Electrostriction in ferroelectrics

Textbooks often explain electrostriction (deformation of a crystal in an external electric field = inverse piezo-electric effect) by a change of the dipole moment in the unit cell. But: an other choice of the unit cell can result in an oppositely directed dipole. . . [1]

To measure what really happens in the crystal, a series of experiments has been performed in the recent years, mainly with synchrotron radiation. [2, 3, 4] Some of these measurements show a strong non-linearity in the Bragg intensity as a function of field strength. This has been explained by 'space-charge effects' because x-rays probe close to the surface and see the electron density. To verify this hypotheses neutron measurements on the samples in question are planned. As a starting point the well characterised material KDP was chosen to test the transferability of the measuring scheme from x-rays to neutrons.

The structural changes in a crystal in an external electric field can be subdivided into

- the deformation of the unit cell, resulting in a shift of Bragg-reflections, and
- the change of the relative atomic coordinates (and the electron density) within the unit cell. This shows up in the change of the integrated intensities $R$ of Bragg-reflections.

To deduce the latter effect in KDP, Reeuwijk et al. [2] measured 58 reflections with synchrotron radiation with several field strengths. Data analysis with a model for the strained crystal gave the following results:

- P shifts downwards (K relative positions fixed),
- $P_{O_4}$ tetrahedra are deformed,
- occupancy of $H$ position changes: more of the bonds to the lower tetrahedron get covalent,
- The measured relative intensity variations $\Delta R/R$ got stable after some hour only. They found $\Delta R/R$ to be strictly linear.

As a test-sample we used $KH_2PO_4$ (KDP) because it shows a large effect, is available in the right dimensions and is already measured with synchrotron radiation [2].

The structure can be seen as $P_{O_4}$ tetrahedra connected by $H$ bonds where the $H$ sites are splitted: the $H$ statistically bonds covalently to one neighbouring $O$ and forms a hydrogen bond to the other $O$. The $C_2$ symmetry connecting both sites is broken by the external field.

unit cell of $KH_2PO_4$
symmetry: $i42d \ E= Fdd2$

The principle set-up and the measuring scheme was the same as with x-rays, besides the time structure: no modulation/demodulation technique is implemented yet and the time per data point is $5s$ instead of $0.02s$.

All measurements were performed with $\lambda = 2.4\AA$.

$$\Delta R(E)/R \quad \text{for the reflections } (004), (440) \quad \text{and } (\bar{4}40), \ E \ | \ c.$$  

- $\Delta R(E)/R$ is of the type $s E^2 + b E$.
- $b$ is an order of magnitude larger compared to the x-ray results.
- Possible explanation: Due to the different time-scale we probed the sample in a stationary state, i.e. after the space charges at the surfaces are formed and evtl. mislocations are settled.
- A detailed data-analysis is missing yet, since the measurements ended last week.

To be continued...