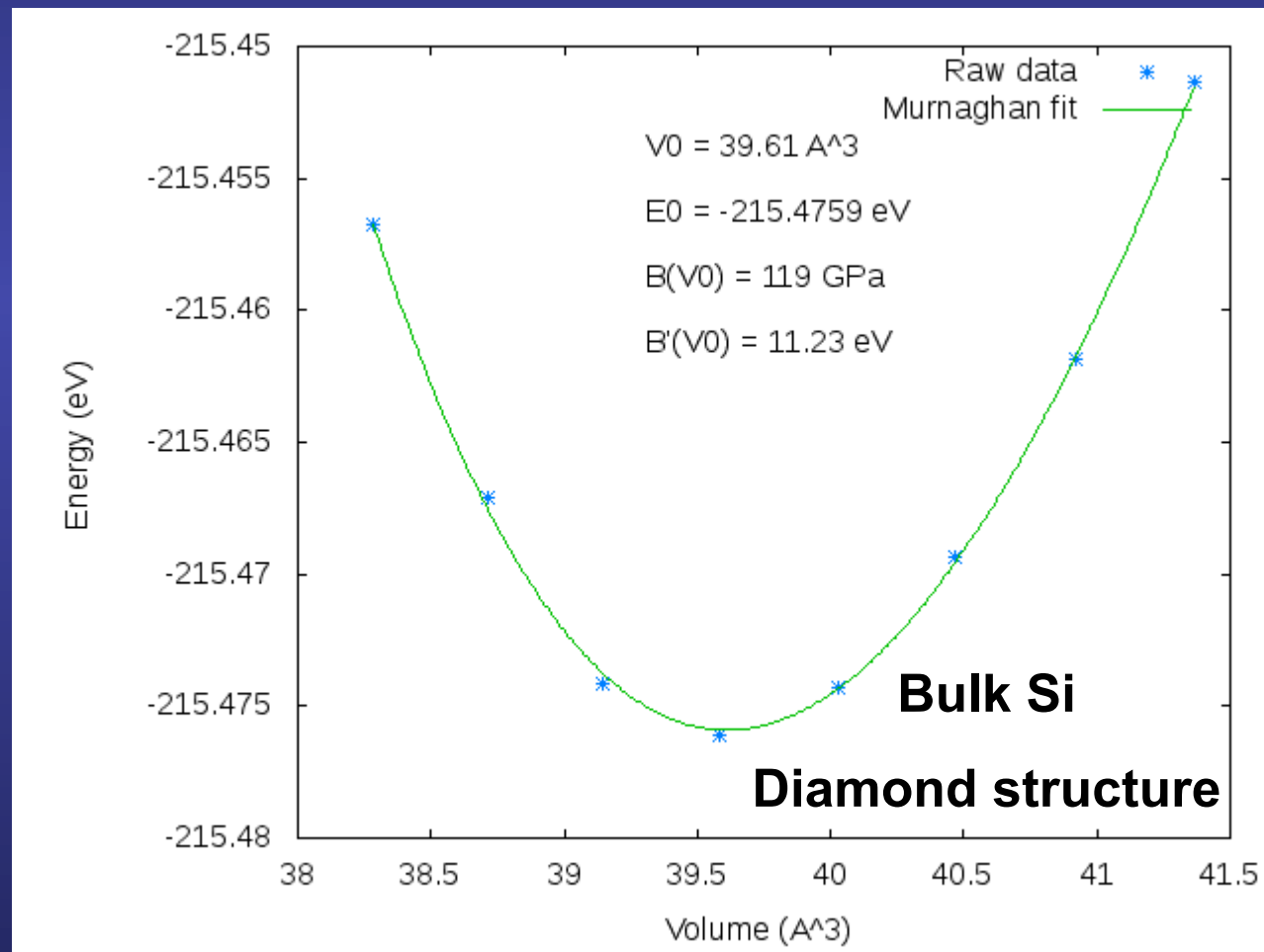


Computing lattice constant, bulk modulus and equilibrium energies of solids



Information required to run a first-principles simulation

Number and species of the atoms in the unit cell,

Lattice vectors and lattice constants

Position of all the atoms

After the Born Oppenheimer approx.,
are assumed to be fixed,
no thermal vibrations ($T = 0$)



N



Ω



$T = 0$

$S = 0$

The most convenient thermodynamic potential in first-principles theoretical analysis is the total energy $E(N, \Omega, S)$ at $T = 0$

It is straightforward to carry out electronic structure calculations at fixed Ω

First test: determine theoretical predictions for Ω_0 and B for the known zero-pressure crystal structure

Definition of some fundamental quantities

Energy $E(N, \Omega, S)$

Pressure $P = -\frac{dE}{d\Omega}$

Bulk modulus $B = -\Omega \frac{dP}{d\Omega} = \Omega \frac{d^2 E}{d\Omega^2}$

Why Ω_0 and B :

- Can be measured with great accuracy.
- Can be extrapolated at $T = 0$

Ω_0 and B can be measured with great accuracy and extrapolated at $T = 0$

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. (Inorganic Crystal Structure Database (ICSD) online.)

H¹ 4K hcp 3.75 6.12																	He⁴ 2K hcp 3.57 5.83																												
Li 78K bcc 3.491	Be hcp 2.27 3.59											B rhomb.	C diamond 3.567	N 20K cubic 5.66 (N ₂)	O complex (O ₂)	F	Ne 4K fcc 4.46																												
Na 5K bcc 4.225	Mg hcp 3.21 5.21	←———— Crystal structure —————→ ←———— a lattice parameter, in Å —————→ ←———— c lattice parameter, in Å —————→										Al fcc 4.05	Si diamond 5.430	P complex	S complex	Cl complex (Cl ₂)	Ar 4K fcc 5.31																												
K 5K bcc 5.225	Ca fcc 5.58	Sc hcp 3.31 5.27	Ti hcp 2.95 4.68	V bcc 3.03	Cr bcc 2.88	Mn cubic complex	Fe bcc 2.87	Co hcp 2.51 4.07	Ni fcc 3.52	Cu fcc 3.61	Zn hcp 2.66 4.95	Ga complex	Ge diamond 5.658	As rhomb.	Se hex. chains	Br complex (Br ₂)	Kr 4K fcc 5.64																												
Rb 5K bcc 5.585	Sr fcc 6.08	Y hcp 3.65 5.73	Zr hcp 3.23 5.15	Nb bcc 3.30	Mo bcc 3.15	Tc hcp 2.74 4.40	Ru hcp 2.71 4.28	Rh fcc 3.80	Pd fcc 3.89	Ag fcc 4.09	Cd hcp 2.98 5.62	In tetr. 3.25 4.95	Sn (α) diamond 6.49	Sb rhomb.	Te hex. chains	I complex (I ₂)	Xe 4K fcc 6.13																												
Cs 5K bcc 6.045	Ba bcc 5.02	La hex. 3.77 ABAC	Hf hcp 3.19 5.05	Ta bcc 3.30	W bcc 3.16	Re hcp 2.76 4.46	Os hcp 2.74 4.32	Ir fcc 3.84	Pt fcc 3.92	Au fcc 4.08	Hg rhomb.	Tl hcp 3.46 5.52	Pb fcc 4.95	Bi rhomb.	Po sc 3.34	At —	Rn —																												
Fr —	Ra —	Ac fcc 5.31	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td>Ce fcc 5.16</td> <td>Pr hex. 3.67 ABAC</td> <td>Nd hex. 3.66</td> <td>Pm —</td> <td>Sm complex</td> <td>Eu bcc 4.58</td> <td>Gd hcp 3.63 5.78</td> <td>Tb hcp 3.60 5.70</td> <td>Dy hcp 3.59 5.65</td> <td>Ho hcp 3.58 5.62</td> <td>Er hcp 3.56 5.59</td> <td>Tm hcp 3.54 5.56</td> <td>Yb fcc 5.48</td> <td>Lu hcp 3.50 5.55</td> </tr> <tr> <td>Th fcc 5.08</td> <td>Pa tetr. 3.92 3.24</td> <td>U complex</td> <td>Np complex</td> <td>Pu complex</td> <td>Am hex. 3.64 ABAC</td> <td>Cm —</td> <td>Bk —</td> <td>Cf —</td> <td>Es —</td> <td>Fm —</td> <td>Md —</td> <td>No —</td> <td>Lr —</td> </tr> </table>															Ce fcc 5.16	Pr hex. 3.67 ABAC	Nd hex. 3.66	Pm —	Sm complex	Eu bcc 4.58	Gd hcp 3.63 5.78	Tb hcp 3.60 5.70	Dy hcp 3.59 5.65	Ho hcp 3.58 5.62	Er hcp 3.56 5.59	Tm hcp 3.54 5.56	Yb fcc 5.48	Lu hcp 3.50 5.55	Th fcc 5.08	Pa tetr. 3.92 3.24	U complex	Np complex	Pu complex	Am hex. 3.64 ABAC	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —
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Ω_0 and B can be measured with great accuracy and extrapolated at $T = 0$

Table 3 Isothermal bulk moduli and compressibilities at room temperature

After K. Gschneidner, Jr., Solid State Physics 16, 275–426 (1964); several data are from F. Birch, in *Handbook of physical constants*, Geological Society of America Memoir 97, 107–173 (1966). Original references should be consulted when values are needed for research purposes. Values in parentheses are estimates. Letters in parentheses refer to the crystal form. Letters in brackets refer to the temperature:

[a] = 77 K; [b] = 273 K; [c] = 1 K; [d] = 4 K; [e] = 81 K.

Bulk modulus in units 10^{12} dyn/cm² or 10^{11} N/m²
Compressibility in units 10^{-12} cm²/dyn or 10^{-11} m²/N

H [a] 0.002 500																	He [d] 0.00 1168				
Li 0.116 8.62	Be 1.003 0.997															B 1.78 0.562	C [d] 4.43 0.226	N [e] 0.012 80	O	F	Ne [a] 0.010 100
Na 0.068 14.7	Mg 0.354 2.82															Al 0.722 1.385	Si 0.988 1.012	P [b] 0.304 3.29	S [c] 0.178 5.62	Cl	Ar [a] 0.013 79
K 0.032 31.	Ca 0.152 6.58	Sc 0.435 2.30	Ti 1.051 0.951	V 1.619 0.618	Cr 1.901 0.526	Mn 0.596 1.68	Fe 1.683 0.594	Co 1.914 0.522	Ni 1.86 0.538	Cu 1.37 0.73	Zn 0.598 1.67	Ga [b] 0.569 1.76	Ge 0.772 1.29	As 0.394 2.54	Se 0.091 11.0	Br	Kr [a] 0.018 56				
Rb 0.031 32.	Sr 0.116 8.62	Y 0.366 2.73	Zr 0.833 1.20	Nb 1.702 0.587	Mo 2.725 0.366	Tc (2.97) (0.34)	Ru 3.208 0.311	Rh 2.704 0.369	Pd 1.808 0.553	Ag 1.007 0.993	Cd 0.467 2.14	In 0.411 2.43	Sn [c] 1.11 0.901	Sb 0.383 2.61	Te 0.230 4.35	I	Xe				
Cs 0.020 50.	Ba 0.103 9.97	La 0.243 4.12	Hf 1.09 0.92	Ta 2.00 0.50	W 3.232 0.309	Re 3.72 0.269	Os (4.18) (0.24)	Ir 3.55 0.282	Pt 2.783 0.359	Au 1.732 0.577	Hg [c] 0.382 2.60	Tl 0.359 2.79	Pb 0.430 2.33	Bi 0.315 3.17	Po (0.26) (3.8)	At	Rn				
Fr (0.020) (50.)	Ra (0.132) (7.6)	Ac (0.25) (4.)																			
			Ce [c] 0.239 4.18	Pr 0.306 3.27	Nd 0.327 3.06	Pm (0.35) (2.85)	Sm 0.294 3.40	Eu 0.147 6.80	Gd 0.383 2.61	Tb 0.399 2.51	Dy 0.384 2.60	Ho 0.397 2.52	Er 0.411 2.43	Tm 0.397 2.52	Yb 0.133 7.52	Lu 0.411 2.43					
			Th 0.543 1.84	Pa (0.76) (1.3)	U 0.987 1.01	Np (0.68) (1.5)	Pu 0.54 1.9	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					

Bulk Si: a covalent solid that crystallizes in the diamond structure

Go to the directory where the exercise on the structure of Si is stored
Inspect the input file, Si.fdf

More information at the [Siesta web page](http://www.icmab.es/siesta)
<http://www.icmab.es/siesta> and follow the link **Documentations, Manual**

```
SystemName      Bulk Silicon
SystemLabel     Si
NumberOfSpecies 1
NumberOfAtoms   2
%block ChemicalSpeciesLabel
  1 14 Si
%endblock ChemicalSpeciesLabel

LatticeConstant 5.43 Ang
%block LatticeVectors
  0.00 0.50 0.50
  0.50 0.00 0.50
  0.50 0.50 0.00
%endblock LatticeVectors

AtomicCoordinatesFormat ScaledByLatticeVectors
%block AtomicCoordinatesAndAtomicSpecies
  0.00 0.00 0.00 1
  0.25 0.25 0.25 1
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
  4 0 0 0.5
  0 4 0 0.5
  0 0 4 0.5
%endblock kgrid_Monkhorst_Pack
```

The theoretical lattice constant of Si for this first example

Diamond structure:

FCC lattice

+ a basis of two atoms

Sampling in k in the first Brillouin zone to achieve self-consistency

Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy E for several values of the volume Ω

Run the code,

```
siesta < Si.fdf > Si.5.43.out
```

The name of the output file is free, but since we are running bulk Si with the experimental lattice constant, this seems very sensible...

For this particular example, run from 5.35 Å up to 5.49 Å in steps of 0.02 Å.
Save each output file in a different file

Save in a file the data needed to plot the energy versus volume curve

```
grep "Total =" Si.*.out > Si.evslc.dat
```

Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy E for several values of the volume Ω

Edit the Si.evslc.dat file and leave only two columns:

diamond	
5.35	-215.456759
5.37	-215.467051
5.39	-215.474158
5.41	-215.476121
5.43	-215.474288
5.45	-215.469333
5.47	-215.461829
5.49	-215.451340

Add a first line with the kind of lattice (cubic, bcc, fcc, diamond...)

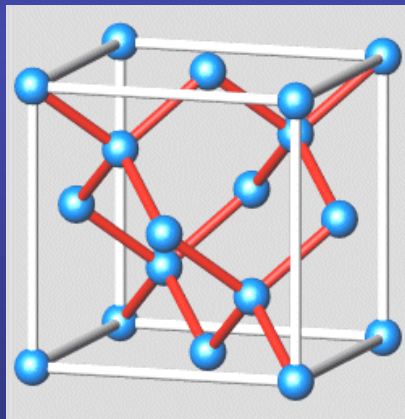
Lattice constant (in Å)

Energy of the unit cell (in eV)

Procedure to compute the equilibrium volume and bulk modulus

Step 1: Given a structure, compute the energy E for several values of the volume Ω

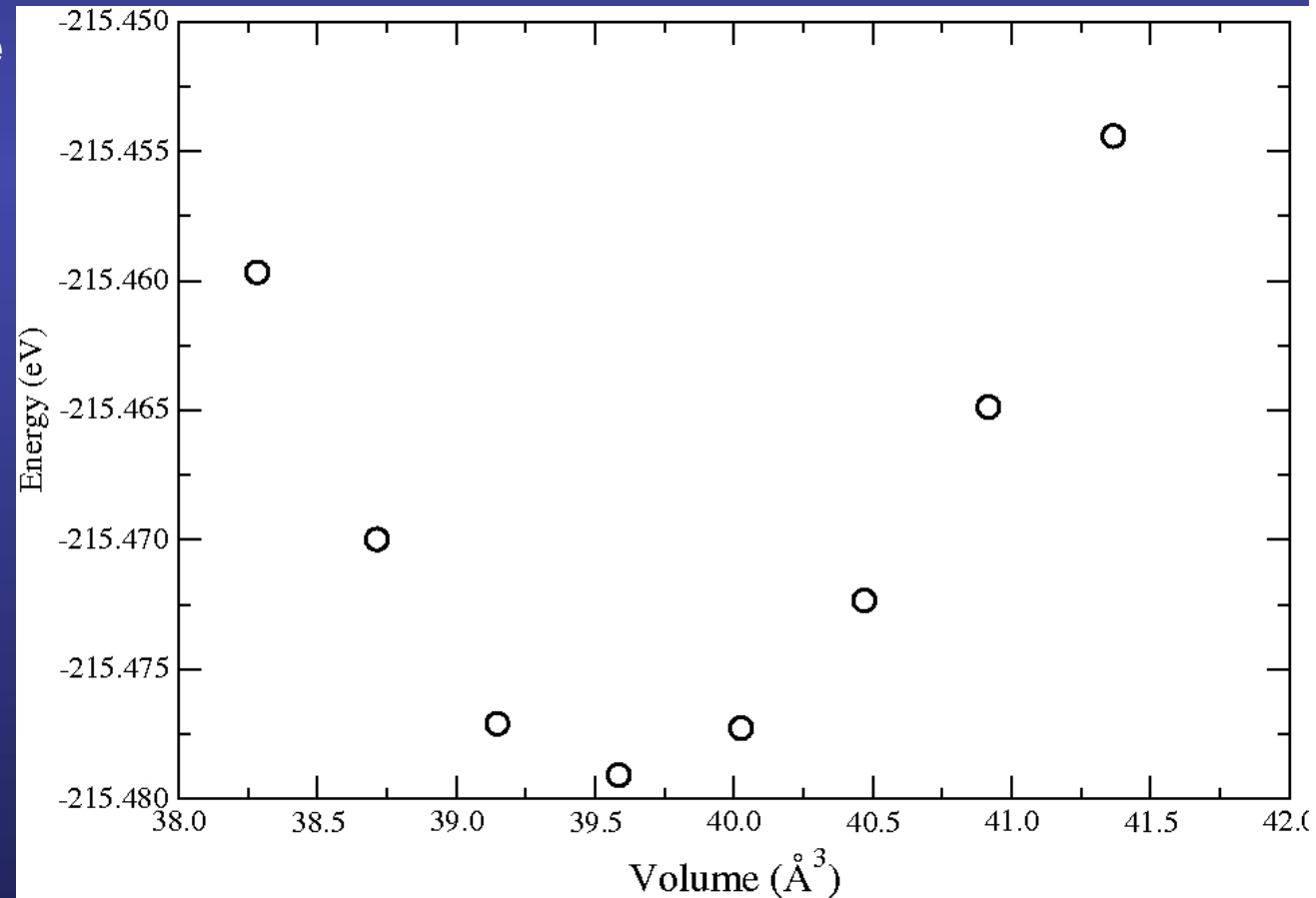
Example: Si in the diamond structure



Number of atoms in the unit cell fixed

Symmetry of the unit cell fixed

Temperature is fixed ($T = 0 \Rightarrow S = 0$)



Procedure to compute the equilibrium volume and bulk modulus

Step 2: Fit to an analytic form, e. g. , the Murnaghan equation of state

$$E(\Omega) = E_0 + \frac{B_0 \Omega}{B'_0} \left[\frac{\left(\frac{\Omega_0}{\Omega}\right)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{\Omega_0 B_0}{B'_0 - 1}$$

F. D. Murnaghan,

Proc. Nat. Acad. Sci. USA, 30, 244 (1944)

B_0 bulk modulus at the equilibrium volume

B'_0 pressure derivative of the bulk modulus at the equilibrium volume

To do this, we have prepared an script in python
`python fit_results.py Si.evslc.dat`

E_0 total energy at the minimum

Procedure to compute the equilibrium volume and bulk modulus

Step 2: Fit to an analytic form, e. g. , the Murnaghan equation of state

$$E(\Omega) = E_0 + \frac{B_0 \Omega}{B'_0} \left[\frac{\left(\frac{\Omega_0}{\Omega}\right)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{\Omega_0 B_0}{B'_0 - 1}$$

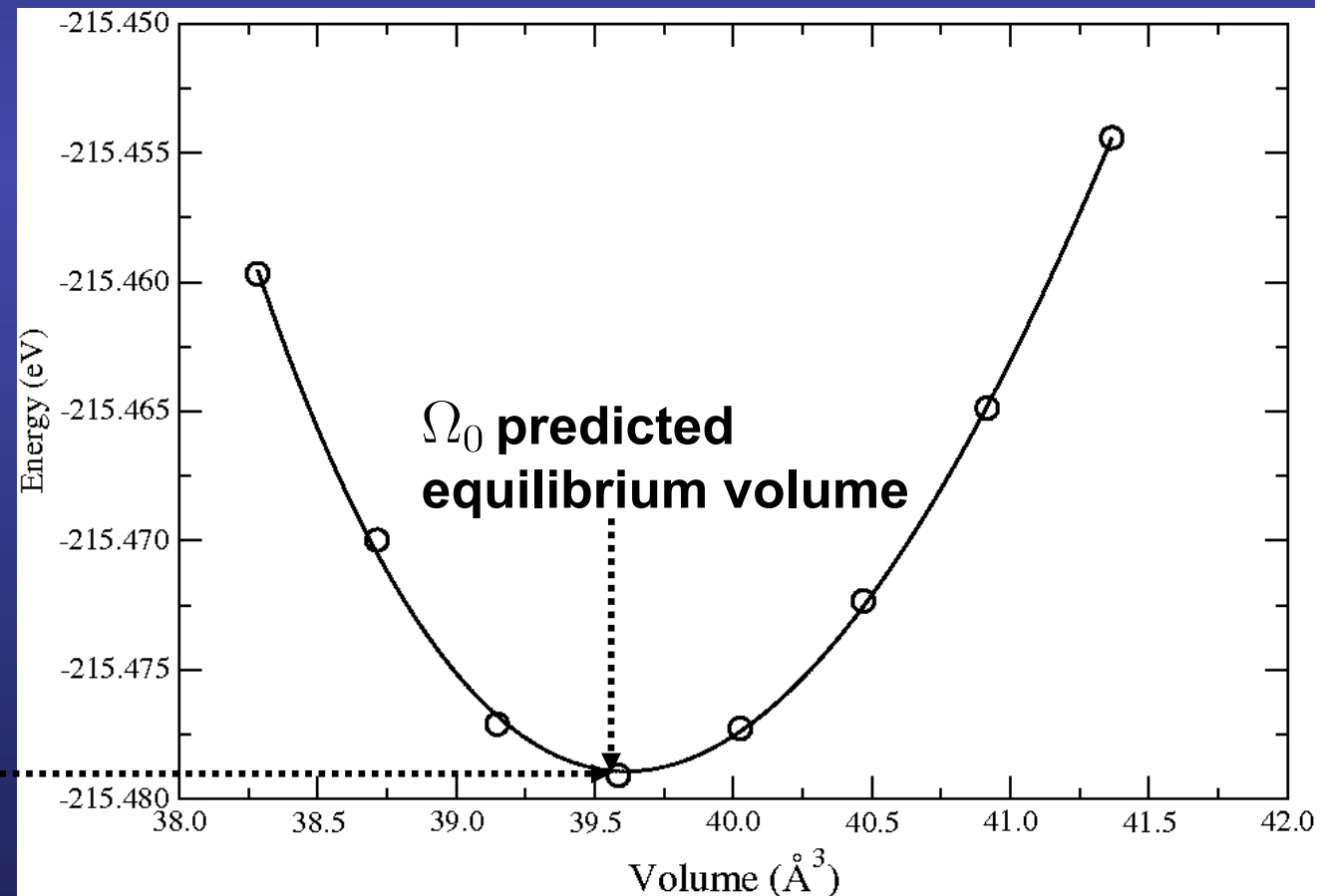
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B_0 bulk modulus at the equilibrium volume

B'_0 pressure derivative of the bulk modulus at the equilibrium volume

E_0 total energy at the minimum



Comparison of predicted equilibrium properties with experimental values are routine tests for calculations

		Exp	LAPW	Other PW	PW	DZP
Au	<i>a</i>	4.08 ^a	4.05 ^b	4.07 ^c	4.05	4.07
	<i>B</i>	173 ^a	198 ^b	190 ^c	191	188
	<i>E_c</i>	3.81 ^a	-	-	4.19	4.03
MgO	<i>a</i>	4.21 ^d	4.26 ^e	-	4.10	4.11
	<i>B</i>	152 ^d	147 ^e	-	168	167
	<i>E_c</i>	10.30 ^d	10.40 ^e	-	11.90	11.87
C	<i>a</i>	3.57 ^a	3.54 ^f	3.54 ^g	3.53	3.54
	<i>B</i>	442 ^a	470 ^f	436 ^g	466	453
	<i>E_c</i>	7.37 ^a	10.13 ^f	8.96 ^g	8.90	8.81
Si	<i>a</i>	5.43 ^a	5.41 ^h	5.38 ^g	5.38	5.40
	<i>B</i>	99 ^a	96 ^h	94 ^g	96	97
	<i>E_c</i>	4.63 ^a	5.28 ^h	5.34 ^g	5.37	5.31
Na	<i>a</i>	4.23 ^a	4.05 ⁱ	3.98 ^g	3.95	3.98
	<i>B</i>	6.9 ^a	9.2 ⁱ	8.7 ^g	8.8	9.2
	<i>E_c</i>	1.11 ^a	1.44 ^j	1.28 ^g	1.22	1.22
Cu	<i>a</i>	3.60 ^a	3.52 ^b	3.56 ^g	-	3.57
	<i>B</i>	138 ^a	192 ^b	172 ^g	-	165
	<i>E_c</i>	3.50 ^a	4.29 ^k	4.24 ^g	-	4.37
Pb	<i>a</i>	4.95 ^a	-	4.88	-	4.88
	<i>B</i>	43 ^a	-	54	-	64
	<i>E_c</i>	2.04 ^a	-	3.77	-	3.51

Accuracy of the xc functionals in the structural and electronic properties

	LDA	GGA
a	-1% , -3%	+1%
B	+10, +40%	-20%, +10%
E_c	+15%	-5%
E_{gap}	-50%	-50%

LDA: crude approximation but sometimes is accurate enough (structural properties, ...).

GGA: usually tends to overcompensate LDA results, not always better than LDA.