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Elasticity in crystals under pressure

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Abstract

The elastic behavior and stability of elemental crystals are studied in the neighborhood of a stable equilibrium state, also called a phase, at finite pressure p . It is shown that two kinds of elastic constants are needed to describe elasticity under pressure. One set, designated as c_{ij} , $i, j = 1-6$, determines stability or lack of it; another set, designated as c_{ij}^p , describes the linear relation between small additional stresses and strains added to the crystal in equilibrium at p . The stress-strain coefficients c_{ij}^p differ from previous formulations of the stress-strain relations by Barron and Klein (1965 *Proc. Phys. Soc.* **85** 523) and Wallace (1972 *Thermodynamics of Crystals* (New York: Wiley)), who give c_{ij} as stress-strain coefficients. Hence we were led to verify the use of the c_{ij}^p using a first-principles numerical calculation example for face centered cubic Al at 1500 kbar. The Gibbs free energy G of the crystal under pressure is shown to provide both a simple definition of equilibrium and an efficient way to calculate all the elastic constants of a general crystal. A computer program finds stable phases by making jumps in structure from an arbitrary initial structure; the jumps converge to minima of G with respect to the structure. In the calculation, 21 elastic constants are evaluated from a special set of G values and the 6×6 elastic constant matrix is tested for stability.

1. Introduction

Linear elasticity theory in crystals in equilibrium states under hydrostatic pressure p concerns two properties of the state: (1) the coefficients of a linear relation between added small strains and the stresses produced in the crystal, (2) the stability of the equilibrium structure. Later a precise definition of equilibrium will be given, but basically equilibrium is a state in which there are no unbalanced stresses, i.e., p is balanced by an internal stress $-p$.

Papers developing the theory include the classic formulations of Barron and Klein [1] and of Wallace [2] as well as some more recent publications that will be cited [3–10]. In [1, 2] two sets of elastic constants are introduced: (1) the set we will designate c_{ij} , $i, j = 1-6$, which we will show are the coefficients of the second-order terms in an expansion of the Gibbs free energy of a non-vibrating crystal $G \equiv E + pV$ (where E is the internal energy and V the volume) in strains around an equilibrium point, (2) a set we will designate by c_{ij}^V , $i, j = 1-6$ which are the coefficients of the second-order terms in an expansion of E in strains around equilibrium. Both [1] and [2] find that the c_{ij} are the coefficients in the stress-strain relations ([1], equation 5.2, [2], equation 2.52). All the papers [1–10], including our own, believe that there is one basic set of elastic constants, the c_{ij} , that fit three properties

of the equilibrium state (stability condition, stress-strain relations, elastic equations of motion). These properties are not derived in [3–10], but reference is made to [1, 2]. Most of [3–10] evaluate the c_{ij} from changes in E produced by strains, we find c_{ij} from changes in G , Wang *et al* [8] find what they consider the basic set from evaluation of the coefficients in stress-strain relations.

What is new in this paper is that we find that the coefficients in stress-strain relations are given by a third set of elastic constants c_{ij}^p , $i, j = 1-6$, which are not specifically introduced or related to the c_{ij} in any of [1–10]. This disagreement with previous papers, particularly [1] and [2], on elasticity under hydrostatic pressure p led us to make a numerical verification of the stress-strain relation by comparison of the stress found by differentiating E with respect to strains in the strained lattice; this calculated stress is shown equal to the sum of the coefficients c_{ij}^p multiplying the strains.

Although we have introduced three sets of elastic constants (c_{ij} , c_{ij}^V , c_{ij}^p), there are only two independent sets since the c_{ij}^V reduce to c_{ij}^V when the strain keeps the volume constant. An important conclusion is that the elastic equations of motion must also use the c_{ij}^p , hence elastic wave velocities should be calculated with the c_{ij}^p .

States of a crystal are the static quantum states which are first-principles solutions of the electronic equations (e.g.,

the Kohn–Sham equations with corrections) with fixed nuclear positions. We are concerned about elastic properties in the subset of states called equilibrium states and in the further subsets which are the stable equilibrium states called phases.

We limit the development here to non-vibrating crystals with one atom per unit cell, i.e., to elements. A state has calculable values of six structural parameters, also called lattice parameters, which could be the sides a, b, c and angles α, β, γ of the unit cell as a parallelepiped, and also has values of E and V . If an external pressure p is present, the Gibbs free energy G can be defined for any state—equilibrium is not required. Definitions of stress, strain, and elastic constants will be given for small perturbations around the equilibrium states which were used as reference states.

Sections 2.1 and 2.2 give the strain expansions of δG and δE around equilibrium and define the corresponding elastic constants c_{ij}, c_{ij}^V .

Section 2.3 derives the linear stress–strain relations at constant pressure and defines the c_{ij}^p .

Section 2.4 provides a numerical check that the stress–strain relations use the c_{ij}^p .

Section 3 describes the minimum path program (MNP) which finds all the c_{ij} of a given structure at a given p from δG , tests that structure for stability and converges to a minimum of G .

Section 4 discusses the consequences of having two sets of elastic constants and gives example of failures to choose the correct set. The advantages of using G in the theory are described; it is noted that the bulk modulus is related to the c_{ij} , not the c_{ij}^p .

2. Expansions in strains around equilibrium states

Equilibrium states can be defined either as states in which all first derivatives of G with respect to strains $\varepsilon_i, i = 1-6$ vanish at constant pressure or in which all but one of the first derivatives of E at constant volume vanish. (The decrease by one is due to the constraint of constant volume V .) Stable equilibrium requires that G or E be a minimum with respect to small strains at constant pressure or constant volume respectively. These definitions come from thermodynamic theory [11]. That theory is here simplified to consideration of a small number of degrees of freedom, namely the six independent strains ε_i . All small homogeneous deformations can be expressed as a superposition of strains [12].

Our strain expansions could be in either Eulerian strains or Lagrangian strains as in [1, 2]. However Lagrangian strains mix first- and second-order displacement gradients, and complicate the separation of first- and second-order strain effects, hence we have chosen the simpler Eulerian form.

2.1. δG expansion in strains

Around an equilibrium state changes in G can be expanded to second order in powers of strains using only second-order terms $\varepsilon_i \varepsilon_j$, since first derivatives of G vanish. Hence we have

$$\frac{\delta G}{V_0} \equiv \frac{G(\underline{\varepsilon}) - G_0}{V_0} = \frac{1}{2} \sum_{i,j=1}^6 c_{ij} \varepsilon_i \varepsilon_j, \quad (1)$$

where G_0 is the value of G at the equilibrium state, V_0 the volume at the equilibrium state and $\underline{\varepsilon}$ is a vector with components $\varepsilon_i, i = 1-6$ that give all components of the strain tensor; then (1) gives a quantitative definition of the c_{ij} at p . The condition for stability that G be a minimum for all small strains is the same as the condition that the quadratic form in ε_i in (1) be positive definite, or, equivalently, that the 6×6 matrix c_{ij} has all positive eigenvalues [2]. The c_{ij} are functions of p and thus determine the stability or instability of a phase at p . The paper by Ackland and Reed [7], equation A14 also gives the expansion (1) of δG around an equilibrium state. The expansion (1) is also given in our previous papers [6].

The simple condition for an equilibrium state in (1) has been criticized as wrong in several ways [3, 4]. These criticisms illustrate misunderstandings of the meaning of the Gibbs free energy. In [3] the authors wrongly state that ‘‘since strained crystal states are essentially non-equilibrium, it is impossible to determine the Gibbs free energy . . . at such states’’ ([3], p 8101), overlooking the fact that the definition here is clearly applicable to such states and is a well-defined thermodynamic state function. In [4] the authors wrongly state that ‘. . . the derivatives $(\partial^2 G / \partial \varepsilon_i \partial \varepsilon_j) / V$, which are not in any case elastic constants’ ([4], p 8784), and ‘. . . strain derivatives of the Gibbs free energy G . . . do not yield properly defined elastic constants’ ([4], p 8785), whereas (1) clearly shows that c_{ij} are the second strain derivatives of G .

At an equilibrium state (1) also provides a direct simple way of evaluating the c_{ij} with one calculation of G needed for each additional c_{ij} by choosing suitable strains with which to find δG . This procedure is used to find the 21 elastic constants for the case of no symmetry in our minimum path program (MNP) (see section 3). This procedure based on δG evaluations is simpler than procedures based on E , which require evaluation of second derivatives of E [10].

The MNP program also uses (1) to find stable equilibrium structures by making a series of jumps in structure that home in on minima of G . We also have used a computational procedure based on (1) for finding equilibrium states of body-centered-tetragonal (bct) or hexagonal close-packed (hcp) structures (each has two structural parameters) which follows the epitaxial Bain path (EBP); the EBP incorporates a minimum of G as one parameter varies at a value of a second structural parameter, then follows the EBP as the second parameter varies until the path shows a second minimum which gives the stable equilibrium state [13].

2.2. δE expansion in strains

From

$$\frac{\delta G}{V_0} = \frac{\delta E}{V_0} + p \frac{\delta V}{V_0} \quad (2)$$

by expanding δV in strains to second order [14]

$$\begin{aligned} \frac{\delta V}{V_0} &\equiv \frac{V(\underline{\varepsilon}) - V_0}{V_0} \cong \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_1 \varepsilon_2 + \varepsilon_2 \varepsilon_3 + \varepsilon_3 \varepsilon_1 \\ &\quad - \frac{1}{4}(\varepsilon_4^2 + \varepsilon_5^2 + \varepsilon_6^2), \end{aligned} \quad (3)$$

Table 1. Lattice parameters a_0 , c_0 and volume/cell V_0 for bct cell of fcc Al at $p = 1500$ kbar and elastic constants c_{ij} , c_{ij}^V , c_{ij}^p in Mbar, referred to bct orthogonal axes at 45° in the x - y plane to fcc orthogonal axes.

<hr/>						
$a_0 = 4.472\,527$ au,						
$c_0 = 6.290\,222$ au,						
$V_0 = a_0^2 c_0 = 125.826\,442$ au ³ /cell						
<hr/>	<hr/>					
ij	11	12	13	33	44	66
<hr/>	<hr/>					
c_{ij}	9.199	2.820	4.881	7.043	3.197	1.214
c_{ij}^V	9.199	1.320	3.381	7.043	3.947	1.964
c_{ij}^p	10.699	2.820	4.881	8.543	3.947	1.964
<hr/>	<hr/>					

$$\delta\sigma_1 = c_{11}^p \varepsilon_1 + c_{12}^p \varepsilon_2 = 0.27 \text{ Mbar.} \quad (14)$$

For the strain $\underline{\varepsilon}^{(1)}$, which changes V , only the c_{11}^p coefficients are correct.

Similarly with $\underline{\varepsilon}^{(4)} \equiv (0, 0, 0, 0.04, 0, 0)$ with $\delta V = 0$ to first order in ε_4 , differentiation of $E(\underline{\varepsilon}^{(4)})$ gives

$$\delta\sigma_4^p(\underline{\varepsilon}^{(4)}) = 0.16 \text{ Mbar} \quad (15)$$

$$c_{44}\varepsilon_4^{(4)} = 0.13 \text{ Mbar} \quad (16)$$

$$c_{44}^V\varepsilon_4^{(4)} = c_{44}^p\varepsilon_4^{(4)} = 0.16 \text{ Mbar.} \quad (17)$$

Again the c_{44}^p coefficient is correct, but also c_{44}^V , whereas c_{44} is not.

3. The minimum path (MNP) programs

The MNP programs use the expansion of δG around any crystal state of any symmetry in strains of that state to find a path to a state at a minimum of G at a given pressure p . That minimum state is then a phase. Thus far the states are restricted to one atom per primitive cell, hence apply to elements, but generalization is possible to more atoms in the cell. In the general one atom per cell state, G has an expansion in strains that is a generalization of (1)

$$\frac{\delta G}{V_0} = \frac{G - G_0}{V_0} = \sum_{i=1}^6 c_i \varepsilon_i + \frac{1}{2} \sum_{i,j=1}^6 c_{ij} \varepsilon_i \varepsilon_j. \quad (18)$$

Terms linear in the ε_i are needed in (18), since the state is not generally an equilibrium state. In (18) G_0 is the value of the Gibbs free energy at the initial state and G the value at a structure strained from the initial state. The coefficients c_i , c_{ij} are evaluated by calculating δG at a set of strains chosen to find the coefficients individually one at a time. There are 27 coefficients c_i , c_{ij} requiring 28 values of G , including G_0 . Since the program is designed to work with any unit cell, a standard set of orthogonal axes is used (x_1 is along \underline{a} , x_2 in \underline{ab} plane $\perp x_1$, $x_3 \perp x_1$ and x_2). These axes will not necessarily coincide with symmetry axes (but will for cubic, tetragonal and orthorhombic symmetries). Hence the program always evaluates 6 c_i and 21 c_{ij} coefficients.

The choice of the 12 strains $\pm\varepsilon_i$, $i = 1-6$, $\varepsilon_j = 0$, $j \neq i$, $j = 1-6$, gives 12 equations for 6 c_i and 6 c_{ii}

$$\frac{\delta G(\pm\varepsilon^{(i)})}{V_0} = \pm c_i \varepsilon_i + \frac{1}{2} c_{ii} \varepsilon_i^2, \quad i = 1-6, \quad (19)$$

where $\pm\varepsilon^{(i)}$ means a strain vector with only one nonzero component $\pm\varepsilon_i$. The sum and difference of δG for $\pm\varepsilon_i$ give linear equations for c_{ii} and c_i respectively.

The choice of the 15 two-component strains (two nonzero strains) $\underline{\varepsilon}^{(ij)} = (\dots \varepsilon_i \dots \varepsilon_j \dots)$, $i, j = 1-6$, $i \neq j$, $i < j$ gives 15 more equations for c_{ij} ,

$$\frac{\delta G(\underline{\varepsilon}^{(ij)})}{V_0} = c_i \varepsilon_i + c_j \varepsilon_j + \frac{1}{2} c_{ii} \varepsilon_i^2 + \frac{1}{2} c_{jj} \varepsilon_j^2 + c_{ij} \varepsilon_i \varepsilon_j. \quad (20)$$

Then (20) is a linear equation for c_{ij} using previously determined values of c_i , c_j , c_{ii} , c_{jj} ; and $c_{ji} = c_{ij}$ fills out the 6×6 symmetric matrix of c_{ij} .

Once the 27 c_i and c_{ij} are calculated, we solve 6 simultaneous linear equations for ε_i that would take the crystal exactly to a minimum of G if the expansion to second order in strains in (18) were exact; these equations are given by

$$\frac{\partial G}{\partial \varepsilon_i} = c_i + \sum_{j=1}^6 c_{ij} \varepsilon_j = 0. \quad (21)$$

Since the expansion to second order in (18) is not exact, the c_i found from (21) are finite, but in the strained state given by the solution of (21) the new c_i are smaller. Repetition of the process starting from the strained state found from (21) converges rapidly toward a minimum of G , using as a convergence criterion that all the c_i are less than a given size.

The program checks whether the curvatures of G with respect to all strains are positive, as would be expected in a 'bowl' of G values around the given state. The check is made by determining whether all six eigenvalues of the c_{ij} matrix are positive. If negative eigenvalues appear indicating negative curvature for some strains the program selects the most negative eigenvalue and takes steps in the direction of decreasing G obtained from the eigenfunction of that eigenvalue leading to a minimum. The check is repeated until all eigenvalues are positive, then (21) is used to converge to a minimum of G . In figure 1 we show both the sequence of jumps in the ε_i from (21) (solid lines, called CASE1) and also steps in a direction to lower G from the eigenfunctions of negative eigenvalues (dashed line, called CASE2) starting from an initial fcc state for Zn and a bcc state for vanadium, both known to be unstable [16, 17]. The sequence of states terminates in rhombohedral states (which are denoted as rh^l and rh^u in [16, 17]).

The MNP programs track down stable phases, they determine elastic constants c_{ij} in equilibrium and they check the stability of any given one-atom-per-cell structure by checking that all eigenvalues of the c_{ij} matrix are positive. We illustrate the application to finding c_{ij} in table 2, which compares c_{ij} for Al and Cu at $p = 0$ with experiment [18, 19] and with a recent first-principles program for calculation of elastic constants using statistical theory to reduce random errors [20]. Comparison to experiment shows that the MNP results are as good as or better than the elaborate procedure in [20].

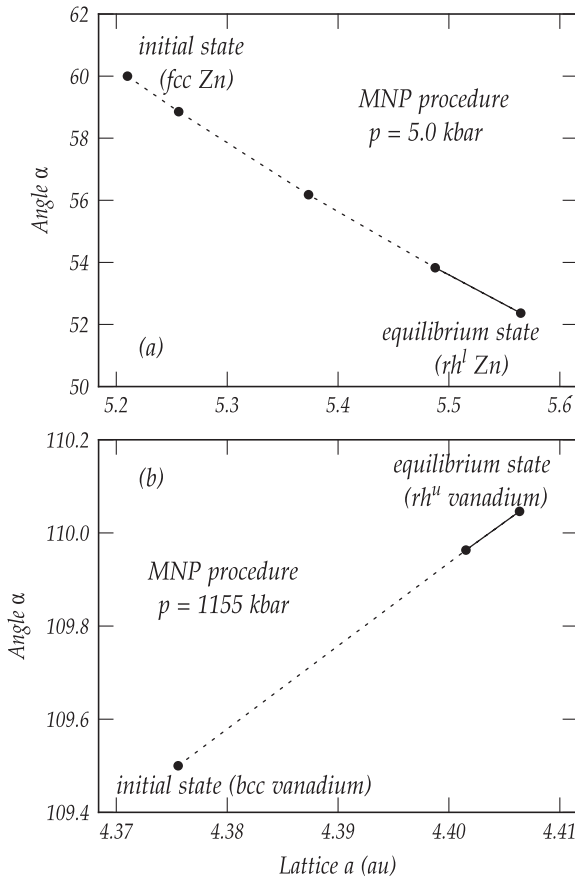


Figure 1. (a) The paths to the minima of G of the rhombohedral phase of Zn at 5.0 kbar starting from an initial fcc phase as found with the MNP procedure. (b) The paths to the minima of G of the rhombohedral phase of vanadium at 1155 kbar starting from an initial bcc phase as found with the MNP procedure. In both (a) and (b) the solid (dashed) lines between the stage's points are CASE1 (CASE2) stages (see the text).

4. Discussion

The new feature introduced in this paper is that one must use two sets of elastic constants to describe the behavior of a crystal under pressure. Previously one set, the c_{ij} , was thought to describe stability, stress–strain relations and the elastic equations of motion. The second set c_{ij}^p needed for stress–strain relations and elastic equations of motion has not explicitly appeared before and its relation to the c_{ij} exhibited, but has implicitly been evaluated by Wang *et al* [8] from direct calculation of stress–strain relations.

The belief that one set of elastic constants fitted all the properties has led to applications of the c_{ij} and c_{ij}^p in some papers, with which we disagree. Thus Landa *et al* [9] used the c_{ij}^V , the form of the c_{ij}^p that applies to strains that keep V constant, to discuss stability in vanadium, whereas the c_{ij} give results in better agreement with experiment [17]. Wang *et al* [8] used directly calculated c_{ij}^p (different notation is used in [8]) to discuss stability in zinc blende lattices under pressure, rather than the c_{ij} . Sin'ko [10] assumes the c_{ij} are the coefficients in the stress–strain relation rather than the c_{ij}^p . Steinle-Neumann *et al* [5] use the c_{ij} to calculate elastic wave velocities in hcp Fe under pressure rather than the c_{ij}^p .

Table 2. Comparison of the MNP results with the experimental data [18, 19] and the calculated data [20] of the lattice constant a , the elastic constants c_{11} , c_{12} , c_{44} of fcc Al and fcc Cu at $p = 0$ and $T = 0$. The experimental data stem from [18] for the lattice constants (extrapolated to 0 K values), and from [19] for the elastic constants (0 K values).

Fcc Al	a (au)	c_{11} (Mbar)	c_{12} (Mbar)	c_{44} (Mbar)
This work	7.646	1.114	0.601	0.329
Exp. [18, 19]	7.620	1.143	0.619	0.316
Theory [20]	7.542	1.200	0.610	0.340
Fcc Cu	a (au)	c_{11} (Mbar)	c_{12} (Mbar)	c_{44} (Mbar)
This work	6.849	1.752	1.145	0.742
Exp. [18, 19]	6.809	1.762	1.249	0.818
Theory [20]	6.726	2.140	1.550	0.990

The key to deriving the new elastic constants c_{ij}^p is the initial simple expansion of δG in strains with only second-order terms $\varepsilon_i \varepsilon_j$ in (1). Then rearrangement in (4) gives δE a simple expansion in first-order and second-order strains with p and the coefficients c_{ij} constants. Hence stresses are straightforwardly found by differentiating E with respect to strain components, which gives the c_{ij}^p as coefficients in (9). To verify that this new stress–strain relation with c_{ij}^p is correct, we make the numerical calculation on fcc Al at 1500 kbar in section 2.4.

We are not clear on why Barron and Klein [1] and Wallace [2] did not find the c_{ij}^p coefficients in stress–strain relations. We note that [1, 2] try to solve a more difficult and more general problem than we do, namely the stress–strain relations in an arbitrary initial state, which will generally contain anisotropic stresses. They do not mention equilibrium, whereas we discuss only small perturbations around equilibrium. The stress–strain formulae for the isotropic applied stress considered here are then obtained by specializing the general formulae.

The bulk modulus $B = -V dp/dV$ from the equation of state $p(V)$ is a stress (δp)–strain (δV) relation along what can be called the equilibrium line, i.e., the succession of equilibrium states as both p and V change. One might then expect B to be related to the c_{ij}^p , which describe stress–strain relations. But the usual stress–strain relation is in a non-equilibrium state at one value of p , whereas B is the stress–strain coefficient for equilibrium states and is in fact related to the c_{ij} by formulae independent of p . In another paper we show that the c_{ij} produce strains along the equilibrium line for a given stress δp , hence prove that B is related to c_{ij} , and give the explicit form of that relation for arbitrary symmetry [21].

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References

- [1] Barron T H K and Klein M L 1965 *Proc. Phys. Soc.* **85** 523
- [2] Wallace D C 1972 *Thermodynamics of Crystals* (New York: Wiley)
- [3] Sin'ko G V and Smirnov N A 2004 *J. Phys.: Condens. Matter* **16** 8101
- [4] Steinle-Neumann G and Cohen R E 2004 *J. Phys.: Condens. Matter* **16** 8783
- [5] Steinle-Neumann G, Stixrude L and Cohen R E 1999 *Phys. Rev. B* **60** 791
- [6] Marcus P M, Ma H and Qiu S L 2002 *J. Phys.: Condens. Matter* **14** L525
Ma H, Qiu S L and Marcus P M 2002 *Phys. Rev. B* **66** 024113
- [7] Ackland G J and Reed S K 2003 *Phys. Rev. B* **67** 174108
- [8] Wang S Q, Ye H Q and Yip S 2006 *J. Phys.: Condens. Matter* **18** 395
- [9] Landa A, Klepeis J, Söderlind P, Naumov I, Velikokhatnyi O, Vitos L and Ruban A 2006 *J. Phys.: Condens. Matter* **18** 5079
Landa A, Klepeis J, Söderlind P, Naumov I, Velikokhatnyi O, Vitos L and Ruban A 2006 *J. Phys. Chem. Solids* **67** 2056
Lee B, Rudd R E, Klepeis J E, Söderlind P and Landa A 2007 *Phys. Rev. B* **75** 180101
- [10] Sin'ko G V 2008 *Phys. Rev. B* **77** 104118
- [11] Landau L D and Lifshitz E M 1980 *Statistical Physics* 3rd edn, part 1 (Oxford: Pergamon)
- [12] Nye J F 1985 *Physical Properties of Crystals* (Oxford: Clarendon)
- [13] Marcus P M, Jona F and Qiu S L 2002 *Phys. Rev. B* **66** 064111
- [14] Qiu S L, Apostol F and Marcus P M 2008 *J. Phys.: Condens. Matter* **20** 345233
- [15] Blaha P, Schwarz K, Madsen Kvasnicka G D and Luitz J 2001 *WIEN2k, An augmented Plane Wave + Local Orbitals Program for calculating Crystal Properties* Karlheinz Schwarz, Techn. Universität Wien, Austria (ISBN 3-9501031-1-2)
Blaha P, Schwarz K and Sorantin P 1990 *Comput. Phys. Commun.* **59** 399
- [16] Qiu S L and Marcus P M 2008 *Eur. Phys. J. B* **66** 1
- [17] Qiu S L and Marcus P M 2008 *J. Phys.: Condens. Matter* **20** 275218
- [18] Touloukian Y S, Kirby R K, Taylor R E and Desai P D 1979 *Thermal expansion metallic elements and alloys Thermophysical Properties of Matter* vol 12 (New York: IFI/Plenum)
Pearson W B 1967 *A Handbook of Lattice Spacing and Structures of Metals and Alloys* (Oxford: Pergamon)
- [19] Simmons G and Wang H 1971 *Single Crystal Elastic Constants and Calculated Aggregate Properties: a Handbook* (Cambridge, MA: MIT Press)
- [20] Page Y L and Saxe P 2001 *Phys. Rev. B* **63** 173103
- [21] Marcus P M and Qiu S L 2009 *J. Phys.: Condens. Matter* at press