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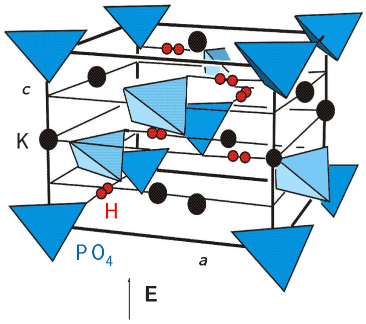
Electrostriction in ferroelectrics

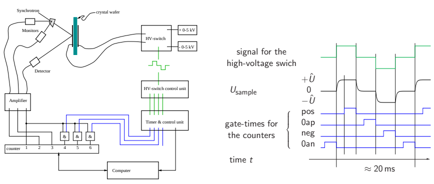
electrostriction

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 planed. As a starting point the well characterised material KDP was chosen to test the transferability of the measuring scheme from x-rays to neutrons.



x-ray measurements



Sketch of an experimental set-up [1] similar to the one used for KDP for the quasi-simultaneous determination of intensities R with and without electric field (modulation/demodulation technique).

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),
- PO_4 tetrahedra are deformed,
- ocuppancy 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.

the sample

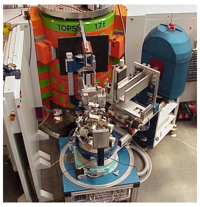
As a test-sample we used KH_2PO_4 (KDP) because it shows a large effect, is available in the right dimensions and is already measured with synchrotron radiation [2].

The structure can be seen as PO_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.

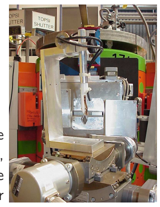
unit cell of KH_2PO_4

symmetry: $I\bar{4}2d \xrightarrow{\mathbf{E}\neq 0} Fdd2$

neutron measurements



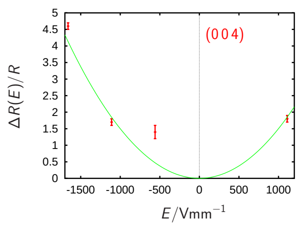
2 axes neutron diffractometer TOPSI at SINQ with diffraction set-up

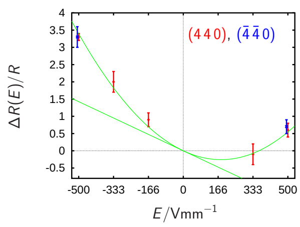


detail with the sample position, view towards the monochromator

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 5 s instead of 0.02 s.
All measurements were performed with $\lambda = 2.4$ Å.

$\Delta R(\mathbf{E})/R$ for the reflections (0 0 4), (4 4 0) and $(\bar{4}\,\bar{4}\,0)$, $\mathbf{E} \parallel c$.





- $\Delta R(\mathbf{E})/R$ is of the type $a\,E^2 + b\,E$.
- 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. . .

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acknowledgements

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references

[1] J. Stahn et al.: *Phys. Rev. B* **63**, 165205 (2001)
[2] S.J. van Reeuwijk et al.: *Physical Review B* **62**, 6192–6197 (2000)
[3] J. Stahn et al.: *Europhys. Lett.* **44**, 714 (1998)
[4] U. Pietsch et al.: *J. Phys. Chem. Solids* **62**, 2129 (2001)