Computational Solid State Physics
2nd Midterm (DFT)

Midterm Exam, December 16th 2024

In this midterm exam you will employ the DFT code `quantum espresso` to simulate elastic anomalies in some cubic metallic alloys with chemical formula AB. You have four hours to solve the assignment; you can consult any books, notes and internet websites, but communicating with other students by any means is strictly forbidden (your test will be invalidated in that case).
The use of AI tools like `ChatGPT` is strictly prohibited and will result in test invalidation.
At the end of the four hours submit your report as a single PDF (named 'NAME_SURNAME.pdf') via email to `lilia.boeri@uniroma1.it`. Include all input files in a separate zipped attachment (named 'NAME_SURNAME_inputs.zip'). Use the subject line: 'Computational Solid State Physics Midterm - NAME SURNAME.'" Please note that NAME SURNAME indicate YOUR name and surname, respectively.

► **Exercise:** In this midterm exam you will use the DFT code `Quantum ESPRESSO` to investigate *strain-induced elastic softening* in metallic alloys under *epitaxial (biaxial) constraint*.
Some binary metallic alloys, such as FeSi or NiAl, can be grown epitaxially in the *CsCl (B2) structure*. These artificially stabilized crystals may exhibit anomalous elastic behavior, becoming *supersoft* under applied strain.
In this exercise, you will simulate the elastic response of a hypothetical binary compound AB in order to verify whether it displays supersoft behavior. The compound is constructed by placing two atomic species A and B in the CsCl structure; each student will be assigned a different AB combination. The CsCl structure, shown in the Appendix, consists of two interpenetrating cubic lattices displaced along the body diagonal. When grown on a substrate, the in-plane lattice constants a and b may expand or contract with respect to their equilibrium value. As a consequence, the system can undergo a tetragonal distortion, with $a = b \neq c$, as illustrated in the figure.

1 Preliminary steps:

- Download and unzip the archive `pseudo.zip` from the e-learning website of the course. The archive contains GGA Norm-Conserving pseudopotentials from the Pseudo-dojo website for selected elements of the periodic table.
- Each student has been assigned a different *student number*, as indicated in the student list file on elearning.
- Consult Table 1 to see what combination of elements corresponds to your student number. Each combination of elements defines a different binary compound with chemical formula AB for which you should perform calculations as described in the text.

2 Electronic properties of hypothetical AB compounds in the B_2 structure, ground-state structure:

2.1 Initial Structure Setup and Convergence of the Relevant Input Parameters:

1. The structural parameters of the B_2 structure are reported in the Appendix. Before setting up the calculation, answer the following questions:

   - How many inequivalent Wyckoff positions are occupied? What is their multiplicity? Are these positions fixed or free? What is the point group? (To answer these questions you may consult the Bilbao Crystallographic Server entry attached to this document.)
   - If A and B were the same element, what type of crystal structure would you obtain? What would be the corresponding space group?
   - What types of symmetry operations can a space group contain?

2. Using the structural data provided in the Appendix, set up an initial input file for a `Quantum ESPRESSO` calculation of your AB binary compound in the CsCl crystal structure. The input file should contain all parameters required to perform a standard self-consistent calculation. For the initial setup, assume a cubic lattice constant $a = 6.0$ Å.

3. Since at this stage you cannot know whether the system you are setting up will be a metal or an insulator, it is safer to use an occupation method that can handle both cases. We will employ the Methfessel–Paxton smearing method, which is computationally efficient and numerically stable, with a fixed smearing value of 0.04 Ry. Therefore, the `&SYSTEM` section of the input file must include the following keywords: `occupations = 'smearing', smearing = 'mp', degauss = 0.04`.

4. Once you have verified that your input file is correctly set up, perform all convergence tests required to achieve a total-energy accuracy of at least 20 meV/atom. Produce a separate plot for each convergence test, accompanied by a brief explanation (maximum 50 words per plot).

2.2 Electronic properties of the ground-state structure

In the second part of the exercise we will relax the crystal structure of the AB crystal to the hypothetical ground-state structure at ambient pressure, and compute the corresponding electronic properties.

1. Explain briefly (max 100 words) what is meant by structural relaxation, and what are the steps that `Quantum ESPRESSO` needs to carry out to perform one.

2. What is the theoretical pressure calculated by `Quantum ESPRESSO` for the initial structure you set up? What are the forces acting on the atoms? Do you expect your final volume to be larger or smaller than the initial one?

3. How many total steps did you need to find the equilibrium structure?

4. **Hint:** To make sure that your relaxation has really converged to the actual equilibrium structure, re-run a second relaxation starting from the final structure of the first relaxation.

5. **Hint:** If your PC is too slow and the relaxation is taking too long, stop it and reduce the k-grid. Write in your report that you had to do this due to slow convergence.

6. Once you are sure that your calculation has reached the theoretical equilibrium volume, write down the final value of the volume and the corresponding lattice constant.

3 Strain:

In the second part of the exercise you will simulate the effect of epitaxial strain by contracting the in-plane lattice constants a, b, and allowing the out-of-plane lattice constant c to relax.
Formally, the effect of strain is described by a strain tensor $\hat{\varepsilon}$, with components ε_{ij} $(i, j = 1, \ldots, 3)$, which relates the strained $(\mathbf{a}'_i)$ and unstrained $(\mathbf{a}_i)$ lattice vectors through

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = (\mathbf{I} + \hat{\varepsilon}) \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} = \begin{pmatrix} 1+\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1+\varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1+\varepsilon_{zz} \end{pmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix}. \tag{1}$$

The diagonal components of the strain tensor describe *normal* strains $(\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz})$, corresponding to relative elongations or contractions along the Cartesian axes, while the off-diagonal components describe *shear* strains $(\varepsilon_{xy}, \varepsilon_{xz}, \varepsilon_{yz})$, corresponding to changes in the angles between the lattice vectors.
A strain deformation introduces a *stress* in the crystal. The stress response is described by a stress tensor $\hat{\sigma}$, whose diagonal components $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ describe normal stresses (pressure), while the off-diagonal components describe shear stresses.
The stress tensor is related to the derivative of the total internal energy of the crystal with respect to strain deformations through

$$\sigma_{ij} = \frac{1}{V} \frac{\partial E}{\partial \varepsilon_{ij}}, \tag{2}$$

where E is the total energy of the system, V is the volume, and ε_{ij} are the components of the strain tensor.
In this exercise you will compute the total energy and the stress tensor of your hypothetical AB crystal for different values of *biaxial in-plane strain* $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon = -0.02, -0.04, \ldots, -0.16$, and use these results to detect possible supersoft behavior.

1. Set up a calculation corresponding to a 10% biaxial in-plane strain $\varepsilon = -0.10$, modifying the `Quantum ESPRESSO` input file as follows: In the `&SYSTEM` section, set `ibrav=0` (custom-defined Bravais lattice), without modifying the value of the in-plane lattice constant. After the `ATOMIC_POSITIONS` block introduce a `CELL_PARAMETERS` block, containing the definitions of the three lattice vectors:
   ```
   CELL_PARAMETERS (alat)
   0.9000000000 0.0 0.0
   0.0 0.9000000000 0.0
   0.0 0.0 1.00000000
   ```
   Here, `alat` indicates that the lattice vectors are expressed in units of a. The above choice corresponds to a 10% negative in-plane strain.

2. Run a self-consistent calculation for this structure, and write down the value of the volume, total energy, and stress tensor.

Answer the following questions (100 words): What are the values of the three diagonal components of the stress tensor? Are they positive/negative? Why? What do you expect will happen if you let the unit cell relax in the out-of-plane (z) direction?

3. Now, relax the crystal in the z direction, while keeping the a, b lattice constants fixed, with a `vc-relax` calculation. To relax the cell only along z, add the instruction `cell_dofree = 'z'` to the `&CELL` section of the input file. Write down the final value of the volume and lattice constant.

   Answer the following questions (100 words): Has the unit cell expanded/contracted in the c direction? What happened to the volume? Is this expected/unexpected, based on the values of the stress tensor you computed before? **Hint:** Also in this case, to make sure your relaxation has really converged, run a second relaxation starting from the relaxed structure.

4. Repeat the operations described for different values of the in-plane biaxial strain $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon = -0.02, -0.04, \ldots, -0.16$. Keep track of the values of in-plane strain, volume, c/a ratio, total energy, and of the three components of the stress tensor.

5. Produce three plots of the energy vs. strain, in-plane stress vs. strain, and c/a ratio vs. strain. In a normal crystal, for small strains the E vs. ε curve is approximately parabolic. In a *supersoft* material, on the other hand, the energy vs. strain has a minimum for a finite value of $\varepsilon \neq 0$, which means that the cubic B_2 structure is so strongly metastable that a relatively small in-plane deformation is enough to destabilize it towards a tetragonal structure.

   Based on your plots, answer the following questions (100 words): Where is the minimum of your energy vs. ε curve? Is your AB crystal supersoft? What happens to the c lattice constant when you apply strain? Why? Are the behaviour of energy vs. strain and stress vs. strain consistent with the definitions in Eqs. (1)–(2)?
   NB: It may not be possible to determine precisely the position of the minimum, if the E vs. strain curve is too flat. In this case, do not overconverge the calculation but briefly discuss what the problem is and how you would in principle solve it if you had enough time.

6. **Bonus question, only if you have finished everything else:**

   Construct a cubic cell with the same lattice constant corresponding to $\varepsilon = -0.10$.

   Answer the following questions: What is the theoretical value of the pressure? Is it smaller/larger than the value of the in-plane stress for the same in-plane lattice constant? Why? What does this say about the elastic behaviour of epitaxially grown crystals?

4 Appendix

4.1 Structural Parameters:

Chemical Formula: AB
Space Group (Lattice): 221 (cubic), 123 (tetragonal).
Atomic coordinates ($WyckoffPositions$)**:** A (1a) B (1b)

4.2 Crystal structure:

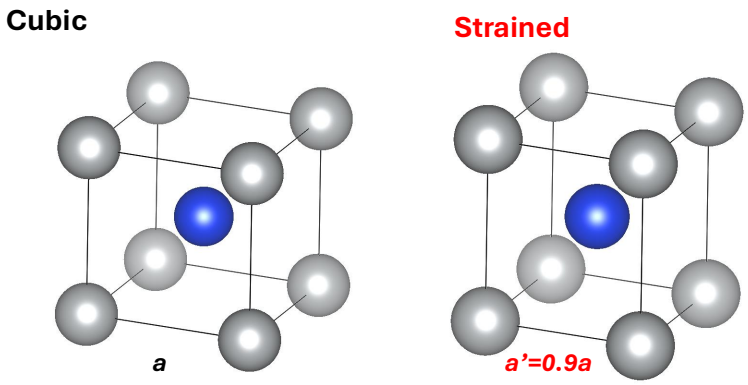

Figure 1: (Left) CsCl crystal structure, undistorded (left) and with a -10% in-plane strain.

4.3 Combinations of element pairs for each student:

St. Number	**Element** A	**Element** B	**St. Number**	**Element** A	**Element** B
1	Sc	Al	31	Fe	Si
2	Ti	Si	32	Co	P
3	V	P	33	Ni	Al
4	Cr	Al	34	Cu	Si
5	Mn	Si	35	Zn	P
6	Fe	P	36	Sc	Si
7	Co	Al	37	Ti	P
8	Ni	Si	38	V	Al
9	Cu	P	39	Cr	Si
10	Zn	Al	40	Mn	P
11	Sc	P	41	Fe	Al
12	Ti	Al	42	Co	Si
13	V	Si	43	Ni	P
14	Cr	P	44	Cu	Al
15	Mn	Al	45	Zn	Si
16	Fe	Si	46	Sc	Al
17	Co	P	47	Ti	Si
18	Ni	Al	48	V	P
19	Cu	Si	49	Cr	Al
20	Zn	P	50	Mn	Si
21	Sc	Si	51	Fe	P
22	Ti	P	52	Co	Al
23	V	Al	53	Ni	Si
24	Cr	Si	54	Cu	P
25	Mn	P	55	Zn	Al
26	Fe	Al	56	Sc	P
27	Co	Si	57	Ti	Al
28	Ni	P	58	V	Si
29	Cu	Al	59	Cr	P
30	Zn	Si	60	Mn	Al

Table 1: List of assigned AB combinations for each student.