

TFY4245/FY8917 Solid State Physics, Advanced Course

NTNU

Problemset 6



Institutt for fysikk

Problem 1, part I

We will here learn that a multi-valued polarization is a natural consequence of the periodicity in a bulk solid. The text below is taken directly from N. Spaldin, Journal of Solid State Chemistry **195**, 2 (2012). We will see that changes in polarization, which are the quantities that are typically measured in experiments, can nevertheless be single valued and well defined.

The length of the problem text here seems outrageous - don't be afraid right now: the actual problems to solve are not so difficult, and most of the text is about providing context.

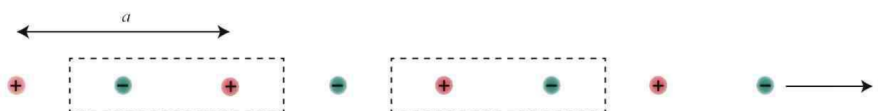


Figure 1: One-dimensional chain of alternating anions and cations, spaced a distance $a/2$ apart, where a is the lattice constant. The dashed lines indicate two representative unit cells which are used in the text for calculation of the polarization. Figure taken from the Spaldin-paper mentioned initially.

Consider the simplest possible example of a one-dimensional chain of singly charged alternating anions and cations (positively and negatively charged ions). Look at Fig. 1 which shows such a chain with the atoms spaced a distance $a/2$ apart so that the lattice constant is a . The first thing to notice is that all of the ions are centers of inversion symmetry: if you sit on any ion and look to the left, then to the right you see no difference. So by definition this lattice is non-polar.

Now let us work out the polarization by calculating the dipole moment per unit length (the definition in three dimensions is dipole moment per unit volume) using in turn the two unit cells shown as the dashed rectangles to compute the local dipole moment.

(a) First, the cell on the left. Take the left edge of the shell as the origin $x = 0$. Compute the polarization of this unit cell in units of $|e|$. If you find a non-zero polarization (which is the correct answer), we have a problem: our non-polar chain has a non-zero polarization.

(b) I am afraid that things will get worse before they get better. Next, let's do the same exercise using the right-most unit cell. Again taking the left edge of the unit cell as the origin, compute the polarization. Do you get the same answer as in (b)?

Problem 1, part II

If we were to repeat the above exercise with many choices of unit cell (convince yourself by choosing a couple of arbitrary unit cells and giving it a try!), we would obtain many values of polarization, with

each value differing from the original value by an integer. We call this collection of polarization values the polarization lattice. In this case it is $\dots, -5/2, -3/2, -1/2, 1/2, 3/2, 5/2, \dots$. Notice that the lattice of polarization values is symmetric about the origin. In fact this is the signature of a non-polar structure: the polarization lattice may or may not contain zero as one of its elements, but it must be centrosymmetric around zero.

Now what is the significance of the spacing (in this case 1) between the allowed values? Well, imagine removing an electron from one of the anions in the lattice (leaving a neutral atom) and moving it by one unit cell to put it on the next anion to the right. Because of the periodic boundary conditions of the infinite lattice, the next anion simultaneously has its electron removed and moved one unit cell to the right, and so it is able to accept the incoming electron and appear unchanged at the end of the process. There has been no change in the physics of the system resulting from the relocation of the electrons by one unit cell to the right. But what has happened to the polarization? Well, in each unit cell a charge of -1 has moved a distance a , changing the dipole moment by $-a$ and the polarization by -1 .

We can clearly perform this thought experiment any number of times, and in either direction, changing the polarization by any integer without changing the physical system! We call the value of polarization resulting from moving one electron by one unit cell the polarization quantum, P_q . In one dimension it is equal to the lattice constant divided by the length of the unit cell, which is of course one (in units of the electronic charge). Going back to the polarization lattice of our non-polar chain, we see that its polarization values correspond to half-polarization quanta. In fact all one-dimensional non-polar systems have polarization lattices of either $0 \pm nP_q$ or $P_q/2 \pm nP_q$.

Endure one more paragraph, and things should start making sense. First, let us think about how we measure electrical polarization, and what a reported measured polarization really means. Look at Fig. 2 - this is a cartoon of a standard way of measuring the electrical polarization using a so-called Sawyer-Tower circuit. On the left the material has become polarized in the up direction as a result of the cation sub-lattice displacing upwards relative to the anion sub-lattice. This could happen, for example during a ferroelectric phase transition with an external electric field applied in the up direction (the light colored cations with the dashed-line bonds indicate their positions in the high-symmetry, paraelectric structure). Electrons accumulate at the upper electrode, and holes (or a depletion of electrons) at the lower electrode in order to screen the surface charge resulting from the ionic displacements. In fact, on each electrode, the accumulated charge per unit area is exactly equal to the polarization of the sample. So if we could measure the amount of charge accumulation we would have a direct measure of the polarization.

But how can we do this? Well, next, imagine reversing the orientation of the polarization - for example by applying an external electric field in the down direction - to reach the configuration on the right. Now electrons accumulate at the lower electrode and holes at the upper electrode to achieve the screening. They achieve this by flowing through the external circuit connecting the two electrodes, where they can be counted by comparing the voltage across the series reference capacitor then using $Q = CV$. The amount of charge per unit area of electrode that flows during the transition is equal to the change in polarization between the up- and down-polarized states; the "absolute" value of polarization which is reported is half of this number.

(a) Now, bearing in mind that what is measured in an experiment is a change in polarization, let us

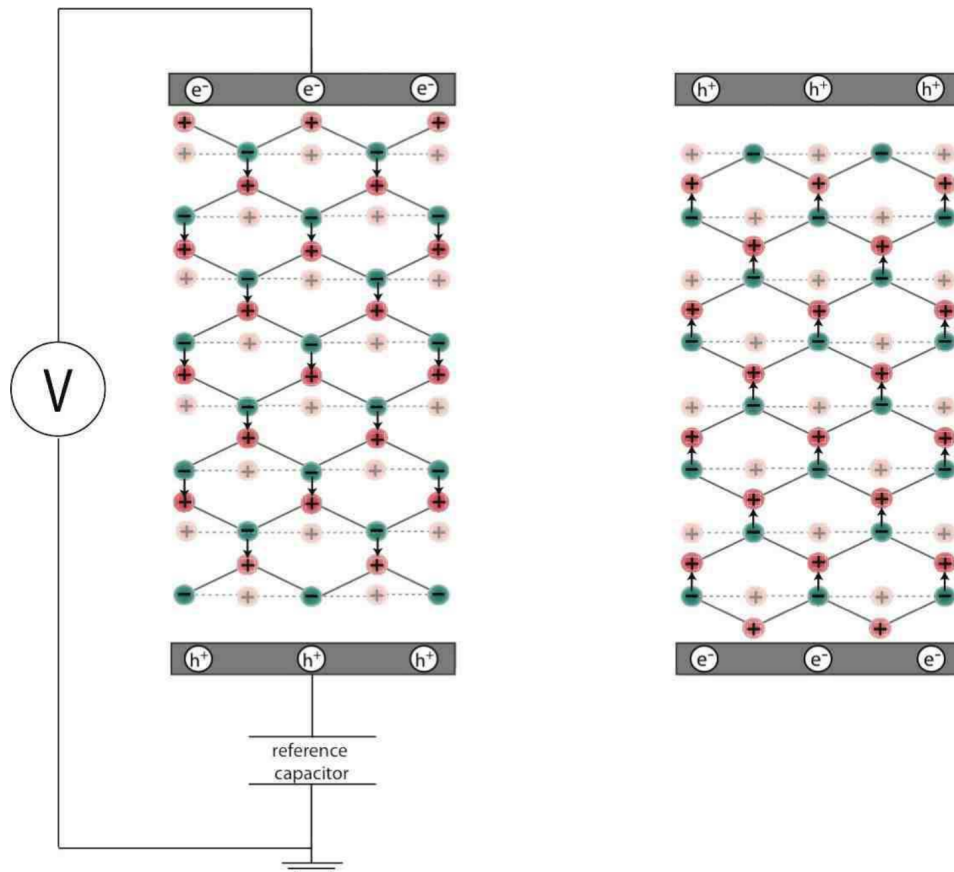


Figure 2: Schematic of the Sawyer-Tower method of measuring ferroelectric polarization. The material on the left is polarized in the up direction and its surface charge is screened by electrons in the upper electrode (grey) and holes in the lower electrode. When the polarization is switched (right), electrons and holes flow through the external circuit to screen the new opposite surface charges, and are counted by comparing the voltage across the material with that across a reference capacitor. Figure taken from the Spaldin-paper mentioned initially.

go back to our cartoon one-dimensional model and make some sense out of this multi-valuedness business. In the upper part of Fig. 3 we reproduce the non-polar one-dimensional chain of Fig. 1, and below it we show a similar chain in which the cations have been displaced by a distance d relative to the anions in the manner of a ferroelectric distortion to create a polar system. Compute the polarization using the two unit cells shown as the dashed rectangles in the lower part of Fig. 3. What is the difference between the polarizations in terms of the polarization quantum?

(b) Next comes the key point: compute now instead the change in polarization between the polar and non-polar chains using each unit cell as our basis. In effect, what is the change in polarization between the upper and lower part of Fig. 3 when you use the left unit cell to compute the change and when you use the right unit cell to compute the change?

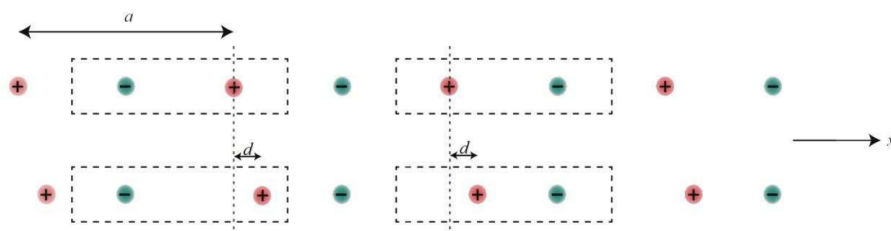


Figure 3: The upper panel reproduces the one-dimensional chain of alternating anions and cations of Fig. 1. In the lower panel, the cations are displaced to the right by a distance d relative to the anions, with the vertical dotted lines indicating their original positions. Figure taken from the Spaldin-paper mentioned initially.

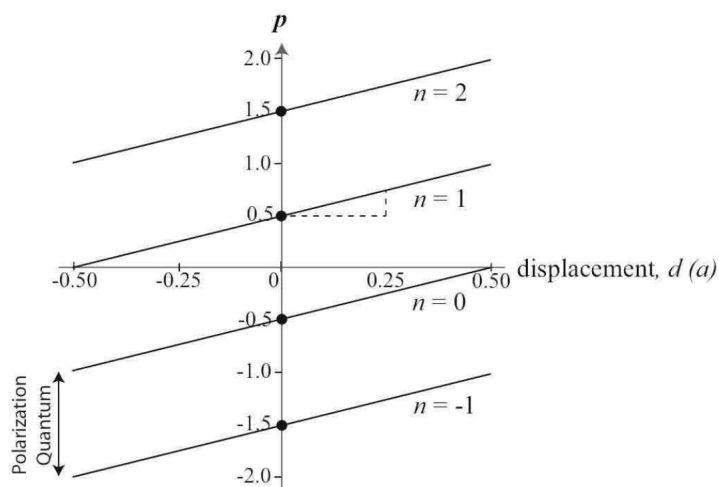


Figure 4: Polarization as a function of the displacement d of the cations in the 1D chain of Fig. 3. The polarization lattice is zero-centered, and the branches are separated by the polarization quantum. Notice that the branches of the lattice run exactly parallel to each other, so that differences in polarization along each branch for the same displacement are identical. Figure taken from the Spaldin-paper mentioned initially.

If you obtained the correct result in (c), one can note that you would in fact have obtained this result whatever unit cell we had chosen to make the calculation. So, while the absolute value of polarization in a bulk, periodic system is multivalued, the change in polarization - which remember is the quantity that can be measured in an experiment - is single valued and well defined. Phew.

Just to really drive the point home, in Fig. 4 we plot the polarization of the ideal one-dimensional ionic chain as a function of the displacement of the cations (as a fraction of the lattice constant) from their non-polar positions. As we calculated earlier, for zero displacement the polarization lattice is centrosymmetric and consists of all half-integer values (black circles). As the displacement increases, the polarization increases linearly and by the same amount along each branch of the polarization lat-

tice (labeled by $n = -1, 0, 1$ etc.) The branches are always separated from each other by the same amount, the polarization quantum, which is equal to 1 in this case. The dashed lines on the $n = 1$ branch show that for a displacement of $0.25a$, the polarization increases from 0.5 to 0.75, and so the change in polarization is 0.25. If the displacement is increased artificially to 0.5 - that is half of the unit cell - the ions end up on top of each other; in our thought experiment this causes the polarization to jump between branches of the polarization lattice.

Problem 2

Consider a first-order phase transition into a ferroelectric state and a Landau free energy $F(P, T)$ with even terms up to and including sixth order. The second order term has a coefficient $g_2 = \gamma(T - T_0)$ where $\gamma > 0$.

- (a) What sign must the fourth order coefficient have?
- (b) Write down the equilibrium condition for the polarization P at zero electric field at the critical temperature T_c , assuming that $P \neq 0$.
- (c) What is the relation between $F[P(T_c), T_c]$ and $F(0, T_c)$?
- (d) Using the results from (b) and (c), derive an explicit expression for the magnitude of the polarization at the critical temperature T_c where the first order phase transition takes place, expressed in terms of the coefficients in the free energy expansion.