Antiferroelectricity

a) PbZrO\textsubscript{3} is antiferroelectric. Does it go through any structural phase transitions?

Yes, the transition to the antiferroelectric state is coupled to a structural phase transition.

In antiferroelectric materials, there is spontaneous polarization of the cells so that neighboring cells have opposite polarization.

Lead Zirconate Oxide (PbZrO\textsubscript{3}) has at high temperature a cubic perovskite structure and at low temperature it goes through a structural phase transition where in one cell the central atom moves up and in the cell above it the atom moves down so the atoms move against each other and the polarizations are pointing towards each other. The result of it is that the macroscopic polarization is zero.

b) How would you observe a phase transition experimentally?

- You can see a phase transition in an x-ray diffraction experiment, because the antiferroelectric ordering is also associated with the motion of the atoms.
- If you measure the susceptibility or the dielectric constant at low frequency you will see a peak near the antiferroelectric phase transition.
- You can also observe a phase transition by measuring the specific heat. When the crystal makes a structural phase transition you can see a kink in the specific heat $c_v$, because there is a change in the free energy when the crystal structure goes through a phase transition, as can be seen in Figure 1:

\[
s = -\frac{\partial f}{\partial T}, \quad c_v = T \frac{\partial s}{\partial T}
\]

Figure 1: Kink in the specific heat when the crystal makes a phase transition.
c) What would the temperature dependence of the pyroelectric constant look like?

The pyroelectric constant \( \frac{\partial P}{\partial T} \) is zero because the macroscopic polarisation is always zero in an antiferroelectric (below and above the phase transition).

The pyroelectric effect is described by a 1\(^{st}\) rank tensor, which is zero when there is inversion symmetry in the crystal, which is the case for an antiferroelectric material.

d) What is the relationship between antiferroelectricity and piezoelectricity?

Figure 2 shows that ferroelectric like materials are classified in 4 kinds: pyroelectrics, ferroelectrics, antipolar and antiferroelectrics.

When you apply an electric field to a piezoelectric crystal it couples to the dipole moments and this can stretch the crystal or makes it shorter.

Figure 2 shows that antiferroelectrics can flip the dipole moments when you apply a high enough electric field. So in every unit cell the polarisation will be the same and then you can get it to expand and to contract. At low fields you do not see a piezoelectric effect. (Reciprocal piezoelectric effect \( = \frac{E_{ij}}{E_k} \)).

Piezoelectricity is described with a 3\(^{rd}\) rank tensor. A 3\(^{rd}\) rank tensor is zero if inversion symmetry exists, like in an antiferroelectric material. However, the applied electric field leads to a symmetry break and so it is possible to see a piezoelectric effect when the applied electric field is high enough as it is explained above.

This problem was also discussed in the Review lectures in 2009: [http://lamp.tu-graz.ac.at/~hadley/ss2/lectures09/19jun09/slide9.html](http://lamp.tu-graz.ac.at/~hadley/ss2/lectures09/19jun09/slide9.html)