

Theoretical Material Science: Exercise Sheet 8**Please hand in solutions by: Wednesday, June 06**, start of the exercise class**Exercise 19** (8 points): *Cohesive properties: Will the stable phase(s) please stand up?*

One of the fundamental questions in materials science is this: Given one or more chemical elements in a certain proportion, which stable structure will they form? The ability of density functional theory (DFT) in the local-density approximation (LDA) to predict, without any empirical parameters, the phase stability and materials parameters of real solids, marked a breakthrough in quantum-mechanics based computational materials science.

At $T=0$ and $p=0$, the quantity that determines phase stability is the total energy $E(V)$, which has the following functional form: ("Murnaghan equation of state"):

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (1)$$

In other words, E is related to the volume V by the following material properties defined at zero pressure: E_0 , the equilibrium energy, V_0 , the equilibrium volume, B_0 , the bulk modulus at zero pressure, and its pressure derivative $B'_0 = \left(\frac{\partial B}{\partial p} \right)_T$ at $p = 0$. The bulk modulus (B) of a solid is defined as:

$$B = -V \left(\frac{\partial P}{\partial V} \right) = -V \left(\frac{\partial^2 E}{\partial V^2} \right) \quad (2)$$

In this exercise, we take E to be the energy at the Born-Oppenheimer surface, and neglect vibrations and finite-temperature effects.

a) $E(V)$ of the diamond phase of Si.

- (i) For a set of five different unit cell volumes (lattice parameters), compute $E(V)$ for diamond Si. Use DFT-LDA and a $12 \times 12 \times 12$ k -point integration grid.
- (ii) By fitting to Eq. (1), determine E_0 , V_0 , and B_0 .
- (iii) Compare your results to the following experimentally known parameters ($T=0$): Lattice parameter $a_0=5.43$ Å, $B_0=98.9$ GPa, cohesive energy $E_{\text{coh}}=4.63$ eV/atom. What are the trends? How do they match the expected properties of LDA? For Si and LDA, use the energy of the spherically symmetric free atom (ensemble average with fractional occupation numbers) as a reference in E_{coh} .

b) *Other phases of Si.*

At Earth atmospheric conditions, Si assumes the diamond structure, but at different conditions, other structures could exist. We here consider fcc and bcc Si.

- (i) Find the fcc and bcc lattice parameter values that correspond to the same Si-Si nearest-neighbour distance as in the experimental diamond structure.
- (ii) Beginning from these rough estimates, use a $12 \times 12 \times 12$ k -point grid and a Gaussian broadening of 0.1 eV about the Fermi level to find the equilibrium lattice parameters, bulk modulus, and cohesive energy for fcc Si and bcc Si as a function of volume.
- (iii) *Only for the calculated lowest-energy geometry*, verify the k -space convergence explicitly by using a $24 \times 24 \times 24$ k -point grid. How good is the convergence? Inspect the printed highest occupied and lowest unoccupied levels: Are fcc and bcc Si semiconductors or metals?
- (iv) Plot the cohesive energy of all three phases into the same graph, as a function of the unit cell volume per atom. According to LDA, which is the most stable phase? Does the prediction agree with experiment? Under pressure, do you expect fcc or bcc Si to become stable?

Please turn over! →

Exercise 20 (4 points): *Trends for cohesive properties in LDA*

Use the same strategy as in the preceding exercise to determine the cohesive properties of

- a) GaAs
- b) ZnSe

Both materials (important semiconductors!) crystallize in the zincblende phase: The same lattice as the diamond phase, but two different elements occupy the two atomic sites. Consider only the zincblende structure, and only $12 \times 12 \times 12$ \mathbf{k} -point grids. Use the free atom reference energies in the detailed instructions as a reference. Compare to the following $T=0$ experimental values:

Material	a [Å]	B_0 [GPa]	E_{coh} [eV/atom]
GaAs	5.648	75.6	3.31
ZnSe	5.668	64.7	2.19

What are the trends that you would expect from DFT-LDA? Do the results match your expectations?

- **Webpage of the lecture:**

http://www.itp.tu-berlin.de/menue/lehre/lv/ss12/wahlpflichtveranstaltungen/theoretische_festkoerperphysik_i_ii_theoretical_material_science/
http://th.fhi-berlin.mpg.de/sitesub/lectures/spring_2012/

- **Lecture:** Tue. & Wed., 10:00 h -12:00 h (sharp!) in room EW 203, TU Berlin

- **Exercise:** Wed., 14:00 h in room EW 229

- **Literature:**

- Ashcroft, Mermin, David: Solid state physics, Saunders College, Philadelphia, 1981
- Kittel: Quantum theory of solids, Wiley, New York, 1963
- Ziman: Principles of the theory of solids, Cambridge University Press, Cambridge, 1964
- Ibach, Lueth: Solid-state physics: an introduction to principles of materials science, Springer, Berlin, 1995
- Madelung: Festkörpertheorie, Springer, Berlin, 1972
- Scherz: Quantenmechanik, Teubner, Stuttgart, 1999
- Dreizler, Gross: Density functional theory: an approach to the quantum many-body problem, Springer, Berlin, 1990
- Parr, Yang: Density-functional theory of atoms and molecules, Oxford University Press, Oxford, 1994
- Anderson: Basic notations of condensed matter physics, Benjamin/Cummings, London, 1984
- Marder: Condensed matter physics, Wiley, New York, 2000
- Martin: Electronic Structure, Cambridge University Press, Cambridge, 2004
- Kohanoff: Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods, Cambridge University Press, Cambridge, 2006

- **"Übungsschein"-criteria:**

- Regular and active participation in the exercises
- Presentation of homework tasks and
- 50% of the homework points.
- Active participation in computational exercises

- **Consultation hours:**

- Prof. Dr. Matthias Scheffler, Dr. Alex Tkatchenko, Dr. Patrick Rinke: by appointment
- Dr. Volker Blum: Available Wed. 16:00 (after the exercise class) or by appointment