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Equilibrium lines and crystal phases under pressure

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Abstract

A crystal phase in equilibrium under changing pressure traces out a line in structure space where each point corresponds to a structure. Along that equilibrium line the structure and all static properties describe the static behavior of the phase, including two sets of elastic constants and the bulk modulus. We discuss and illustrate the calculation of the equilibrium line and the properties from both the Gibbs free energy and the internal energy. We show that the bulk modulus, which gives a stress to strain ratio along the equilibrium line, has a universal relation independent of pressure to that set of elastic constants which control the stability, but not to the set of elastic constants appearing in the stress–strain relations at constant pressure.

1. Introduction

Equilibrium is a basic concept for discussion of phases and their linear elastic properties under hydrostatic pressure p . In a phase in a state of equilibrium, which will be defined precisely later, there are no forces present that move the crystal phase away from that state. The linear elasticity theory of the phase concerns the linear relation between small stresses and strains in the neighborhood of the equilibrium state.

When p changes the crystal state moves along a one-dimensional continuum of states in structure space, where a point corresponds to one structure. For crystals with one atom per cell, which we consider here, structure space has six dimensions, which can be the sides a, b, c and angles between sides α, β, γ of the unit cell. We shall call the one-dimensional continuum the equilibrium line and calculate the properties of the states on the line. The properties include p , the six structure parameters, volume V , internal energy E , Gibbs free energy $G \equiv E + pV$ (for a non-vibrating crystal), elastic constants c_{ij} , $i, j = 1-6$ and bulk modulus B . Each phase has an equilibrium line threading through the six-dimensional structure space; the properties along the line listed above then describe the static behavior as a function of pressure of the corresponding phase, which can be thought of as a quantum state of the infinite periodic crystal.

Of particular interest are the c_{ij} (defined later) which determine if the phase is stable or unstable, and B which relates stress changes (changes in p) to strain changes (changes in volume V) along the equilibrium line. Other elastic constants

called c_{ij}^V and c_{ij}^p enter stress–strain relations for arbitrary structures around the equilibrium state [1].

The purpose of this paper is to define the equilibrium line and show how to calculate it and the crystal properties along it, including the elastic constants and B . We show that B has a universal relation to the c_{ij} , the same at every p and not explicitly dependent on p , and derive that universal relation.

Section 2 defines equilibrium, shows how to find the direction of the equilibrium line, and illustrates the lines for body-centered-tetragonal (bct), body-centered-cubic (bcc) and face-centered-cubic (fcc) Al. The universal relation between the bulk modulus and one set of elastic constants is derived.

Section 3 comments on difficulties in calculating equilibrium lines.

2. Equilibrium, equilibrium lines and the bulk modulus

A state, by which we mean a solution of the electronic equations for fixed nuclear positions, is in equilibrium under pressure p if the internal stresses are isotropic with magnitude $-p$; then the internal stresses balance the applied pressure and the state is stationary. In an equilibrium state at pressure p_0 , volume V_0 the quantitative measure of stress is

$$\frac{1}{V_0} \left(\frac{\partial E}{\partial \varepsilon_i} \right)_{\varepsilon_j=0} = -p_0(\delta_{i1} + \delta_{i2} + \delta_{i3}),$$

$$i, j = 1-6, \quad j \neq i. \quad (1)$$

Hence at constant pressure p_0

$$\begin{aligned} \frac{1}{V_0} \left(\frac{\partial G}{\partial \varepsilon_i} \right)_{\varepsilon_j=0} &= \frac{1}{V_0} \left(\frac{\partial E}{\partial \varepsilon_i} \right)_{\varepsilon_j=0} + \frac{P_0}{V_0} \left(\frac{\partial V}{\partial \varepsilon_i} \right)_{\varepsilon_j=0} \\ &= \frac{1}{V_0} \left(\frac{\partial E}{\partial \varepsilon_i} \right)_{\varepsilon_j=0} + p_0(\delta_{i1} + \delta_{i2} + \delta_{i3}) = 0, \\ &i, j = 1-6, \quad j \neq i, \end{aligned} \quad (2)$$

and the first derivatives of G with respect to strain all vanish, which is a simple definition of equilibrium and agrees with a basic thermodynamic theorem. The expansion of V in strains used in (2) to evaluate $\partial V/\partial \varepsilon_i$ is given in [2].

Equilibrium states can be either stable, in which case G is a minimum with respect to the ε_i , or unstable, in which case strains exist which decrease G . The equilibrium states on one line belong to a particular phase, which can then be appropriately called stable or unstable at each p .

The neighboring equilibrium states to the equilibrium state p_0 , V_0 lie on the equilibrium line along which we can write

$$\begin{aligned} \left(\frac{dE}{dV} \right)_{V_0, p_0} &= -p_0; \\ \left(\frac{d^2 E}{dV^2} \right)_{V_0, p_0} &= - \left(\frac{dp}{dV} \right)_{V_0, p_0} = \frac{B_0}{V_0}, \end{aligned} \quad (3)$$

where the total derivatives are at the equilibrium point and B_0 is the bulk modulus there. Hence for small changes from the equilibrium at p_0 , V_0 along the equilibrium line we have from (3)

$$\delta E \equiv E - E_0 = -p_0 \delta V + \frac{B_0}{2V_0} (\delta V)^2, \quad (4)$$

$$\delta G \equiv G - G_0 = \delta E + p_0 \delta V = \frac{B_0}{2V_0} (\delta V)^2. \quad (5)$$

To find a strain which changes the crystal along the direction of the equilibrium line we have to find a strain for which δG satisfies (5). Introduce the expansion of δG in strains ε_i , $i = 1-6$ [2], which starts with second-order terms $\varepsilon_i \varepsilon_j$ since $\partial G/\partial \varepsilon_i = 0$, $i = 1-6$ from (2). Hence at constant p

$$\frac{\delta G}{V_0} = \frac{1}{2} \sum_{i,j=1}^6 c_{ij} \varepsilon_i \varepsilon_j, \quad (6)$$

which defines the c_{ij} as coefficients in the Taylor expansion of δG .

We now assume stresses exist in the crystal which correspond to a pressure change δp added to p

$$\delta \sigma_i = -\delta p(\delta_{i1} + \delta_{i2} + \delta_{i3}), \quad i = 1-6, \quad (7)$$

and calculate a special strain $\varepsilon_i^{\text{eq}}$ which produces $\delta \sigma_i$ from

$$-\delta p(\delta_{i1} + \delta_{i2} + \delta_{i3}) = \sum_{j=1}^6 c_{ij} \varepsilon_j^{\text{eq}}, \quad i = 1-6. \quad (8)$$

Substitution of (8) in (6) gives, using (3) and $\delta V = V_0(\varepsilon_1 + \varepsilon_2 + \varepsilon_3)$,

$$\begin{aligned} \frac{\delta G}{V_0} &= -\frac{\delta p}{2} \sum_{j=1}^6 (\delta_{i1} + \delta_{i2} + \delta_{i3}) \varepsilon_j^{\text{eq}} = \frac{-\delta p \delta V}{2V_0} \\ &= - \left(\frac{\delta p}{\delta V} \right) \frac{\delta V^2}{2V_0} = \frac{B_0}{2} \left(\frac{\delta V}{V_0} \right)^2. \end{aligned} \quad (9)$$

Thus (9) shows that δG from $\varepsilon_i^{\text{eq}}$ is in agreement with the behavior of G along the equilibrium line in (5), hence $\varepsilon_i^{\text{eq}}$, $i = 1-6$ gives a strain which moves the crystal along the equilibrium line.

We introduce the 6×6 compliance matrix $\{s_{ij}\}$, $i, j = 1$ to 6 reciprocal to $\{c_{ij}\}$

$$\{s_{ij}\} = \{c_{ij}\}^{-1}. \quad (10)$$

Consider (8) as a matrix times a vector equation and multiply by matrix $\{s_{ij}\}$. The sum of the first three rows of the product gives

$$\sum_{i,j=1}^3 s_{ij}(-\delta p) = \varepsilon_1^{\text{eq}} + \varepsilon_2^{\text{eq}} + \varepsilon_3^{\text{eq}} = \frac{\delta V}{V_0}, \quad (11)$$

or from (3) and (11)

$$B_0 = -V_0 \frac{\delta p}{\delta V} = \left(\sum_{i,j=1}^3 s_{ij} \right)^{-1}. \quad (12)$$

The formula (12) gives a universal relation between B and the s_{ij} , $i, j = 1-3$ which can also be expressed as rational fractions in terms of the c_{ij} , $i, j = 1-6$ (see Nye [3, p 147]). The relation (12) is the same as the one derived by Nye [3, p 146] at $p = 0$, but here generalized to crystals under pressure.

Figure 1(a) shows the sweeps of total internal energy E at constant V (called $E_V(c/a)$ curves). The minima of $E_V(c/a)$ curves give the equilibrium states of the bct, bcc and fcc phases of Al. The total-energy calculations were made with the well-tested WIEN2k band structure program [4] using a two-atom bct cell; the parameters such as R_{MT} , k -points in the Brillouin zone, etc used in the calculations can be found in [5].

The equilibrium lines for the bct, bcc and fcc phases of Al obtained from figure 1(a) are plotted in the two-dimensional structure space of the bct structure, coordinates c/a and V , as shown in figure 1(b). The states marked by open circles and open triangles are stable, the states marked by symbol \times are unstable. The stability of each of the equilibrium states is determined by a calculation of the eigenvalues of the 6×6 c_{ij} , $i, j = 1-6$ matrix. A minimum path (MNP) program which converges on minima of G finds the c_{ij} from trial sets of strains in (6) and calculates the eigenvalues [1]. A negative eigenvalue means the expansion in (6) is not positive definite, hence indicates instability [1, 6, 7].

The pressure values shown in figure 1(b) are obtained from figure 2, which shows the equation of state $p(V)$ for the bct, bcc phase and the fcc phase of Al. The p values come from dE/dV in (3). The Gibbs free energy $G = E + pV$ can then be calculated at each equilibrium volume. This procedure is the same as we used in our calculations of the equilibrium states of

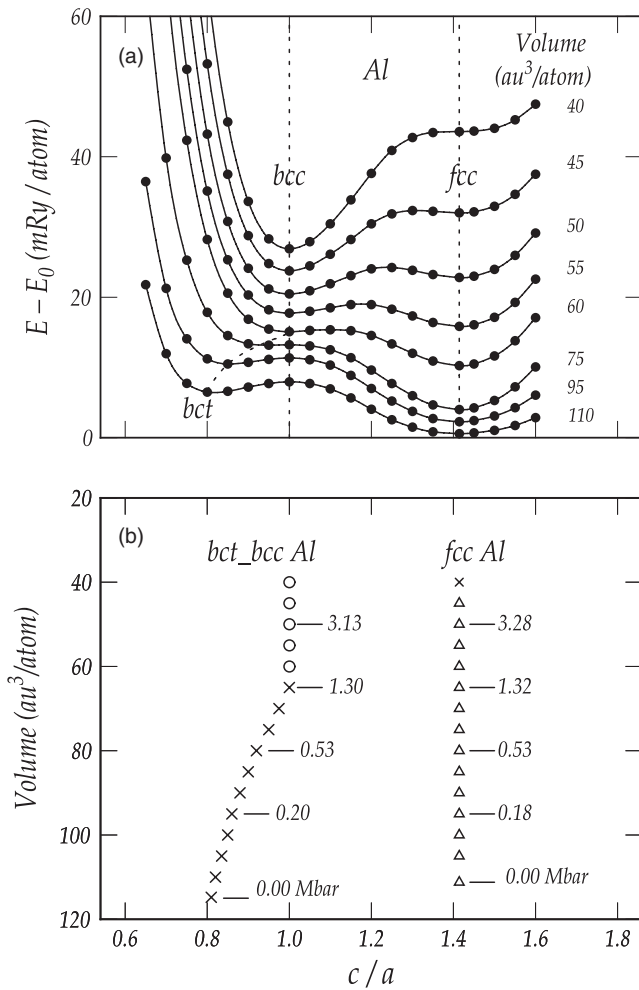


Figure 1. (a) Total internal energy as a function of c/a (called $E_V(c/a)$ curves) of Al at selected volumes; the reference energy E_0 is the total energy of fcc Al at $V = 110 \text{ au}^3/\text{atom}$. For clarity the $E_V(c/a)$ curves at volumes from 95 to $40 \text{ au}^3/\text{atom}$ are shifted toward E_0 by 6.60, 59.5, 237, 323, 448 and 620 mRyd/atom , respectively. The vertical dashed lines indicate the fcc phase at $c/a = 1.414$ and the bcc phase at $c/a = 1$. The curved dashed line denotes the bct phase which merges into bcc phase at $V = 65 \text{ au}^3/\text{atom}$. The solid lines interpolate between the calculated points. (b) Equilibrium lines for the bct_bcc and fcc phases of Al obtained from (a). The open circles and open triangles represent stable states, the crosses represent unstable states. The pressure values shown in (b) are obtained from figure 2.

vanadium [6] and Zn [7]. The bct_bcc phase is shown unstable until it becomes bcc and at $p > 1.3 \text{ Mbar}$.

Figure 3 shows $G(p)$ along the bct_bcc and fcc equilibrium lines. The inset shows the energy difference curve $G^{\text{bct_bcc}}(p) - G^{\text{fcc}}(p)$ indicating the phase transition from bcc to fcc at 2.7 Mbar .

3. Discussion

The concept of an equilibrium line in structure space is implicit in the equation of state $p(V)$, which is a function defined along the equilibrium line. We note that the equilibrium line and $p(V)$ are not easy to find in lower symmetry structures. For cubic structures with just one lattice parameter,

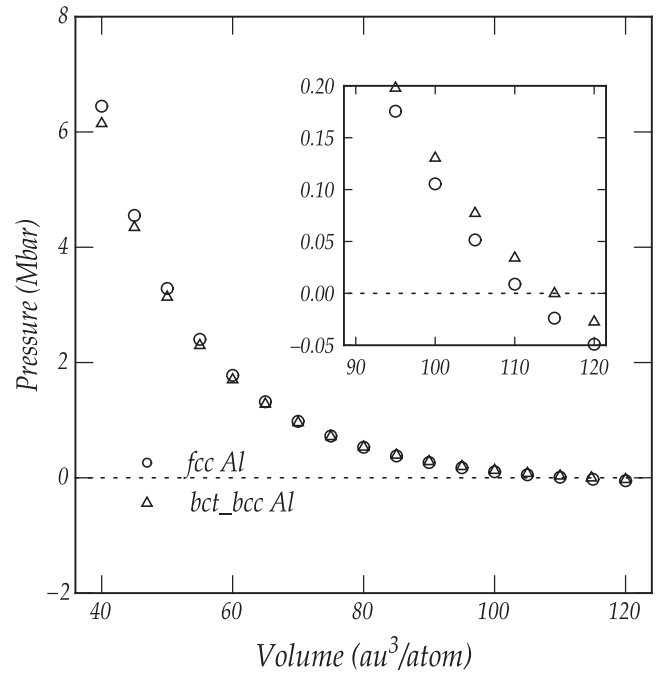


Figure 2. $p(V)$ curves for bct_bcc phase (open triangles) and fcc phase (open circles) of Al. The crossing of the $p(V)$ curve and the dashed line ($p = 0$) gives the equilibrium volume: $V_0^{\text{fcc}} = 111.2 \text{ au}^3/\text{atom}$, $V_0^{\text{bct}} = 114.8 \text{ au}^3/\text{atom}$.

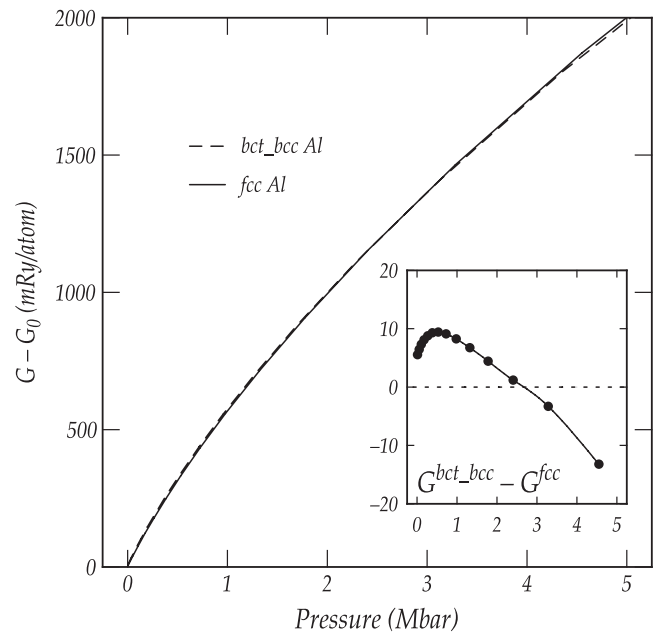


Figure 3. Gibbs free energies of the bct_bcc phase and the fcc phase of Al as a function of pressure, where $G_0 = -485.638965 \text{ mRyd/atom}$. The inset shows the free energy difference curve $G^{\text{bct_bcc}}(p) - G^{\text{fcc}}(p)$ of Al indicating the phase transition from bcc to fcc phase at 2.7 Mbar . The solid line interpolates between the calculated points.

the line and $E(V)$ and $p(V)$ are immediate. For lower symmetries additional minimizations of E with respect to lattice parameters are needed. We have chosen to show the equilibrium line for bct structure with two lattice parameters,

and to use sweeps of E at constant V to locate equilibrium states at V from minima of E , which give the equilibrium states immediately. This procedure is less work than finding minima of G at constant p , which would require a search for minima with respect to two lattice parameters.

We have shown that the stress–strain relation at constant pressure uses different coefficients than the c_{ij} , which we have called c_{ij}^p [1]. Hence use of c_{ij}^p to find the strain along the equilibrium line from additional stress δp would give the wrong strain (the c_{ij} must be used, as in (8)). However Sin’ko [8] assumed the stress–strain relation at constant pressure had as coefficients c_{ij} rather than c_{ij}^p , hence found the correct relation of B to the c_{ij} . Sin’ko limited the formulae he derived for B as a function of the c_{ij} to certain Bravais symmetry cases, whereas (12) applies to all symmetry cases.

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