3.2.3 Ionic Polarization
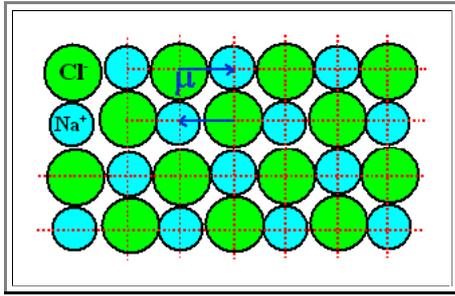
Consider a simple ionic crystal, e.g. **NaCl**.

The lattice can be considered to consist of **Na⁺ - Cl⁻** dipoles as shown below.

Each **Na⁺ - Cl⁻** pair is a *natural dipole*, no matter how you pair up two atoms.

The polarization of a given volume, however, is *exactly zero* because for every dipole moment there is a neighboring one with exactly the same magnitude, but opposite sign.

Note that the dipoles *can not rotate*; their direction is fixed.

In an electric field, the ions feel forces in opposite directions. For a field acting as shown, the lattice distorts a little bit (hugely exaggerated in the drawing)
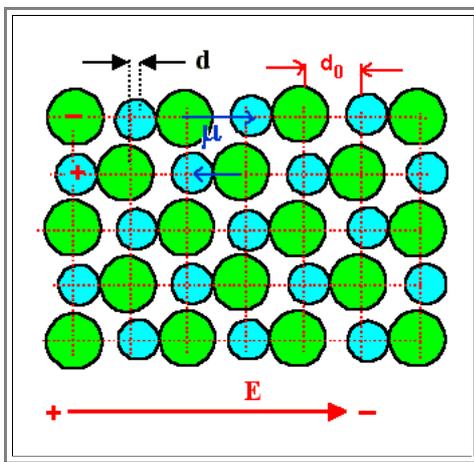
The **Na⁺** ions moved a bit to the right, the **Cl⁻** ions to the left.

The dipole moments between adjacent **NaCl** - pairs in field direction are now different and there is a *net dipole moment* in a finite volume now.

From the picture it can be seen that it is sufficient to consider *one* dipole in field direction. We have the following situation:
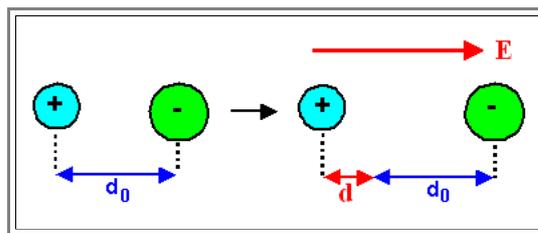
Shown is the situation where the distance between the ions *increases* by d; the symmetrical situation, where the distance *decreases* by d, is obvious.

How large is d? That is easy to calculate:

The force F_1 increasing the distance is given by

$$F_1 = q \cdot E$$

With q = net charge of the ion.

The restoring force F_2 comes from the binding force, it is given as the derivative of the binding potential. Assuming a *linear relation* between binding force and deviation from the equilibrium distance d_0, which is a good approximation for $d \ll d_0$, we can write

$$F_2 = k_{IP} \cdot d$$

● With k_{IP} being the "*spring constant*" of the bond. k_{IP} can be calculated from the bond structure, it may also be expressed in terms of other constants that are directly related to the shape of the interatomic potential, e.g. the *modulus of elasticity* or *Youngs modulus*.

● If we do that we simply find

$$k_{IP} = Y \cdot d_0$$

● With Y = Youngs Modulus, and d_0 = equilibrium distance between atoms.

▸ From force equilibrium. i.e. $F_1 - F_2 = 0$, we immediately obtain the following relations:

● *Equilibrium distance d*

$$d = \frac{q \cdot E}{Y \cdot d_0}$$

● *Induced dipole moment* μ (on top of the existing one)

$$\mu = \frac{q^2 \cdot E}{Y \cdot d_0}$$

● *Polarization P*

$$P = \frac{N \cdot q^2 \cdot E}{Y \cdot d_0}$$

▸ Of course, this is only a very rough approximation for an *idealized* material and just for the case of increasing the distance. Adding up the various moments - some larger, some smaller - will introduce a factor **2** or so; but here we only go for the principle.

▸ For *real* ionic crystals we also may have to consider:

● More complicated geometries (e.g. CaF_2, with ions carrying different amount of charge).

● This example was deliberately chosen: The dielectric constant of CaF_2 is of paramount interest to the semiconductor industry of the **21**st century, because CaF_2 is pretty much the only usable material with an index of refraction n (which is directly tied to the DK via $\epsilon_r = n^2$) that can be used for making lenses for lithography machines enabling dimensions of about **0,1** μm.

● If the field is not parallel to a major axis of the crystal (this is automatically the case in polycrystals), you have to look at the components of μ in the field direction and average over the ensemble.

▸ Still, the basic effects is the same and ionic polarization can lead to respectable dielectric constants ϵ_r or susceptibilities χ.

● Some values are given in the link.

Questionaire

Multiple Choice questions to 3.2.3