown in figure 2(a), and compared with the values in [4] in figure 2(b).

From the EOS in figure 2 the p dependence of the equilibrium states found in figure 1 can be obtained. Three branches, one for each of the three phases, are shown in

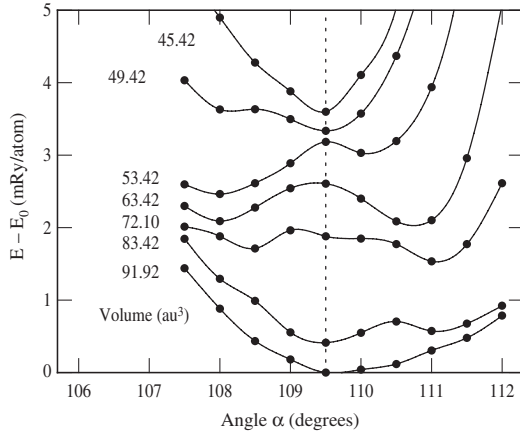


Figure 1. Total internal energy as a function of angle α (called $E(\alpha)$ curves) of the 1-atom rh unit cell of vanadium at selected volumes; E_0 is the total energy of bcc vanadium at $V = 91.92 \text{ au}^3$. For clarity the $E(\alpha)$ curves at volumes from 83.42 to 45.42 au^3 are shifted toward E_0 by 4.272, 33.572, 87.072, 208.272, 282.572 and 382.272 mRyd/atom, respectively. The solid lines interpolate between the calculated points. The vertical dashed line indicates the bcc phase at $\alpha^{\text{bcc}} = 109.47^\circ$ at which the curvatures of the $E(\alpha)$ curves are a function of volume and change sign from positive to negative and then back to positive again. The minima on the right side of the vertical dashed line are the rh^{u} phase, while the minima on the left side are the rh^{l} phase.

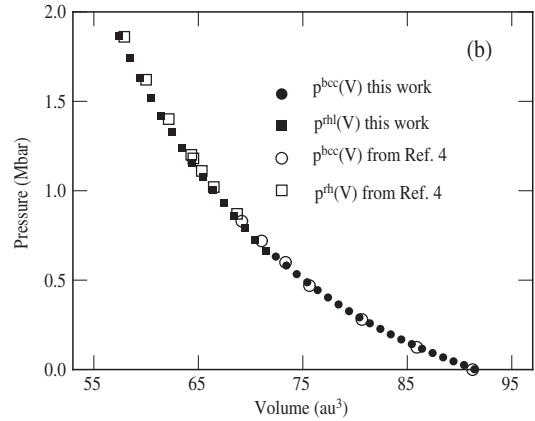
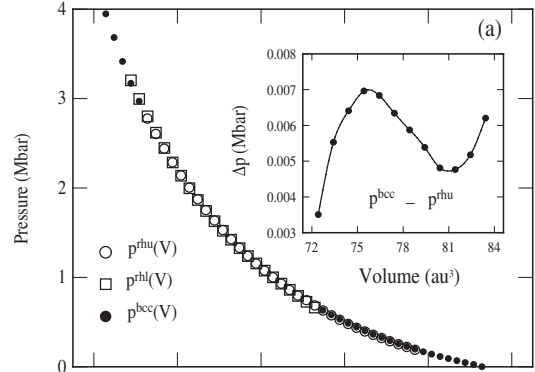


Figure 2. (a) $p(V)$ curves for the bcc phase (filled circles), rh^{u} phase (open circles) and rh^{l} phase (open squares) of vanadium which are calculated using equation (2). The inset shows the difference $p^{\text{bcc}} - p^{\text{rh}^{\text{u}}}$ in the pressure range in which both bcc and rh^{u} phases coexist. (b) $p(V)$ data from [4] (open symbols), and for rh^{u} and bcc phases (filled symbols) from this work.

figure 3, with the ground state and phase appearances and disappearances and unstable states indicated. The arrows indicate the phase transitions among the three phases of vanadium. Figure 3 here may be compared with figure 2 of [4]. The general structure is similar, but the structure in the lower part of the p scale is all at smaller p values.

Figures 4–6 show how three first-order phase transitions are found from crossings of the $G^{\text{ph}}(p)$ curves, i.e., $\text{bcc} \rightarrow \text{rh}^{\text{u}}$, $\text{rh}^{\text{u}} \rightarrow \text{rh}^{\text{l}}$, $\text{rh}^{\text{l}} \rightarrow \text{bcc}$. The theory predicts four phase transitions among the phases of vanadium (figure 3). There are two $\text{bcc} \rightarrow \text{rh}^{\text{u}}$ transitions: one is identified at 0.32 Mbar as a thermodynamic transition that is not observed (figure 4(b)), and one at 0.65 Mbar as an instability transition (figure 7(a)) which is observed. The transition $\text{rh}^{\text{l}} \rightarrow \text{bcc}$ at 2.97 Mbar is identified as a thermodynamic transition (figure 6). The transition $\text{rh}^{\text{u}} \rightarrow \text{rh}^{\text{l}}$ appears at 1.15 Mbar to be both a thermodynamic transition (figure 5(b)) and an instability transition (figure 3).

To check the instability pressures of bcc vanadium figure 8(a) shows two calculations of $c_{44}(p)$, which are compared to the calculation by Landa *et al* [2]. These are the two calculations mentioned in section 2. Both show the first instability pressure of vanadium around 0.6 Mbar in good agreement with the experiment indicating that both calculations include proper pressure corrections. In contrast, the c_{44} values calculated in [2] do not show an instability that is in agreement with experiment, which is apparently due to the neglect of the pressure correction.

Table 1 summarizes all the critical pressures, i.e., of existence of phases, thermodynamic phase transitions between phases and of instability of vanadium. For comparison the results from Lee *et al* [4] are also included.

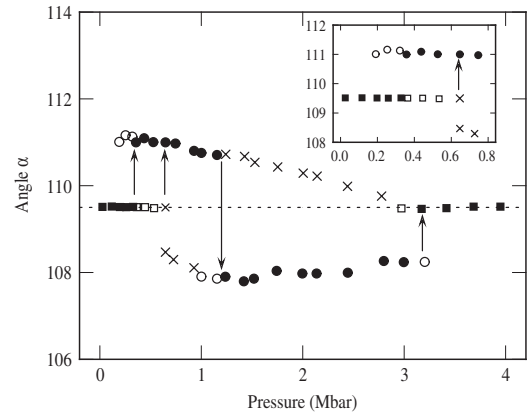


Figure 3. The angles $\alpha^{\text{bcc}}(p)$, $\alpha^{\text{rh}^{\text{u}}}(p)$, $\alpha^{\text{rh}^{\text{l}}}(p)$ of the equilibrium states of vanadium as functions of pressures as predicted by theory. The filled symbols represent ground states, the open symbols represent metastable states, the crosses represent unstable states. The arrows indicate the phase transitions among the three phases of vanadium. The inset shows $\alpha^{\text{bcc}}(p)$ and $\alpha^{\text{rh}^{\text{u}}}(p)$ in an expanded pressure range from 0 to 0.8 Mbar.

4. Discussion

There are two calculation procedures that satisfy thermodynamic principles that can be used to find equilibrium states

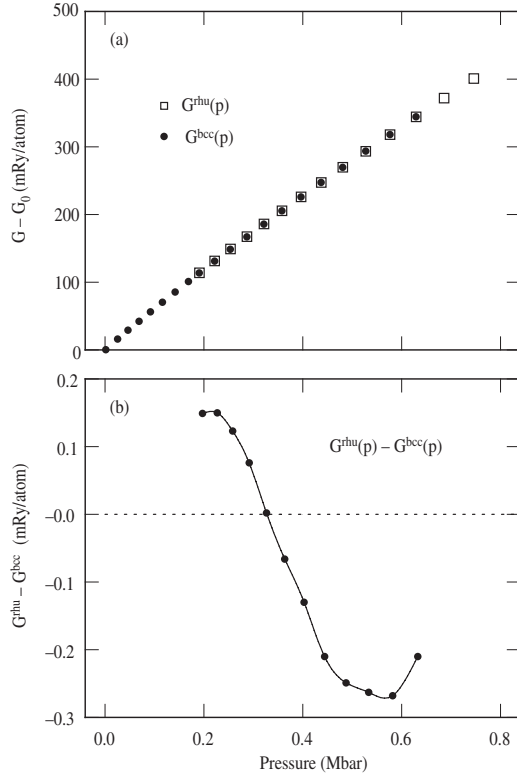


Figure 4. (a) Gibbs free energies in the bcc and rh^u phases in the pressure range from 0 to 0.8 Mbar. (b) The energy difference curve of $G^{rh^u}(p) - G^{bcc}(p)$ indicating the phase transition from bcc to rh^u phase at 0.32 Mbar. The solid lines interpolate between the calculated points.

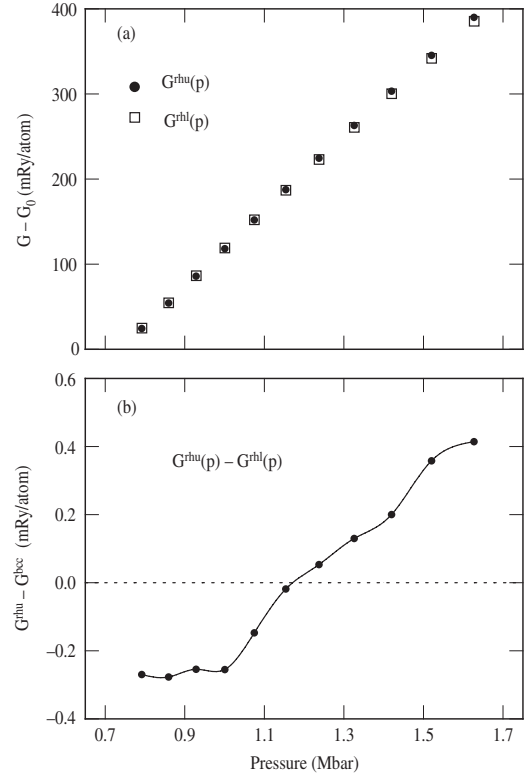


Figure 5. (a) Gibbs free energies in the rh^u and rh^l phases in the pressure range from 0.7 to 1.7 Mbar. (b) Energy difference curve of $G^{rh^u}(p) - G^{rh^l}(p)$ indicating the phase transition from rh^u to rh^l occurs at 1.15 Mbar. The solid lines interpolate between the calculated points.

Table 1. Critical pressures of vanadium.

Critical point	Pressure (Mbar)	
	This work	Lee <i>et al</i> [4]
Existence of rh^u phase	0.19	0.73
Phase transition bcc \rightarrow rh^u	0.32	0.84 ^a
Existence of rh^l phase	0.65	1.03
Instability of bcc phase (1st)	0.65	1.20
Phase transition $rh^u \rightarrow rh^l$	1.15	1.19
Instability of bcc phase (2nd)	2.97	2.49
Phase transition $rh^l \rightarrow$ bcc	2.97	2.80

^a Mention is made in [4] without details that all-electron calculations give this transition pressure to be 0.6 Mbar.

of homogeneous crystals under pressure. The first procedure finds minima of the internal energy E at constant volume V with respect to structure. Then for a structure with two parameters, e.g., the α , a of rhombohedral phases, the complete equilibrium state, i.e., including pressure, is found in two stages: the first stage makes a one-parameter calculation of $E(\alpha)$ at V to give various equilibrium states at that V from the minima $E_m^{ph}(V)$, where ph gives the phases, rh^u , bcc, rh^l . The second stage finds $p(V)$ from several adjacent values of V using (2). A disadvantage of the procedure is that finding all the elastic constants from the calculation of E is complicated. Note that p is not constant along the $E_V(\alpha)$ curve, hence there is a different p at each of the minima α_m^{ph} corresponding to a particular

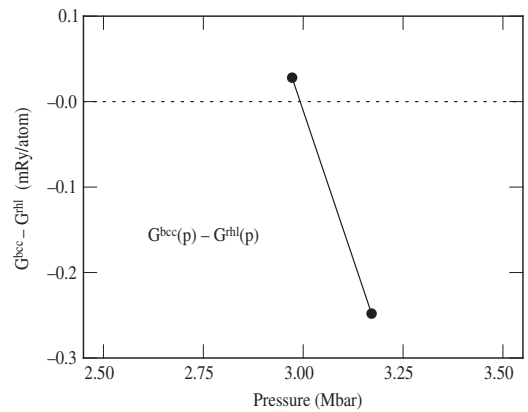


Figure 6. Energy difference of $G^{bcc}(p) - G^{rh^l}(p)$ as a function of pressure indicating the phase transition from rh^l to bcc phase at 2.97 Mbar. Notice that the bcc and rh^l phases coexist in a very narrow pressure range near 3 Mbar as shown in figure 3.

phase at that V . The second thermodynamic procedure finds the minima of the Gibbs free energy at a constant p . For equilibrium states of rh phases G is required to be a minimum in two variables a and α . This is more complicated than the first procedure, but calculation of elastic constants as functions of pressure is easier than with the first procedure.

The large discrepancy in critical pressures for vanadium phases between this work and [4] indicates a difficulty in the

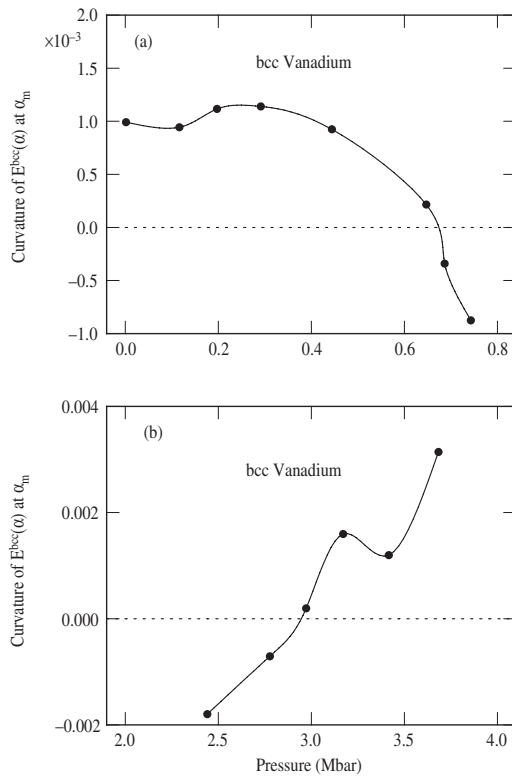


Figure 7. (a) Curvature of the $E(\alpha)$ curve at $\alpha^{\text{bcc}} = 109.47^\circ$ as a function of pressure which changes its sign at $p = 0.65$ Mbar, the first instability pressure of the bcc phase. (b) Curvature of the $E(\alpha)$ curve at $\alpha^{\text{bcc}} = 109.47^\circ$ in the high pressure region which gives the second instability pressure of the bcc phase at 2.97 Mbar which is the same as the phase transition pressure from rh^1 to bcc phase shown in figure 6. In both (a) and (b) the solid lines interpolate between the calculated points.

enthalpy formula in [4] (their equation (3)). We have noted above that finding equilibrium states at a pressure p from the Gibbs free energy (or enthalpy) requires minimizing with respect to all structural variables, i.e., for rh phase both α and V . But in equation (3) of [4] for enthalpy V is not a variable; only the constant V_0 , the volume at $\delta = 0$, appears as α is varied. This omission of variable V is a possible source of error.

The theory indicates that the phase transition at 0.6 Mbar is not a second-order thermodynamic phase transition as suggested in [1] and [4]. A better description is to call it an instability transition in which the bcc phase loses its stability and makes a finite (discontinuous) structural change. In a second-order transition under pressure the symmetry of the initial phase is broken, but as the pressure changes the new structure changes steeply but continuously. In both types of transition (instability or second-order) the initial phase disappears and is not even metastable.

In summary the calculation here shows that theory can analyze complicated phase situations. From the minima of E as a function of structure at constant V , the existence and vanishing of phases can be found as minima appear and disappear as V changes. From the minimum E values separate equations of state can be determined and used to find separate

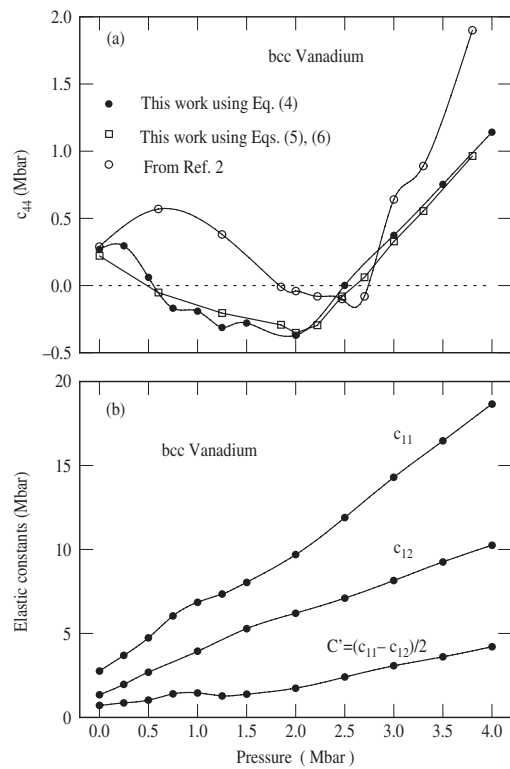


Figure 8. Elastic constants of bcc vanadium as a function of pressure. (a) The filled circles are c_{44} data of vanadium calculated in this work using equation (4). The open circles are c_{44} values calculated in [2]. The open squares are c_{44} values calculated in this work using equations (5) and (6) at the same pressures as used in the c_{44} calculations in [2], the corresponding equilibrium lattice parameters at these pressures needed for the calculations are deduced from the equation of state in [2]. (b) The elastic constants c_{11} , c_{13} and $C' = (c_{11} - c_{12})/2$ of bcc vanadium as a function of pressure calculated in this work using equation (4). In both (a) and (b) the solid lines interpolate between the calculated points.

$G(p)$ functions for each phase. Then the crossings of $G(p)$ curves determine phase transition pressures. The vanishing of eigenvalues of the c_{ij} matrix determines instability pressures.

Acknowledgments

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