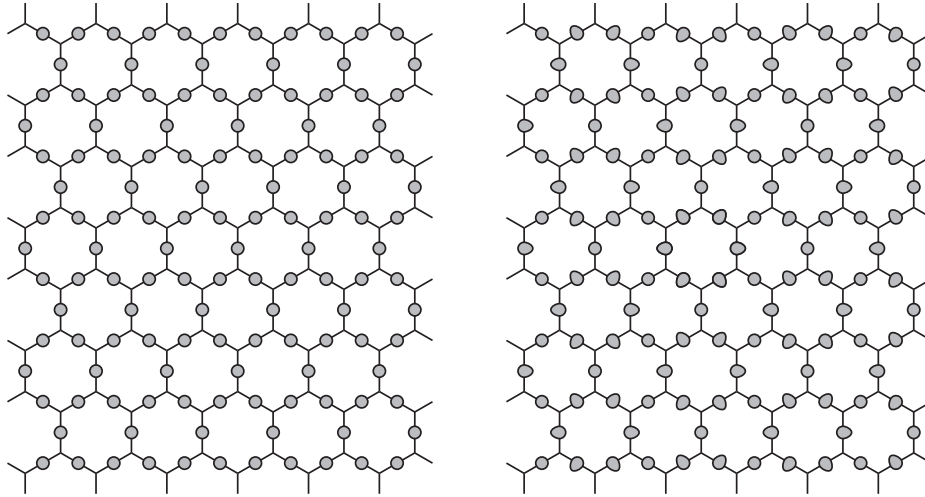


Physics 725: Assignment 2

(to be submitted by Thursday, February 14, 2019)

1. A two-dimensional network of atoms undergoes a structural phase transition as a function of temperature. The high-temperature (high-symmetry) phase is shown below on the left, and the low-temperature (broken-symmetry) phase on the right.



To start, focus on the non-deformed crystal. Its structure, called a Kagomé lattice, is the link-vertex dual of a honeycomb. (Have a look at the paper [Prog. Theor. Phys. Vol. 6 No. 3 \(1951\) pp. 306–308.](#))

- Sketch the lattice with lines drawn between nearest-neighbour atoms instead. What you should get is a tiling of the plane by hexagons and corner-sharing triangles.
- Both the Kagomé and honeycomb lattices can be viewed as triangular lattices that have been depleted in a regular way. In each case, depleted by what fraction?
- Describe the Kagomé lattice in terms of a set of primitive lattice vectors and a basis. Work in units where each lattice vector has length a .
- Determine the corresponding reciprocal lattice vectors and identify a Brillouin zone (BZ) using the Wigner-Sietz construction.

Now consider the crystal after it has been cooled through the critical temperature.

- How many times larger is the primitive unit cell?
- How many elements are in the basis?
- Construct the BZ of the deformed crystal and find two vectors in reciprocal space that can fold the BZ of the non-deformed crystal into it.

BONUS → (h) Find a suitable order parameter for the transition. Build a Ginzburg-Landau functional as a power series that includes only terms allowed by symmetry.

2. **Barium titanate**, a member of the perovskite family, is a piezoelectric material with the chemical formula BaTiO_3 . It exists in a variety of structural arrangements, depending on temperature and pressure. Two common ones are the cubic and tetragonal arrangements, which are separated by a phase transition at temperature $T_c = 403$ K. In the higher-temperature cubic phase, the barium and oxygen atoms form a cubic cage, and one titanium atom sits at each cube centre. (The alternative view is also valid: the titanium and oxygen atoms form a cubic cage, and one barium atom sits at each cube centre.) In the low-temperature tetragonal phase, the barium atoms displace in tandem along one of the orthogonal axes of the cubic system, and the titanium atoms do the same. The oxygen atoms sitting adjacent to each titanium along the line of displacement move in the opposite direction.

Barium titanate is described by the following set of lattice vectors:

$$\mathbf{a}_1 = a\mathbf{e}_x, \quad \mathbf{a}_2 = a\mathbf{e}_y, \quad \mathbf{a}_3 = c\mathbf{e}_z.$$

Atoms reside within each unit cell at these positions:

$$\begin{aligned} \boldsymbol{\tau}_{\text{Ba}} &= \eta\mathbf{e}_z, & \boldsymbol{\tau}_{\text{O1}} &= \frac{a}{2}(\mathbf{e}_x + \mathbf{e}_y), \\ \boldsymbol{\tau}_{\text{Ti}} &= \frac{a}{2}(\mathbf{e}_x + \mathbf{e}_y) + \left(\frac{c}{2} + \eta'\right)\mathbf{e}_z, & \boldsymbol{\tau}_{\text{O2}} &= \frac{a}{2}\mathbf{e}_x + \left(\frac{c}{2} + \eta''\right)\mathbf{e}_z, \\ & & \boldsymbol{\tau}_{\text{O3}} &= \frac{a}{2}\mathbf{e}_y + \left(\frac{c}{2} + \eta''\right)\mathbf{e}_z. \end{aligned}$$

In the cubic phase, $a = c = 4.00$ Å and $\eta = \eta' = \eta'' = 0$. In the tetragonal phase, $a = 3.99$ Å and $c = 4.04$ Å; the atomic displacements are $\eta = 0.06$ Å, $\eta' = 0.11$ Å, and $\eta'' = -0.03$ Å.

- Draw a diagram of the unit cell in the cubic and tetragonal phases.
- Explain what symmetries are broken as the system is cooled across the phase transition.
- Determine the BZ for BaTiO_3 . How is it different for temperatures $T > T_c$ and $T < T_c$.
- The ionization states of the atoms are roughly Ba^{2+} , Ti^{4+} , and O^{2-} . Compute the dipole moment per unit cell in the two phases.

Suppose we perform an X-ray powder diffraction experiment on a sample of BaTiO_3 .

- Compute the structure factor $S_{\mathbf{G}} = \sum_{\boldsymbol{\tau}} f_{\boldsymbol{\tau}} e^{i\mathbf{G}\cdot\boldsymbol{\tau}}$, allowing for $a \neq c$ and nonzero values of η and η' . The form factors are complex-valued, but their imaginary components are only significant near an absorption line, so we will assume that they are real. A good phenomenological model is

$$f(G) = \sum_{j=1}^4 a_j \exp[-b_j(G/4\pi)^2] + c,$$

with coefficients taken from the following table:

atom	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
O^{2-}	3.75040	16.5151	2.84294	6.59203	1.54298	0.319201	1.62091	43.3486	0.242060
Ba^{2+}	20.1807	3.21367	19.1136	0.28331	10.9054	20.0558	0.77634	51.746	3.02902
Ti^{4+}	19.5114	0.178847	8.23473	6.67018	2.01341	-0.29263	1.5208	12.9464	-13.28

The functional dependence of $f(G)$ means that the form factors change with the Bragg scattering angle. If you want to neglect that effect, you can assume that they are roughly constant in the vicinity of $G = |\mathbf{G}| = 2\pi/a$; in that case, use $f_{\text{Ba}^{2+}} = 51.0$, $f_{\text{Ti}^{4+}} = 17.3$, and $f_{\text{O}^{2-}} = 8.68$.

- Produce a plot of the square intensity $|S_{\mathbf{G}}|^2$ versus angular position $|\mathbf{G}| \sim \sin \phi/2$. Include the first five powder diffraction peaks, and discuss how one might distinguish the cubic and tetragonal phases.