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# Lattice parameters of aluminium in the Mbar range by first-principles

F Jona and P M Marcus

Department of Materials Science and Engineering, State University of New York, Stony Brook, NY 11794-2275, USA

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## Abstract

Using the WIEN2k band-structure program in the generalized gradient approximation (GGA) and a procedure based on minimization of the Gibbs free energy at 0 K, we calculate the lattice parameters of face-centred-cubic (fcc) and of hexagonal-close-packed (hcp) aluminium in the pressure range from 1.8 to 3.3 Mbar. The results are compared to the experimental data published by Akahama *et al.* The agreement between theory and experiment is better than 1% for the lattice parameters and the axial ratio, and better than 2% for the equation of state. The rigid-lattice transition pressure from intersection of Gibbs free-energy curves is 1.92 Mbar.

## 1. Introduction

The characterization of aluminium as one of the simplest metals with a close-packed face-centred-cubic (fcc) structure and no 3d electrons has made it an attractive system for several theoretical and experimental studies starting about 30 years ago. The theoretical interest was stimulated by the absence of d electrons at ambient pressure and by the consequences of lowering the energy and partial filling of the 3d band with increasing hydrostatic pressure. The calculations aimed at the determination of the equation of state (EOS) and relative phase stability as a function of pressure. A common feature of the studies reported in the last 20 years is a sequence of structure changes with increasing pressure from fcc to hcp and then to bcc (body-centred cubic), a sequence similar to that observed in the transition-series elements with increasing atomic number.

Early theoretical work [1] and a shock-compression experiment [2] had failed to find a pressure-induced transition up to 3 Mbar (300 GPa) and 10 Mbar, respectively, but a 1982 study by McMahan and Moriarty [3, 4] concentrating on *energy* (as opposed to enthalpy or Gibbs free energy) differences between the fcc, hcp and bcc structures predicted the sequence mentioned above and gave values for the transition pressures involved. A problem, however, was that the two methods used for the calculations predicted notably different transition pressures: the generalized pseudopotential technique (GPT) predicted 3.6 Mbar for the fcc–hcp transition,

while the all-electron linear muffin-tin-orbital (LMTO) method within the so-called atomic-sphere approximation (ASA) predicted 1.2 Mbar. A 1983 study by Lam and Cohen [5] by the *ab initio* self-consistent pseudopotential (AP) technique found the same sequence of structures, but predicted the rigid-lattice fcc-hcp transition to occur 'at about 2 Mbar'. These authors did calculate the enthalpy  $H = E + pV$  ( $E$  = energy per atom,  $V$  = volume per atom,  $p$  = pressure) and used Murnaghan's EOS to fit the calculated energies and then obtain the pressure from the derivative  $-dE/dV$ , but found the volume changes at the transition to be small, and hence concluded that the stable phase could be determined by comparing total energies without the  $pV$  term, as was done in [3] and [4]. The contribution of the vibrational energy was considered 'probably not important' in determining phase stability and it was therefore not included in the total-energy calculations.

The discrepancies among the predictions of the fcc  $\rightarrow$  hcp transition pressure (1.2, 3.6 and 2.0 Mbar) were left unchallenged until an experiment by Ruoff and co-workers [6], using the diamond-anvil-cell (DAC) technique, measured the EOS and the crystal structure of Al up to 2.19 Mbar ( $V/V_0 = 0.50$ ,  $V_0$  is the volume at  $p = 0$ ) and found no evidence for a transition. This result prompted Boettger and Trickey [7] to make a new calculation using a linear combination of Gaussian-type orbitals-fitting function (LCGTO-FF) combined with a rough estimate for the impact of zero-point motion on the transition. These authors used the crossing of enthalpy curves to determine the fcc  $\rightarrow$  hcp transition pressure, albeit treating the hcp phase at ideal  $c/a$  only. The transition was thus predicted to occur at  $2.05 \pm 0.2$  Mbar ( $V/V_0 = 0.51$ ), neglecting both zero-point and thermal-phonon contributions. Estimates of these contributions moved the transition pressure to upper bounds of 2.82 Mbar at 0 K and 2.90 Mbar at room temperature. These results, the authors conclude, suggest that the DAC experiment of Ruoff and co-workers [6] came close to observing the fcc  $\rightarrow$  hcp transition.

All the above theoretical studies adopted the local-density approximation (LDA) to density-functional theory. A more recent work, by Sin'ko and Smirnov [8], uses the full-potential linear muffin-tin orbital (FPLMTO) technique with the generalized gradient approximation (GGA) together with the Debye treatment of the vibrating lattice to calculate the EOS, the elastic constants and their dependence on volume, and the phase stability of Al. From the crossing of Gibbs free-energy curves in their figure 1 we read about 1.7 Mbar for the rigid-lattice fcc  $\rightarrow$  hcp transition pressure, and about 2.2 Mbar after inclusion of zero-point vibrations.

The definitive statement about the transition was made recently by Akahama *et al* [9] with a powder x-ray diffraction and DAC experiment at pressures up to 3.33 Mbar. In this experiment, as in the one by Ruoff and co-workers, no pressure-transmitting medium was used, which may at the outset suggest some doubts about the hydrostaticity of the applied pressure. However, the authors note that the very low errors in the measured average pressure, together with the closeness of the results obtained with different anvil culet sizes, indicate that the Al sample (a foil) acted as a good pressure-transmitting medium. The fcc  $\rightarrow$  hcp transition was found to occur at  $2.17 \pm 0.1$  Mbar ( $V/V_0 = 0.509$ ). Thus this result is in general agreement with theoretical predictions, and hence provides experimental evidence for the important role played by d electrons in the transition owing to the gradual filling of the initially unoccupied 3d band as the crystal is compressed. An additional valuable product of the Akahama *et al* experiment is the publication of the pressure dependence of the lattice constants of both fcc and hcp Al in the range from 1.8 to 3.33 Mbar, which inspired the present theoretical work.

None of the published theoretical studies on Al reported directly on the dependence of the lattice constants upon pressure, with the possible exception of [1] for fcc Al in the lower-pressure region up to about 1 Mbar. All the theoretical studies used the LDA except [8] and they all used the procedure of minimizing the energy  $E$  with respect to structural deformations under

the constraint of constant volume  $V$ , a procedure which requires knowledge of the function  $p(V)$  to fix the value of the pressure  $p$ . By contrast, in the present work we follow our well-tested procedure [10] of determining equilibrium structure at a pressure  $p$  by minimizing the Gibbs free energy per atom  $G = E + pV - TS$  (at 0 K, where  $G$  is equivalent to the enthalpy;  $T =$  temperature,  $S =$  entropy) with respect to structure. In the present cases of fcc Al, which we treat as body-centred tetragonal (bct) with structural parameters  $a_{\text{bct}}$  and  $c_{\text{bct}}$ , and hcp Al, with structural parameters  $a_{\text{hcp}}$  and  $c_{\text{hcp}}$ ,  $G$  is minimized with respect to both the  $a$  and the  $c$  parameters (here we drop the subscripts for brevity) at a given  $p$ . This procedure directly yields the pressure dependence of  $a$ ,  $c$ ,  $E$  and  $G$  in both phases. The treatment of fcc Al in bct symmetry permits use of the epitaxial Bain path for the tetragonal structure at a given pressure. We determine the equilibrium lattice parameters at the minimum of  $G$  on the epitaxial Bain path at that pressure. The usual procedure of evaluating  $E$  at constant  $V$  does not give the pressure  $p$  directly.

Some details of the calculations are given in section 2; the results are presented in section 3 and discussed in section 4.

## 2. Computation details

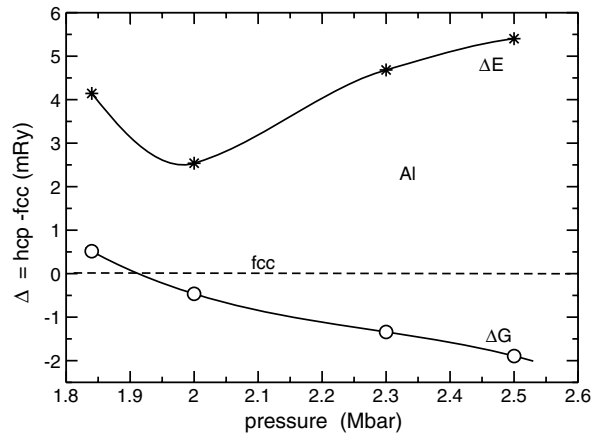
The calculations were done with the WIEN2k computer program developed by Blaha *et al* [11]. This program uses the FPLAPW (full-potential linearized augmented plane-wave) method for computation of the electronic structure of solids from the Kohn–Sham equations of density functional theory [12, 13] in the generalized gradient approximation (GGA). The procedure for finding the minima of the Gibbs free energy  $G$  (at  $T = 0$  K) as a function of the tetragonal or hexagonal lattice parameters  $a$  and  $c$  has been described in detail elsewhere [14] and will be only briefly summarized here.

For any value of the pressure  $p \neq 0$  one chooses a value of  $a = a_1$  and varies the value of  $c$  until one finds the values  $c = c_1$  and  $E = E_1$  at which the slope of the energy  $E$  is  $(\partial E/\partial c)_a = -p a_1^2 \sin \gamma/2$ , where  $\gamma$  is the angle between the  $a$  and  $b$  vectors ( $90^\circ$  for bct structures,  $120^\circ$  or  $60^\circ$  for hcp structures). This condition on the slope of  $E$  makes the stress  $\sigma_3$  in the  $c$  direction equal to  $-p$  [10], which is the epitaxial boundary condition. Then  $G_1 = E_1 + pV_1$  is the value of the free energy at 0 K on the so-called epitaxial Bain path (EBP) at  $a_1$  and at pressure  $p$  ( $V_1$  is calculated from  $a_1$  and  $c_1$ ). The procedure is repeated for a sequence of choices of  $a$ , providing values of  $G$  until a minimum of  $G$  is reached; this minimum gives the equilibrium structure and  $G$  at the chosen pressure  $p$ . Thus by choosing different values of  $p$  one determines an equilibrium path along which  $G(p)$ ,  $a(p)$ ,  $c(p)$  and  $V(p)$  are determined *directly*, i.e., with no need of constant-volume calculations to find equilibrium and the equilibrium pressure from  $-(dE/dV)$ .

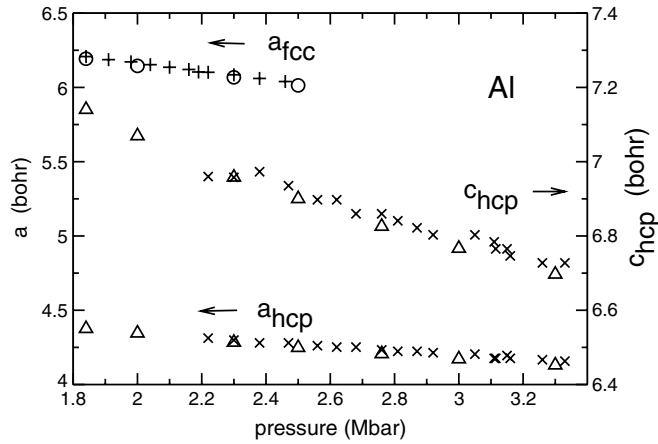
The parameters used in the WIEN program for fcc and hcp Al were: muffin-tin radius  $\text{RMT} = 1.9$  bohr; plane-wave cutoff  $\text{RK}_{\text{max}} = 10.0$ ; largest vector in the charge-density Fourier expansion  $\text{GMAX} = 16$  bohr $^{-1}$ ;  $k$ -point sampling in the Brillouin zone of 16 000 points (about 1000 in the irreducible wedge IBZ) mostly for fcc Al, and 8000 (about 500 in the IBZ) mostly for hcp Al; criterion for energy convergence  $1 \times 10^{-6}$  Ryd.

## 3. Results

The calculations determined the pressure dependence of the lattice constants and the Gibbs free energy for both fcc and hcp Al. The crossing point of the two functions  $G_{\text{hcp}}(p)$  and  $G_{\text{fcc}}(p)$  defines the rigid-lattice transition pressure between the fcc and the hcp structures. Figure 1 depicts the difference between the two functions and shows that the crossing occurs at about



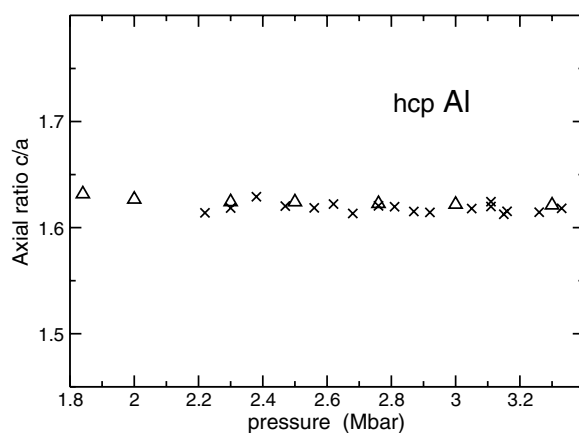
**Figure 1.**  $\Delta G$  is the difference between the Gibbs free energies  $G_{\text{hcp}}$  (solid) and  $G_{\text{fcc}}$  (dashed), shown here as a function of pressure  $p$ . The crossing occurs at approximately 1.92 Mbar and represents the rigid-lattice transition pressure.  $\Delta E$  is the difference  $E_{\text{hcp}} - E_{\text{fcc}}$ , which does not vanish at any pressure.



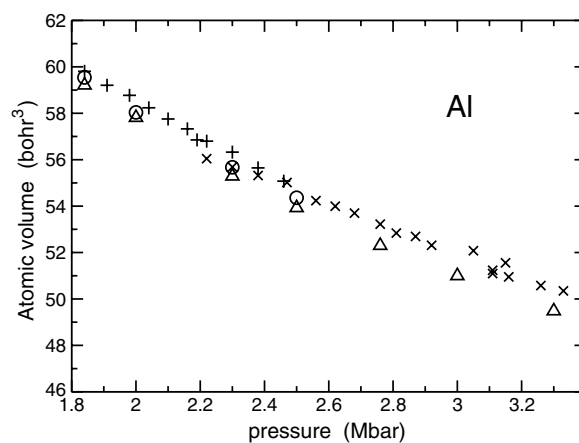
**Figure 2.** Lattice constants of fcc and hcp Al versus pressure. For  $a_{\text{fcc}}$  the plusses are experimental; the open circles, theoretical. For  $a_{\text{hcp}}$  and  $c_{\text{hcp}}$  the crosses are experimental; the open triangles, theoretical.

1.92 Mbar. This value is 0.25 Mbar lower than the experimental value of 2.17 Mbar, but of course it does not contain the contributions of zero-point and thermal phonons. Although we do not calculate this contribution here, we expect that it will move the crossing-point pressure toward larger pressures, since the zero-point energies will raise *both*  $G$  curves, but the  $G_{\text{hcp}}$  will be raised more than the  $G_{\text{fcc}}$  owing to the contributions of optical modes in the hcp lattice. Hence the crossing will occur at a higher pressure than the rigid-lattice value.

Figure 2 show the pressure dependence of the lattice parameters, both experimental (plusses for fcc  $a_{\text{fcc}}^{\text{exp}}$ ; crosses for hcp  $a_{\text{hcp}}^{\text{exp}}$  and  $c_{\text{hcp}}^{\text{exp}}$ ) and theoretical (open circles for fcc  $a_{\text{fcc}}^{\text{theo}}$ ; open triangles for hcp  $a_{\text{hcp}}^{\text{theo}}$  and  $c_{\text{hcp}}^{\text{theo}}$ ). The agreement between theory and experiment is very good: about 0.2 to 0.4% for fcc and 0.4 to 0.8% for hcp.



**Figure 3.** Axial ratio  $c/a$  for hcp Al versus pressure. Crosses: experimental data. Open triangles: theoretical results.



**Figure 4.** Volume per atom of fcc and hcp Al versus pressure. Plusses: fcc experimental. Crosses: hcp experimental. Open circles: fcc theoretical. Open triangles: hcp theoretical.

Figure 3 depicts the pressure dependence of the axial ratio  $c/a$  for hcp Al (crosses experimental; open triangles theoretical). The agreement is also good here, varying from 0.1 to 0.4% depending on the pressure.

Finally, figure 4 shows the equation of state (again, plusses and crosses, experimental, fcc and hcp, respectively; open circles and open triangles, theoretical, fcc and hcp, respectively). Here the agreement between theory and experiment is less good: from a minimum of 0.4% at low pressures to a maximum of 2.1% above 3 Mbar.

#### 4. Discussion

Agreement at the 1% level of the first-principles theoretical lattice parameters with experimental data over a wide range of pressure has been obtained here for Al in two phases, and for Ba in three phases [15]. As noted in [15], this agreement supports the conclusion

that 1% accuracy in structure determination under pressure has been attained in the data, in the WIEN band-structure program, and in the procedure based on minimizing the Gibbs free energy at constant pressure.

We should not expect closer agreement between theory and experiment than 1% for two reasons: (1) the effect of lattice motion, particularly zero-point motion, which can expand the measured lattice in the 1% range, and (2) the inherent inaccuracy of the band calculations, which appears to be at the 1% level. Some information on these effects is available for fcc Al: Quong and Liu [16] have shown that the lattice constant  $a$  of fcc Al expands 0.1% due to zero-point motion at  $p = 0$  and another 0.4% at 300 K (in agreement with experiment). The zero-point effect will probably be larger for hcp Al owing to optical modes. A study of the accuracy of band calculations on fcc Al by Qiu *et al* [17] found values of lattice parameter  $a$  at 0 K and  $p = 0$  calculated with inclusion of zero-point motion from Debye theory. Comparison of the values of  $a$  with experiment showed that the GGA overestimates  $a$  by about 0.6% and the LDA underestimates  $a$  by about 1%.

The rigid-lattice transition pressure between fcc and hcp Al should also be well established by our calculation, but probably not as well as the lattice parameters. The relative  $G$  values of two phases compare band-structure energy calculations in two different symmetries, so the convergence error in the number of  $k$ -points is different, whereas the calculation of lattice parameters in one phase compares energies for structures with the same symmetry and same convergence error in number of  $k$ -points. Our value of 1.92 Mbar is in reasonable agreement with the 2.05 Mbar found in [7], the 1.7 Mbar found in [8] and the 2 Mbar in [5].

The experimental value of the transition pressure  $p_t$  is given as 2.17 Mbar in [9], which includes the effects of lattice vibrations. Such effects have not been evaluated accurately in the theory, although in [8] Debye theory finds that  $p_t$  increases by 0.5 Mbar from zero-point vibrations. However, [8] estimates the effects of zero-point vibrations by using Debye theory, which substantially overestimates the zero-point energy by failing to take account of the lowering of vibration frequencies by dispersion. We note that the value of 2.17 Mbar is the pressure of the first appearance of the hcp phase for increasing pressure. The fcc phase is then shown to disappear at 2.45 Mbar in figure 3 of [9], although the text states that the fcc structure was detected up to 2.65 Mbar. A fluctuation model of the transition would probably find a value of the thermodynamic transition pressure between 2.17 Mbar and the higher values at which the fcc phase disappears.

Also plotted in figure 1 is  $\Delta E = E_{\text{hcp}} - E_{\text{fcc}}$  as a function of pressure, which shows that  $\Delta E$  does not vanish at any pressure. Thus comparison of energies  $E$  at the same pressure will not give relative instabilities of phases. In [3–5] phase stabilities have been found by comparison of energies at the same volume; hence the phases are at different pressures. This comparison is physically incorrect, because phase transitions take place at the same pressure. However, the sequence of phase stabilities from fcc to hcp with increasing pressure is correct. We show why the sequence is correct, but the transition occurs at a pressure lower than the thermodynamic pressure  $p_t$  at which  $\Delta G$  would vanish, where

$$\Delta G = G_{\text{hcp}} - G_{\text{fcc}} = \Delta E + p\Delta V = E_{\text{hcp}}(p) - E_{\text{fcc}}(p) + p[V_{\text{hcp}}(p) - V_{\text{fcc}}(p)], \quad (1)$$

and  $E$ ,  $G$  and  $V$  are considered functions of  $p$  for each phase.

We illustrate the comparison of energies at the same volume by noting that, at  $p = 2.3$  Mbar,  $V_{\text{fcc}} = 55.86$  bohr<sup>3</sup>/atom and  $V_{\text{hcp}} = 55.23$  bohr<sup>3</sup>/atom, and  $\Delta E(2.3 \text{ Mbar}) = 4.7$  mRyd (see figure 1); hence the fcc phase is more stable. The comparison of the energies of the two phases at the same volume, say, at  $V_{\text{hcp}}(2.3 \text{ Mbar}) = 55.23$  bohr<sup>3</sup>, will increase  $E_{\text{fcc}}$  by the work of compression from  $V_{\text{fcc}}$  to  $V_{\text{hcp}}$ , which requires pressures greater than 2.3 Mbar,

**Table 1.** Calculated pressure dependence of the lattice constants of fcc and hcp Al. Units of pressure are Mbar, units of lattice constants are bohr.

Pressure	$a_{\text{fcc}}$	$a_{\text{hcp}}$	$c_{\text{hcp}}$	$c/a$
1.84	6.193	4.376	7.140	1.632
2.00	6.145	4.345	7.069	1.627
2.30	6.068	4.284	6.958	1.624
2.50	6.014	4.248	6.900	1.624
2.76		4.207	6.826	1.623
3.00		4.172	6.766	1.622
3.30		4.131	6.697	1.621

i.e., to  $E'_{\text{fcc}}$ , given by

$$E'_{\text{fcc}} = E_{\text{fcc}}(2.3 \text{ Mbar}) + \int_{V_{\text{hcp}}}^{V_{\text{fcc}}} p \, dV. \quad (2)$$

Then at  $V_{\text{hcp}}$  the energy difference is

$$\Delta E' = E_{\text{hcp}} - E'_{\text{fcc}} = \Delta E - \int_{V_{\text{hcp}}}^{V_{\text{fcc}}} p \, dV < 0 \quad (3)$$

and now the hcp phase is more stable. However, the work term

$$\int_{V_{\text{hcp}}}^{V_{\text{fcc}}} p \, dV = \bar{p}(V_{\text{fcc}} - V_{\text{hcp}}) = -\bar{p}\Delta V > 0, \quad (4)$$

which is subtracted from  $\Delta E$  to give  $\Delta E'$ , is larger than  $p(V_{\text{fcc}} - V_{\text{hcp}})$  at  $p = 2.3 \text{ Mbar}$ , which enters  $\Delta G$  in (1) at  $p = 2.3 \text{ Mbar}$ , because  $\bar{p} > 2.3 \text{ Mbar}$ . Hence the  $\Delta E'$  at  $V = V_{\text{hcp}}$  makes the hcp phase more stable with respect to fcc than  $\Delta G$  at  $2.3 \text{ Mbar}$  would make it, and the calculated transition pressure would be too low. However, contrary to the statements in [3–5] that the  $p\Delta V$  term can be ignored, the term is critical in obtaining the relative stability of phases at the same pressure, as should be done.

The basic experimental data in [9] are values of  $a(p)$  and  $c(p)$  for fcc and hcp Al. It is regrettable that previous papers on Al under pressure such as [7, 8] did not plot or tabulate the values of  $a(p)$  and  $c(p)$ , so that we could check their accuracy against the new data. In [7] the constant close-packed value of  $c/a$  was assumed and it would be of interest to see how that assumption affects  $a$  and  $c$ . Figure 3 here shows that  $c/a$  decreases by 0.7% between 1.8 and 3.2 Mbar. In [8] it is stated that  $c/a$  was varied at each  $V$  to minimize  $E$ , but no values of  $c/a$  are given. Table 1 provides our calculated  $a(p)$  and  $c(p)$  values of fcc and hcp Al for future reference.

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