A database of structural energies of aluminium from *ab initio* calculations

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Abstract. We present a database of 171 aluminium structures with coordination number ranging from 0 to 12 and nearest-neighbour distance from 2.0 Å to 5.7 Å. The purpose of the database is further to test and refine empirical and semi-empirical models of metallic bonding. Each structure is specified by the atomic positions and the unit cell used and a total energy per atom is given. Full details of the first-principles total energy calculations are given along with the estimated errors involved. Examples of densities of states are also given for a few of the structures.

1. Introduction

Total energy calculations from first principles to simulate complex systems of condensed matter have steadily improved over the past few years. The use of more efficient algorithms and access to more powerful computers has led to much larger systems being attempted now than was previously possible. Still there are many situations where attempting to model from first principles is impractical. These are processes that are large on the atomic scale, such as crack formation, needing thousands of atoms. At present, first-principles calculations can handle tens or hundreds of atoms depending on the atomic species.

We are therefore forced to use empirical or semi-empirical models. These models have been developed particularly with reference to metallic bonding and span from those that are calculated partly from first principles such as effective-medium theory [1, 2] to simpler empirical schemes such as Finnis–Sinclair potentials [3, 4]. Others are based on a tight-binding form for the electronic structure [5].

If these models are to be useful they must obviously describe accurately the material in question. In most cases the model is constrained to give some experimental constants of the bulk material such as the lattice constant and bulk modulus. It is then hoped that the model represents the material adequately. However, the atomic configurations that occur in the modelling of complex problems are often very different from the geometry of the stable crystal structure (and small deviations from it) about which one has experimental information, e.g. at a rough surface or a grain boundary.

Hence our approach here. A large database of *ab initio* total energies for a very wide range of different structures has been calculated for aluminium. This database has already been used to test some models [6, 7]. Now the complete database is published here to

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make it available to others for the purpose of further refining and testing models of metallic bonding. The size and range of the database is wider than had been produced before by more than an order of magnitude. Since completing this work Ercolessi (see [8]) has done something similar with a very large number of configurations but a narrower range of coordination number.

The layout of the paper is as follows. Section 2 discusses the *ab initio* techniques used to calculate the energies of the structures. Section 3 gives the database results and the following section gives an estimate of the errors involved in calculating the energies. Finally a brief summary is given in section 5.

2. Method of calculation

The energy of each structure in the database was calculated *ab initio* using the density functional theory formulation of quantum mechanics in the local density approximation for exchange and correlation in the usual way; see [9] for a review.

As usual with metals, the states in the Brillouin zone had to be sampled at a large number of k points to include accurately the effect of the sharp discontinuity at the Fermi level. The $k \cdot p$ method was used to obtain the band energies and wave functions at a large number of k points. The method works by first generating a set of wave functions at one particular point, and then using them as a basis set for calculating those for other k points for the same potential. There is no restriction on the k point used to generate the wave functions, neither does it need to be only one point—it can be a set of points. This method has been described in more detail by Robertson and Payne [10]. The calculation then proceeds by iteration to self-consistency. After each iteration the energy was evaluated using the Harris–Foulkes energy functional [11]

$$H = \sum_i \epsilon_i w_i - E_H[n_{in}(r)] + E_{XC}[n_{in}(r)] - \int d^3r \, \mu_{XC}[n_{in}(r)]n_{in}(r) + E_{nn} \tag{1}$$

where E_H is the Hartree energy, E_{XC} is the exchange–correlation energy, E_{nn} is the nuclear-nuclear interaction, μ_{XC} is the exchange–correlation potential, ϵ_i is the ith eigenvalue, w_i is the corresponding occupation probability and $n_{in}(r)$ is the input charge density. This expression is made up of terms that are functions of the input charge density and a term that is the weighted sum of the output eigenvalues. This energy functional is stationary at the ground-state density, so the errors will be second order with respect to the charge density. This energy functional was chosen over the Kohn–Sham functional because it does not require knowledge of the output charge density or of the output kinetic energy. Although it would not have been computationally expensive to calculate these quantities, this provided a small saving in time. The errors in the $k \cdot p$ method were analysed thoroughly [10, 12] and a discussion of this error is given later in section 4. Using the $k \cdot p$ method, calculations were several orders of magnitude faster than with previous methods and this allows one to use much larger k point sets than would otherwise have been possible.

The pseudopotential used was a modified Heine–Abarenkov local pseudopotential. This pseudopotential was tested by Goodwin *et al* [13]. Tests on it included calculating the bulk modulus, binding energy and some phonon frequencies. It was found to give good agreement with more accurate norm-conserving pseudopotentials and reasonable agreement with experimental results. A summary of these results is given in table 1. In any case the purpose was not to obtain an accurate database specifically for aluminium; the purpose was to have a database for some metal on which one could test models of metallic bonding. It does not matter that it is a slightly fictional metal, very similar to real aluminium, defined

Table 1. Pseudopotential data: The bulk modulus, binding energy for FCC structure and phonon frequencies in units of 10^{13} radians per second for aluminium calculated with the local pseudopotential, experimental values and a result of a norm-conserving pseudopotential.

	Bulk modulus	E_b	ω_{phon}	
	(Mbar)	(eV/atom)	L(X)	T(X)
Calculated (local)	0.79	3.68	5.68	3.11
Experimental	0.74	3.40	6.08	3.65
Calculated (norm)	—	3.67	—	—

precisely by its pseudopotential. A local pseudopotential was used, as the $k \cdot p$ method developed by Robertson and Payne [10] was for local pseudopotentials only. A non-local version was not developed. A plane-wave basis set was used with 190 eV cut-off energy, and the exchange and correlation function of Ceperley and Alder [14] as parametrized by Perdew and Zunger [15]. Each structure was calculated with a $8 \times 8 \times 8$ Monkhorst–Pack set of k points.

Firstly 18 structures were taken and their total energy calculated to self-consistency. All structures were modelled using orthorhombic supercells and the structures were chosen so that in each structure all the atoms are equivalent by symmetry. This makes it easier to deduce something about the interaction from the database. For these 18 structures the nearest-neighbour distance was fixed at 2.85 Å and vacuum was modelled by an additional distance of 2.85 Å. The breakdown on the types of structures is as follows:

(i) six three-dimensional structures: FCC, BCC, simple hexagonal, vacancy lattice based on FCC with one atom missing per unit cube, simple cubic and diamond;

(ii) three consisting of one layer of atoms: close-packed layer, square layer, graphite;

(iii) five structures that involved two layers of atoms (termed slabs): square slab, close-packed slab and three FCC slabs using a pair of 110, 100 and 111 layers respectively;

(iv) a line structure, a girder structure, a dimer and an atom.

The wide range of situations included were chosen to be representative of situations that could be found in a real solid. The low-coordination ones are typical of atoms approaching a surface, the intermediate ones are typical of atoms in a surface and the higher-coordination ones are for atoms in the bulk or around a crack or a vacancy. With hindsight other structures such as rearrangements at constant volume, for instance 'frozen' phonons or sheared structures, would have been useful to have in the database, but these are not represented here.

In order to create a much larger database, ten of these structures were chosen and total energies calculated for dilated and contracted forms of these structures. By expanding or contracting the supercell the nearest-neighbour distance was varied from 2 Å to 5 Å. To calculate the total energy self-consistently for these structures would have taken a great deal of time. Therefore the input charge density was derived from the original self-consistent calculations and only one iteration of the system was taken, thus dispensing with self-consistency. We had shown earlier that the self-consistent charge densities for all the original 18 structures aside from the free atom could all be expressed to good accuracy as the sum of spherical, slightly contracted, atomic charge densities [16]. Moreover the use of the Harris–Foulkes functional [11] reduces errors to second order. To test the validity of this approach, a range of coordination and the extremes of distance variation for the simple cubic structure were tested [16]. The error in abandoning self-consistency is discussed in

Table 2. The energies (per atom) of the basic 18 structures calculated self-consistently. As all the cells are orthorhombic only the lattice parameters have been given. Also given are N_a, the number of atoms in the cell, and the positions of the atoms.

Structure	Unit cell dimensions (Å)			N_a	Atomic positions (cell units)	Energy (eV/atom)
	a	b	c			
Atom	5.70000	5.70000	5.70000	1	(0.0000,0.0000,0.0000)	−54.95
Dimer	8.55000	5.70000	5.70000	2	(0.3333,0.0000,0.0000)	−55.66
					(0.6666,0.0000,0.0000)	
Line	2.85000	5.70000	5.70000	1	(0.0000,0.0000,0.0000)	−56.28
Graphite	5.70000	8.55000	4.93634	4	(0.0000,0.0000,0.0000)	−56.95
					(0.0000,0.3333,0.0000)	
					(0.0000,0.5000,0.5000)	
					(0.0000,0.8333,0.5000)	
Girder	5.70000	2.85000	7.98700	2	(0.0000,0.2500,0.1545)	−57.04
					(0.0000,0.7500,0.8455)	
Square layer	5.70000	2.85000	2.85000	1	(0.0000,0.0000,0.0000)	−57.29
Diamond	6.58175	4.65400	4.65400	4	(0.0000,0.0000,0.0000)	−57.42
					(0.2500,0.5000,0.0000)	
					(0.5000,0.5000,0.5000)	
					(0.7500,0.0000,0.5000)	
Square slab	8.55000	2.85000	2.85000	2	(0.0000,0.0000,0.0000)	−57.64
					(0.3333,0.0000,0.0000)	
CP layer	2.85000	4.93630	5.70000	2	(0.0000,0.0000,0.0000)	−57.49
					(0.5000,0.5000,0.0000)	
Simple cubic	2.85000	2.85000	2.85000	1	(0.0000,0.0000,0.0000)	−57.91
FCC (110)	7.12500	2.85000	4.03050	2	(0.0000,0.0000,0.0000)	−57.54
					(0.2000,0.5000,0.5000)	
CP slab	8.55000	4.93630	2.85000	4	(0.0000,0.0000,0.0000)	−57.89
					(0.0000,0.5000,0.5000)	
					(0.3333,0.0000,0.0000)	
					(0.3333,0.5000,0.5000)	
FCC (100)	7.34710	4.03050	4.03050	4	(0.0000,0.0000,0.0000)	−57.85
					(0.2743,0.5000,0.0000)	
					(0.2743,0.0000,0.5000)	
					(0.0000,0.5000,0.5000)	
Vacancy	4.03050	4.03050	4.03050	3	(0.5000,0.5000,0.0000)	−58.10
					(0.5000,0.0000,0.5000)	
					(0.0000,0.5000,0.5000)	
Simple hexagonal	2.85000	4.93630	2.85000	2	(0.0000,0.0000,0.0000)	−58.12
					(0.5000,0.5000,0.0000)	
BCC	3.29090	3.29090	3.29090	2	(0.0000,0.0000,0.0000)	−58.24
					(0.5000,0.5000,0.5000)	
FCC (111)	2.85000	4.93634	8.02702	4	(0.0000,0.0000,0.0000)	−57.97
					(0.5000,0.5000,0.0000)	
					(0.0000,0.3333,0.2899)	
					(0.5000,0.8333,0.2899)	
FCC	4.03050	4.03050	4.03050	4	(0.0000,0.0000,0.0000)	−58.31
					(0.5000,0.5000,0.0000)	
					(0.5000,0.0000,0.5000)	
					(0.0000,0.5000,0.5000)	

more detail in section 4. Other computational details are as for the fully self-consistent calculations except a $30 \times 30 \times 30$ Monkhorst–Pack grid of k points was used. In total a further 153 structure's total energies were calculated in this way.

Table 3. The results for the remaining 153 structures obtained using non-self-consistent calculations. The orthorhombic cell dimensions, total energy per atom and the nearest-neighbour distances, r_0, are given.

Structure	Unit cell (Å)			Energy (eV/atom)	r_0 (Å)
	a	b	c		
Graphite	5.7000	8.5500	4.93634	−56.979	2.85
Graphite	5.7000	8.1500	4.70540	−57.120	2.72
Graphite	5.7000	7.8500	4.53220	−57.198	2.62
Graphite	5.7000	7.5500	4.35899	−57.244	2.52
Graphite	5.7000	7.2000	4.15692	−57.214	2.40
Graphite	5.7000	7.0000	4.04145	−57.139	2.33
Graphite	5.7000	6.8000	3.92598	−57.008	2.27
Graphite	5.7000	6.6000	3.81051	−56.802	2.20
Graphite	5.7000	6.4500	3.72391	−56.643	2.15
Graphite	5.7000	6.2000	3.57957	−56.068	2.07
Square layer	3.3500	3.3500	5.7000	−56.697	3.35
Square layer	3.2500	3.2500	5.7000	−56.824	3.25
Square layer	3.1500	3.1500	5.7000	−56.945	3.15
Square layer	3.0500	3.0500	5.7000	−57.074	3.05
Square layer	2.9500	2.9500	5.7000	−57.190	2.95
Square layer	5.7000	2.8500	2.8500	−57.307	2.85
Square layer	2.7500	2.7500	5.7000	−57.396	2.75
Square layer	2.6500	2.6500	5.7000	−57.460	2.65
Square layer	2.5500	2.5500	5.7000	−57.482	2.55
Square layer	2.4500	2.4500	5.7000	−57.424	2.45
Square layer	2.4000	2.4000	5.7000	−57.366	2.40
Square layer	2.3500	2.3500	5.7000	−57.276	2.35
Square layer	2.3000	2.3000	5.7000	−57.149	2.30
Square layer	2.2500	2.2500	5.7000	−56.962	2.25
Square layer	2.2000	2.2000	5.7000	−56.738	2.20
Square layer	2.1000	2.1000	5.7000	−56.081	2.10
Square layer	5.7000	2.0000	2.0000	−54.976	2.00
Close-packed layer	3.5500	6.1487	5.7000	−56.726	3.55
Close-packed layer	3.3000	5.7157	5.7000	−57.038	3.30
Close-packed layer	3.1000	5.3693	5.7000	−57.294	3.10
Close-packed layer	2.9500	5.1095	5.7000	−57.469	2.95
Close-packed layer	2.8500	4.9363	5.7000	−57.565	2.85
Close-packed layer	2.7500	4.7631	5.7000	−57.645	2.75
Close-packed layer	2.6500	4.5899	5.7000	−57.684	2.65
Close-packed layer	2.5500	4.4167	5.7000	−57.671	2.55
Close-packed layer	2.5000	4.3301	5.7000	−57.633	2.50
Close-packed layer	2.4000	4.1569	5.7000	−57.477	2.40
Close-packed layer	2.3500	4.0703	5.7000	−57.330	2.35
Close-packed layer	2.3000	3.9837	5.7000	−57.149	2.30
Close-packed layer	2.2500	3.8971	5.7000	−56.901	2.25
Close-packed layer	2.2000	3.8105	5.7000	−56.589	2.20
Close-packed layer	2.1500	3.7239	5.7000	−56.183	2.15
Close-packed layer	2.1000	3.6373	5.7000	−55.674	2.10
Close-packed layer	2.0500	3.5507	5.7000	−55.008	2.05
Close-packed layer	2.0000	3.4641	5.7000	−54.196	2.00
Line	3.2000	5.7000	5.7000	−56.115	3.20
Line	3.1000	5.7000	5.7000	−56.183	3.10
Line	3.0000	5.7000	5.7000	−56.242	3.00
Line	2.9000	5.7000	5.7000	−56.296	2.90
Line	2.8500	5.7000	5.7000	−56.323	2.85

Table 3. *Continued.*

| Structure | Unit cell (Å) | | | Energy | r_0 |
	a	b	c	(eV/atom)	(Å)
Line	2.8000	5.7000	5.7000	−56.342	2.80
Line	2.7000	5.7000	5.7000	−56.384	2.70
Line	2.6000	5.7000	5.7000	−56.414	2.60
Line	2.5000	5.7000	5.7000	−56.449	2.50
Line	2.4000	5.7000	5.7000	−56.492	2.40
Line	2.3000	5.7000	5.7000	−56.505	2.30
Line	2.2000	5.7000	5.7000	−56.414	2.20
Line	2.1000	5.7000	5.7000	−56.155	2.10
Line	2.0000	5.7000	5.7000	−55.659	2.00
Square slab	8.5500	3.8500	3.8500	−56.633	3.85
Square slab	8.5500	3.4000	3.4000	−57.063	3.40
Square slab	8.5500	3.1500	3.1500	−57.357	3.15
Square slab	8.5500	3.0000	3.0000	−57.545	3.00
Square slab	8.5500	2.8500	2.8500	−57.708	2.85
Square slab	8.5500	2.7500	2.7500	−57.785	2.75
Square slab	8.5500	2.6500	2.6500	−57.831	2.65
Square slab	8.5500	2.5500	2.5500	−57.828	2.55
Square slab	8.5500	2.5000	2.5000	−57.792	2.50
Square slab	8.5500	2.4500	2.4500	−57.740	2.45
Square slab	8.5500	2.4000	2.4000	−57.659	2.40
Square slab	8.5500	2.3500	2.3500	−57.545	2.35
Square slab	8.5500	2.1000	2.1000	−56.196	2.10
FCC (100) slab	7.3471	5.7000	5.7000	−56.758	4.03
FCC (100) slab	7.3471	5.2000	5.2000	−57.106	3.68
FCC (100) slab	7.3471	4.8500	4.8500	−57.365	3.43
FCC (100) slab	7.3471	4.6000	4.6000	−57.552	3.25
FCC (100) slab	7.3471	4.4000	4.4000	−57.698	3.11
FCC (100) slab	7.3471	4.2500	4.2500	−57.804	3.00
FCC (100) slab	7.3471	4.1000	4.1000	−57.898	2.90
FCC (100) slab	7.3471	4.0305	4.0305	−57.931	2.85
FCC (100) slab	7.3471	3.9000	3.9000	−57.983	2.76
FCC (100) slab	7.3471	3.8000	3.8000	−58.007	2.69
FCC (100) slab	7.3471	3.7000	3.7000	−58.003	2.62
Diamond	7.6500	5.409 37	5.409 37	−56.715	3.31
Diamond	6.5817	4.654 00	4.654 00	−57.425	2.85
Diamond	6.4500	4.560 84	4.560 84	−57.500	2.79
Diamond	6.3000	4.454 77	4.454 77	−57.573	2.73
Diamond	6.1000	4.313 35	4.313 35	−57.652	2.64
Diamond	5.9500	4.207 29	4.207 29	−57.685	2.58
Diamond	5.8000	4.101 22	4.101 22	−57.682	2.51
Diamond	5.6500	3.995 15	3.995 15	−57.645	2.45
Diamond	5.4500	3.853 73	3.853 73	−57.518	2.36
Diamond	4.8500	3.429 47	3.429 47	−56.192	2.10
Simple cubic	5.7000	5.7000	5.7000	−55.056	5.70
Simple cubic	5.3000	5.3000	5.3000	−55.234	5.30
Simple cubic	4.9000	4.9000	4.9000	−55.473	4.90
Simple cubic	4.5000	4.5000	4.5000	−55.777	4.50
Simple cubic	4.1000	4.1000	4.1000	−56.182	4.10
Simple cubic	3.6000	3.6000	3.6000	−56.834	3.60
Simple cubic	3.5000	3.5000	3.5000	−56.991	3.50
Simple cubic	3.4000	3.4000	3.4000	−57.153	3.40
Simple cubic	3.3000	3.3000	3.3000	−57.307	3.30

Table 3. *Continued.*

Structure	Unit cell (Å)			Energy (eV/atom)	r_0 (Å)
	a	*b*	*c*		
Simple cubic	3.2000	3.2000	3.2000	−57.470	3.20
Simple cubic	3.1000	3.1000	3.1000	−57.640	3.10
Simple cubic	3.0000	3.0000	3.0000	−57.800	3.00
Simple cubic	2.9000	2.9000	2.9000	−57.927	2.90
Simple cubic	2.8500	2.8500	2.8500	−57.988	2.85
Simple cubic	2.8000	2.8000	2.8000	−58.014	2.80
Simple cubic	2.7000	2.7000	2.7000	−58.076	2.70
Simple cubic	2.6000	2.6000	2.6000	−58.041	2.60
Simple cubic	2.5000	2.5000	2.5000	−57.917	2.50
Simple cubic	2.3500	2.3500	2.3500	−57.451	2.35
Simple cubic	2.1500	2.1500	2.1500	−55.776	2.15
Simple cubic	2.0000	2.0000	2.0000	−53.229	2.00
Vacancy	5.2500	5.2500	5.2500	−56.840	3.71
Vacancy	4.9500	4.9500	4.9500	−57.161	3.50
Vacancy	4.7000	4.7000	4.7000	−57.444	3.32
Vacancy	4.5500	4.5500	4.5500	−57.624	3.22
Vacancy	4.4000	4.4000	4.4000	−57.792	3.11
Vacancy	4.2500	4.2500	4.2500	−57.959	3.00
Vacancy	4.1000	4.1000	4.1000	−58.099	2.90
Vacancy	4.0305	4.0305	4.0305	−58.140	2.85
Vacancy	4.0000	4.0000	4.0000	−58.159	2.83
Vacancy	3.9000	3.9000	3.9000	−58.200	2.76
Vacancy	3.8500	3.8500	3.8500	−58.206	2.72
Vacancy	3.7500	3.7500	3.7500	−58.163	2.65
Vacancy	3.6500	3.6500	3.6500	−58.076	2.58
Vacancy	3.5500	3.5500	3.5500	−57.945	2.51
Vacancy	3.4500	3.4500	3.4500	−57.727	2.44
Vacancy	3.3500	3.3500	3.3500	−57.398	2.37
Vacancy	3.2500	3.2500	3.2500	−56.901	2.30
Vacancy	3.1500	3.1500	3.1500	−56.214	2.23
Vacancy	3.0500	3.0500	3.0500	−55.324	2.16
FCC	6.1305	6.1305	6.1305	−56.384	4.33
FCC	5.7305	5.7305	5.7305	−56.742	4.05
FCC	5.4305	5.4305	5.4305	−57.046	3.84
FCC	5.2305	5.2305	5.2305	−57.266	3.70
FCC	5.1305	5.1305	5.1305	−57.376	3.63
FCC	5.0305	5.0305	5.0305	−57.488	3.56
FCC	4.9305	4.9305	4.9305	−57.605	3.49
FCC	4.8305	4.8305	4.8305	−57.719	3.42
FCC	4.7305	4.7305	4.7305	−57.828	3.35
FCC	4.6305	4.6305	4.6305	−57.943	3.27
FCC	4.5305	4.5305	4.5305	−58.040	3.20
FCC	4.4305	4.4305	4.4305	−58.139	3.13
FCC	4.3305	4.3305	4.3305	−58.228	3.06
FCC	4.2305	4.2305	4.2305	−58.301	2.99
FCC	4.1305	4.1305	4.1305	−58.342	2.92
FCC	4.0305	4.0305	4.0305	−58.345	2.85
FCC	3.7305	3.7305	3.7305	−58.092	2.64
FCC	3.4305	3.4305	3.4305	−57.180	2.42
FCC	3.2305	3.2305	3.2305	−55.848	2.28
FCC	3.1305	3.1305	3.1305	−54.817	2.21

3. Results

Tables 2 and 3 give the complete database. Table 2 gives the 18 different structures calculated to self-consistency all with interatomic spacing $r_0 = 2.85$ Å. The remaining 153 structures are given in table 3. The atomic positions for the latter are the same as for the original structures given in table 2. This dataset can be accessed directly over telnet by using **ftp tcm1.phy.cam.ac.uk** and typing **anonymous** for the login name, and user name and address for the password. The data are in the **Al-structures** directory and all the files can be copied in the usual way with the **get** command.
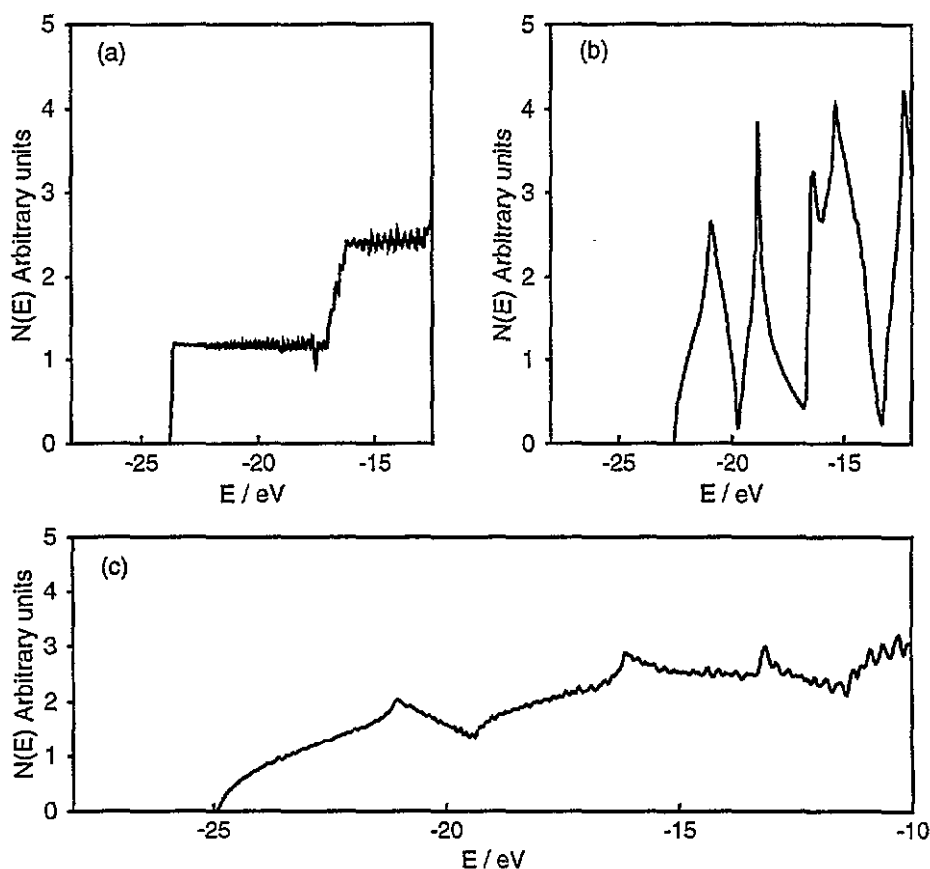
Figure 1. The density of states for three structures: (a) a close-packed layer, with dimensions of the unit cell $a = 2.85$ Å, $b = 4.9363$ Å, $c = 5.7$ Å; (b) a simple cubic structure, with unit cell $a = b = c = 2.85$ Å; (c) a diamond structure, with unit cell $a = 6.58175$ Å, $b = c = 2.85$ Å.

Furthermore the density of states for some of the structures were calculated by constructing a histogram of the energy eigenvalues. Graphs of the density of states for the close-packed layer, simple cubic and diamond structures are given in figure 1. The graphs are given only to show how the densities of states produced by the eigenvalues behave. Figure 1(a) gives the close-packed layer's density of states and has a stepped form similar to that of a two-dimensional non-interacting electron gas. Figure 1(c) shows the simple cubic density of states and gives a roughly parabolic form as would be expected for a three-dimensional non-interacting density of states. The density of states for aluminium in

the diamond structure is rather similar to the valence band of silicon with the third minimum in figure 1(b) corresponding to the band gap of Si. The Fermi level for all three cases lies around -12 eV.

4. Estimation of errors

The following gives an estimate of the errors in the calculations given in the last section. There are four main groups of error: the error from using the local density approximation for the exchange and correlation energy, the pseudopotential error, the errors in the finite sampling and the $k \cdot p$ method, and the error due to the non-self-consistency of the second set of calculations. The pseudopotential, as commented on in section 2, appeared to be reasonable and any errors involved in it are ignored. In any case, for purposes of testing different types of bonding model we can regard it as a database for a fictitious metal defined by the local pseudopotential and very similar to aluminium. Similarly the error due to the local density approximation is not discussed here. This leaves two remaining errors to be estimated. These have been analysed in depth in three papers [10, 12, 16] and the following is a summary of the errors with an estimate of the numerical accuracy of the results given in section 3.

Firstly the $k \cdot p$ and finite-sampling errors: these can be split up into four lots. There is the finite-sampling error in the eigenvalue sum, the finite-sampling error in charge density, the $k \cdot p$ error in the eigenvalue sum and the $k \cdot p$ error in the charge density. The two finite-sampling errors arise from the discrete sampling in the Brillouin zone. These are general to total energy pseudopotential calculations and can be reduced by finer k point sampling. Indeed the purpose of using the $k \cdot p$ method was to generate quickly the energy at so many k points that the error from discrete k point sampling was rendered negligible [12]. However, there remains the error from the $k \cdot p$ method itself.

The root of the problem is that the $k \cdot p$ method uses a basis set derived from one point (or possibly set of points) and uses this rather than the original basis set, in this case plane waves. When these two errors were analysed [12] it was found that the $k \cdot p$ error in the charge density was negligible. However, the $k \cdot p$ error in the eigenvalue sum was found to be significant. The total error of all four sources was estimated as no more than 0.05 eV per atom. It should be noted that the sign of this error is always positive and it increases with increasing size of Brillouin zone and hence with decreasing size of unit cell.

Secondly we have the error due to non-self-consistency. To treat the remaining 153 structures only one iteration was taken, so leading to an error in the total energy calculated, as compared to a full self-consistent calculation. This error is always negative, being largest in magnitude for dilated structures. The magnitude of the error is estimated by comparing the calculations for $r_0 = 2.85$ Å in table 3 with the corresponding self-consistent ones in table 2. The difference for the ten structures of table 3 was a RMS value of 0.05 eV with a maximum of 0.08 eV. Taking the worst possible case a combined error on the latter calculations due to residual errors and also the lack of self-consistency gave an error of 0.13 eV, but this is very much a maximum; we believe that the systematic trends are represented considerably more accurately.

5. Conclusion

This paper has presented a database of 171 first-principles total energy calculations for aluminium. It provides a tool for developing and testing empirical or semi-empirical models

of metallic bonding. The first 18 structures were calculated self-consistently using the $k \cdot p$ method with the coordination number varying from zero to twelve, and all with interatomic spacing of 2.85 Å close to that of bulk FCC aluminium. The remaining 153 calculations dispensed with complete self-consistency and calculated dilations or contractions of ten of the original calculations, using the Harris–Foulkes functional to reduce the resulting error to second order. In these the interatomic spacing varied from 0.7 to 2.0 times that of the original 18. An uncertainty of up to 130 meV in the given energies can be assumed for the non-self-consistent calculations and a smaller error of up to 50 meV for the original 18 calculations.

As mentioned in the introduction an example of the use of this database can be seen in Robertson *et al* [7]. Tests on over 24 empirical models were made. There were general constraints on the form of the functions used and at most nine free parameters to fit the models to the data. It was found that at best the models would give a RMS error of 0.11 eV per atom when optimized. Although this was deemed unsatisfactory for using them, only a small selection of the many possibilities of functional forms were looked at. It is therefore not inconceivable that an alternative empirical model approach can be a better fit to the data than the one studied. By using this database there is available a test to gauge the accuracy of such an empirical model.

Acknowledgments

References

[1] Jacobsen K W, Nørskov J K and Puska M J 1987 *Phys. Rev.* B **35** 7423
[2] Daw M S and Baskes M I 1984 *Phys. Rev.* B **29** 6443
[3] Finnis M W and Sinclair J E 1984 *Phil. Mag.* A **50** 45
[4] Sutton A P and Chen J 1990 *Phil. Mag. Lett.* **61** 2480
[5] Pettifor D G 1989 *Phys. Rev. Lett.* **63** 2480
[6] Robertson I J, Payne M C and Heine V 1991 *Europhys. Lett.* **15** 301
[7] Robertson I J, Heine V and Payne M C 1993 *Phys. Rev. Lett.* **70** 1944
[8] Ercolessi F and Adams J B 1994 *Europhys. Lett.* **26** 583
[9] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos 1992 *Rev. Mod. Phys.* **64** 1045
[10] Robertson I J and Payne M C 1990 *J. Phys.: Condens. Matter* **2** 9837
[11] Harris J 1985 *Phys. Rev.* B **31** 1770
      Foulkes W M C and Haydock R 1989 *Phys. Rev.* B **39** 12520
[12] Robertson I J and Payne M C 1991 *J. Phys.: Condens. Matter* **3** 8841
[13] Goodwin L, Needs R J and Heine V 1990 *J. Phys.: Condens. Matter* **2** 351
[14] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[15] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[16] Robertson I J, Payne M C and Heine V 1991 *J. Phys.: Condens. Matter* **3** 8351