

Computational Solid State Physics

Makeup Test (DFT)

January 12th 2026

In this midterm exam you will employ the DFT code `quantum espresso` to understand the electronic structure properties of XB_3C_3 compounds. You have two 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 two 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 Makeup - NAME SURNAME.' Please note that NAME SURNAME indicate YOUR name and surname, respectively.

► **Exercise:** In this makeup exam you will use the DFT code `Quantum ESPRESSO` to investigate the electronic structure of XB_3C_3 compounds; here X is an alkali metal, alkaline earth, or lanthanide. XB_3C_3 compounds were first synthesized in 2020 using laser heating at high pressure. Once formed, some of these compounds remain metastable at ambient pressure. Their crystal structure is shown in Fig. 1: B and C atoms form an alternating cage-like framework that encloses the larger X atom at the center of the cage. Depending on the nature of X , XB_3C_3 compounds can exhibit different physical properties, such as superconductivity, ferroelectricity, and structural instabilities. In this exercise, you will study the electronic properties of a specific XB_3C_3 compound. Each student will be assigned a different X atom.

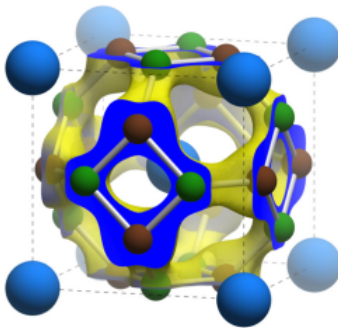


Figure 1: Crystal Structure of XB_3C_3 : Blue, Green and Brown sphere indicate X , B and C atoms respectively.

1 Preliminary steps

- Download and unzip the archive `pseudo.zip` from the course e-learning platform. The archive contains GGA norm-conserving pseudopotentials from the PseudoDojo library for boron, carbon,

and selected elements of the periodic table.

- Each student has been assigned a different *student number*, as indicated in the student list available on the e-learning platform.
- Using your student number, consult Appendix Table 3 to identify the element X assigned to you. Each element X defines a different XB_3C_3 compound for which you must perform the calculations described below.

| | |
|--------------------------|--------------------------|
| Chemical formula | XB_3C_3 |
| Space group | 223 (cubic) |
| Wyckoff positions | X (2a), B (6c), C (6d) |

Table 1: Structural information for the XB_3C_3 compound.

2 Electronic properties of XB_3C_3 in the ground-state structure:

2.1 Initial Structure Setup:

2.1.1 The structural parameters of the XB_3C_3 compound are reported in Table 1. Before setting up the calculations, answer the following:

- What type of Bravais lattice does this structure belong to?
- How many atoms are there in the unit cell and what are their crystallographic positions?
- How many formula units are contained in each unit cell?

(Answer in max 100 words total. You may consult the Bilbao Crystallographic Server entry attached to this document.)

2.1.2 Using the structural data provided in Table 1, set up an initial input file for a Quantum ESPRESSO calculation of your XB_3C_3 compound. The input file must contain all the parameters required to perform a standard self-consistent (SCF) calculation. For the initial setup:

- Assume a cubic lattice constant $a = 10$ a.u..
- Since at this stage you cannot know whether the system is metallic or insulating, use an occupation scheme that is appropriate for both cases. In particular, employ the Methfessel-Paxton smearing method with a fixed smearing width of 0.04 Ry. Therefore, the `&SYSTEM` section of the input file must include: `occupations = 'smearing', smearing = 'mp', degauss = 0.04`.
- Do not perform a convergence study on the kinetic energy cutoff or the **k**-point sampling. Assume `ecutwfc = 40` Ry and a uniform $2 \times 2 \times 2$ grid in reciprocal space.

2.1.3 Report the volume of the unit cell and the corresponding pressure (in kbar) obtained from your SCF calculation.

2.1.4 Based on the calculated pressure, would you expect the unit cell to shrink or expand if relaxed to zero pressure? Explain your reasoning (max 50 words).

2.2 Relaxation to the ground-state structure

In the second part of the exercise we will relax the crystal structure of the XB_3C_3 compound to its hypothetical ground-state structure at ambient pressure.

2.2.1 Relax the structure to zero pressure: what are the corresponding volume and pressure? What is the lattice constant? Is the result consistent with your expectations? Why? (100 words).

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

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.

3 Electronic Structure

Once you have found the ground-state structure, you will compute the corresponding electronic structure and Density of States, and discuss the main implications.

3.1 Pristine Compound:

3.1.1 Explain what is meant by an electronic band-structure calculation and describe briefly how Quantum ESPRESSO computes it (max 100 words).

3.1.2 Compute and plot the electronic band structure of your XB_3C_3 compound along a high-symmetry path in reciprocal space. To reduce the computational load, use the minimal path $M - \Gamma - X$. If the calculation is slow, reduce the number of points along each segment (10 points/segment are sufficient). You can find a list of special \mathbf{k} -points in table 2.

3.1.3 Compute the corresponding density of states (DOS) using a $6 \times 6 \times 6$ \mathbf{k} -point grid and the tetrahedron method.

3.1.4 Explain briefly how Quantum ESPRESSO computes the DOS (max 100 words).

3.1.5 Using your band structure and DOS, answer the following (max 200 words total): (i) What is the Fermi level of your system and how did you determine it? (ii) Is the system metallic or insulating? Justify your answer. (iii) If metallic, report $N(E_F)$ (DOS at the Fermi level). If insulating, report the band gap.

Hint: For the above plots, you may use the attached python scripts; remember to update the name of the relevant `dat` files, the name and coordinates of the special \mathbf{k} -points, the position of the Fermi level, the total number of valence electrons, etc.

3.2 Rigid-Band Doping:

The rigid-band approximation is a quick-and-dirty way to estimate the effect of doping on a crystal without explicitly introducing dopants in the calculation. In practice, one assumes that the band structure (and DOS) remains unchanged upon doping, and simulates the effect of adding/removing carriers by shifting the Fermi level accordingly.

Based on the results you obtained in the previous section, answer the following:

| Label | Coordinates (k_x, k_y, k_z) (fractional) |
|----------|--|
| Γ | $(0, 0, 0)$ |
| X | $(\frac{1}{2}, 0, 0)$ |
| M | $(\frac{1}{2}, \frac{1}{2}, 0)$ |
| R | $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ |

Table 2: High-symmetry **k**-points for the Brillouin zone of XB_3C_3 (coordinates in units of the reciprocal lattice vectors).

3.2.1 Where would the Fermi level fall if you added/subtracted one or two electrons per formula unit (f.u.)?

3.2.2 Which physical properties would be affected by this change, and why?

3.3 Physical Doping:

Now replace the X atoms with the Y atoms indicated in Appendix Table 3. Without relaxing the crystal structure (i.e. keeping the same lattice parameters and atomic positions), compute the electronic structure and DOS of the resulting YB_3C_3 compounds. Answer the following:

3.3.1 Which of the rigid-band cases from the previous section (electron- or hole-doped, and by how many electrons per f.u.) is the appropriate reference for comparison?

3.3.2 State whether the substitution is consistent with a rigid-band picture, and justify your answer (max 100 words).

Bonus question:

In this exercise, we have used coarse numerical settings and simplified models to keep the calculations manageable. Assume you were studying this system as part of a real research project. Describe how you would improve the quality and reliability of your results, both from a numerical and a physical point of view, justifying your choices (max 200 words).

4 Appendix

4.1 X/Y element for each student

| St. Number | Element X | Element Y |
|------------|-------------|-------------|
| 1 | Li | Be |
| 2 | Be | Sc |
| 3 | K | Ca |
| 4 | Ca | K |
| 5 | Na | Mg |
| 6 | Mg | Sc |
| 7 | Sc | Ca |
| 8 | Rb | Sr |
| 9 | Y | Sr |
| 10 | Sr | La |
| 11 | La | K |

Table 3: Combinations of X and Y elements for each student.

PERIODIC TABLE OF ELEMENTS

| 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 | | | | | | | | | | | | | | | | | |
|--|---------------------------------|------------------------------------|-------------------------------------|---------------------------------|----------------------------------|---------------------------------|----------------------------------|----------------------------------|------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|---------------------------------|----------------------------------|-----------------------------------|----------------------------------|---------------------------------|
| 1 H Hydrogen 1.008 | 2 He Helium 4.0026 | | | | | | | | | | | | | | | | |
| 3 Li Lithium 6.94 | 4 Be Beryllium 9.0122 | | | | | | | | | | | | | | | | |
| 11 Na Sodium 22.990 | 12 Mg Magnesium 24.305 | | | | | | | | | | | | | | | | |
| 19 K Potassium 39.098 | 20 Ca Calcium 40.078 | 21 Sc Scandium 44.956 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 | 25 Mn Manganese 54.938 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933 | 28 Ni Nickel 58.693 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.630 | 33 As Arsenic 74.922 | 34 Se Selenium 78.971 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.798 |
| 37 Rb Rubidium 85.468 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.906 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.95 | 43 Tc Technetium (98) | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.91 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.87 | 48 Cd Cadmium 112.41 | 49 In Indium 114.82 | 50 Sn Tin 118.71 | 51 Sb Antimony 121.76 | 52 Te Tellurium 127.60 | 53 I Iodine 126.90 | 54 Xe Xenon 131.29 |
| 55 Cs Caesium 132.91 | 56 Ba Barium 137.33 | 57-71 Lanthanoids (Lanthanides) | 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.95 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.21 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.22 | 78 Pt Platinum 195.08 | 79 Au Gold 196.97 | 80 Hg Mercury 200.59 | 81 Tl Thallium 204.38 | 82 Pb Lead 207.2 | 83 Bi Bismuth 208.98 | 84 Po Polonium (209) | 85 At Astatine (210) | 86 Rn Radon (222) |
| 87 Fr Francium (223) | 88 Ra Radium (226) | 89-103 Actinoids (Actinides) | 104 Rf Rutherfordium (267) | 105 Db Dubnium (268) | 106 Sg Seaborgium (269) | 107 Bh Bohrium (270) | 108 Hs Hassium (271) | 109 Mt Meitnerium (272) | 110 Ds Darmstadtium (281) | 111 Rg Roentgenium (282) | 112 Cn Copernicium (285) | 113 Nh Nihonium (286) | 114 Fl Flerovium (289) | 115 Mc Moscovium (290) | 116 Lv Livermorium (293) | 117 Ts Tennessine (294) | 118 Og Oganesson (294) |
| For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses. | | | | | | | | | | | | | | | | | |
| 57 La Lanthanum 138.91 | 58 Ce Cerium 140.12 | 59 Pr Praseodymium 140.91 | 60 Nd Neodymium 144.24 | 61 Pm Promethium (145) | 62 Sm Samarium 150.36 | 63 Eu Europium 151.96 | 64 Gd Gadolinium 157.25 | 65 Tb Terbium 158.93 | 66 Dy Dysprosium 162.50 | 67 Ho Holmium 164.93 | 68 Er Erbium 167.26 | 69 Tm Thulium 168.93 | 70 Yb Ytterbium 173.05 | 71 Lu Lutetium 174.97 | | | |
| 89 Ac Actinium (227) | 90 Th Thorium 232.04 | 91 Pa Protactinium 231.04 | 92 U Uranium 238.03 | 93 Np Neptunium (237) | 94 Pu Plutonium (244) | 95 Am Americium (243) | 96 Cm Curium (247) | 97 Bk Berkelium (247) | 98 Cf Californium (251) | 99 Es Einsteinium (252) | 100 Fm Fermium (257) | 101 Md Mendelevium (258) | 102 No Nobelium (259) | 103 Lr Lawrencium (260) | | | |

Figure 2: Caption

Wyckoff Positions of Group *Pm-3n* (No. 223)

| Multiplicity | Wyckoff letter | Site symmetry | Coordinates |
|--------------|----------------|-----------------|--|
| 48 | <i>l</i> | 1 | (x,y,z) $(-x,-y,z)$ $(-x,y,-z)$ $(x,-y,-z)$ (z,x,y) $(z,-x,-y)$ $(-z,-x,y)$ $(-z,x,-y)$ (y,z,x) $(-y,z,-x)$ $(y,-z,-x)$ $(-y,-z,x)$ $(y+1/2,x+1/2,-z+1/2)$ $(-y+1/2,-x+1/2,-z+1/2)$ $(y+1/2,-x+1/2,z+1/2)$ $(-y+1/2,x+1/2,z+1/2)$ $(x+1/2,z+1/2,-y+1/2)$ $(-x+1/2,z+1/2,y+1/2)$ $(-x+1/2,-z+1/2,-y+1/2)$ $(x+1/2,-z+1/2,y+1/2)$ $(z+1/2,y+1/2,-x+1/2)$ $(z+1/2,-y+1/2,x+1/2)$ $(-z+1/2,y+1/2,x+1/2)$ $(-z+1/2,-y+1/2,-x+1/2)$ $(-x,-y,-z)$ $(x,y,-z)$ $(x,-y,z)$ $(-x,y,z)$ $(-z,-x,-y)$ $(-z,x,y)$ $(z,x,-y)$ $(z,-x,y)$ $(-y,-z,-x)$ $(y,-z,x)$ $(-y,z,x)$ $(y,z,-x)$ $(-y+1/2,-x+1/2,z+1/2)$ $(y+1/2,x+1/2,z+1/2)$ $(-y+1/2,x+1/2,-z+1/2)$ $(y+1/2,-x+1/2,-z+1/2)$ $(-x+1/2,-z+1/2,y+1/2)$ $(x+1/2,-z+1/2,-y+1/2)$ $(x+1/2,z+1/2,y+1/2)$ $(-x+1/2,z+1/2,-y+1/2)$ $(-z+1/2,-y+1/2,x+1/2)$ $(-z+1/2,y+1/2,-x+1/2)$ $(z+1/2,-y+1/2,-x+1/2)$ $(z+1/2,y+1/2,x+1/2)$ |
| 24 | <i>k</i> | <i>m</i> .. | $(0,y,z)$ $(0,-y,z)$ $(0,y,-z)$ $(0,-y,-z)$ $(z,0,y)$ $(z,0,-y)$ $(-z,0,y)$ $(-z,0,-y)$ $(y,z,0)$ $(-y,z,0)$ $(y,-z,0)$ $(-y,-z,0)$ $(y+1/2,1/2,-z+1/2)$ $(-y+1/2,1/2,-z+1/2)$ $(y+1/2,1/2,z+1/2)$ $(-y+1/2,1/2,z+1/2)$ $(1/2,z+1/2,-y+1/2)$ $(1/2,z+1/2,y+1/2)$ $(1/2,-z+1/2,-y+1/2)$ $(1/2,-z+1/2,y+1/2)$ $(z+1/2,y+1/2,1/2)$ $(z+1/2,-y+1/2,1/2)$ $(-z+1/2,y+1/2,1/2)$ $(-z+1/2,-y+1/2,1/2)$ |
| 24 | <i>j</i> | ..2 | $(1/4,y,y+1/2)$ $(3/4,-y,y+1/2)$ $(3/4,y,-y+1/2)$ $(1/4,-y,-y+1/2)$ $(y+1/2,1/4,y)$ $(y+1/2,3/4,-y)$ $(-y+1/2,3/4,y)$ $(-y+1/2,1/4,-y)$ $(y,y+1/2,1/4)$ $(-y,y+1/2,3/4)$ $(y,-y+1/2,3/4)$ $(-y,-y+1/2,1/4)$ $(3/4,-y,-y+1/2)$ $(1/4,y,-y+1/2)$ $(1/4,-y,y+1/2)$ $(3/4,y,y+1/2)$ $(-y+1/2,3/4,-y)$ $(-y+1/2,1/4,y)$ $(y+1/2,1/4,-y)$ $(y+1/2,3/4,y)$ $(-y,-y+1/2,3/4)$ $(y,-y+1/2,1/4)$ $(-y,y+1/2,1/4)$ $(y,y+1/2,3/4)$ |
| 16 | <i>i</i> | .3. | (x,x,x) $(-x,-x,x)$ $(-x,x,-x)$ $(x,-x,-x)$ $(x+1/2,x+1/2,-x+1/2)$ $(-x+1/2,-x+1/2,-x+1/2)$ $(x+1/2,-x+1/2,x+1/2)$ $(-x+1/2,x+1/2,x+1/2)$ $(-x,-x,-x)$ $(x,x,-x)$ $(x,-x,x)$ $(-x,x,x)$ $(-x+1/2,-x+1/2,x+1/2)$ $(x+1/2,x+1/2,x+1/2)$ $(-x+1/2,x+1/2,-x+1/2)$ $(x+1/2,-x+1/2,-x+1/2)$ |
| 12 | <i>h</i> | <i>mm2</i> .. | $(x,1/2,0)$ $(-x,1/2,0)$ $(0,x,1/2)$ $(0,-x,1/2)$ $(1/2,0,x)$ $(1/2,0,-x)$ $(0,x+1/2,1/2)$ $(0,-x+1/2,1/2)$ $(x+1/2,1/2,0)$ $(-x+1/2,1/2,0)$ $(1/2,0,-x+1/2)$ $(1/2,0,x+1/2)$ |
| 12 | <i>g</i> | <i>mm2</i> .. | $(x,0,1/2)$ $(-x,0,1/2)$ $(1/2,x,0)$ $(1/2,-x,0)$ $(0,1/2,x)$ $(0,1/2,-x)$ $(1/2,x+1/2,0)$ $(1/2,-x+1/2,0)$ $(x+1/2,0,1/2)$ $(-x+1/2,0,1/2)$ $(0,1/2,-x+1/2)$ $(0,1/2,x+1/2)$ |
| 12 | <i>f</i> | <i>mm2</i> .. | $(x,0,0)$ $(-x,0,0)$ $(0,x,0)$ $(0,-x,0)$ $(0,0,x)$ $(0,0,-x)$ $(1/2,x+1/2,1/2)$ $(1/2,-x+1/2,1/2)$ $(x+1/2,1/2,1/2)$ $(-x+1/2,1/2,1/2)$ $(1/2,1/2,-x+1/2)$ $(1/2,1/2,x+1/2)$ |
| 8 | <i>e</i> | .32 | $(1/4,1/4,1/4)$ $(3/4,3/4,1/4)$ $(3/4,1/4,3/4)$ $(1/4,3/4,3/4)$ $(3/4,3/4,3/4)$ $(1/4,1/4,3/4)$ $(1/4,3/4,1/4)$ $(3/4,1/4,1/4)$ |
| 6 | <i>d</i> | -4 <i>m</i> . 2 | $(1/4,1/2,0)$ $(3/4,1/2,0)$ $(0,1/4,1/2)$ $(0,3/4,1/2)$ $(1/2,0,1/4)$ $(1/2,0,3/4)$ |
| 6 | <i>c</i> | -4 <i>m</i> . 2 | $(1/4,0,1/2)$ $(3/4,0,1/2)$ $(1/2,1/4,0)$ $(1/2,3/4,0)$ $(0,1/2,1/4)$ $(0,1/2,3/4)$ |
| 6 | <i>b</i> | <i>mmm</i> .. | $(0,1/2,1/2)$ $(1/2,0,1/2)$ $(1/2,1/2,0)$ $(0,1/2,0)$ $(1/2,0,0)$ $(0,0,1/2)$ |
| 2 | <i>a</i> | <i>m-3</i> . | $(0,0,0)$ $(1/2,1/2,1/2)$ |

Figure 3: Caption