Testing the switching of polar structure of Magnetite by an ac electric field using time resolved diffraction

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At Petra III we investigated polar structural switching of Magnetite by an applied ac electric field by developing and using a time resolved diffraction technique. The 120K Verwey transition in magnetite [1] is the classical example of charge ordering (CO), even though it has been under debate [2, 3]. Only very recently the complex CO-structure has been solved and in contrast to e.g. $LuFe_2O_4$ it is polar [4], in agreement with theory [5].
However, ferroelectricity implies also switchability by an electric field, and the macroscopic indications of this are unclear, although a first report appeared already in 1982 [6] and very recently in 2011 Schrettle and co-workers proposed that magnetite is a relaxor ferroelecric below ∼40 K rather than a normal ferroelectric, based on their observation of frequency dependent of dielectric properties [7].
The basic problem with the low temperature ferroelectric phase of magnetite is the presence resid ual conductivity as visible in the figure 1. For this reason, halfway convincing- looking P(E) loops are obtained only at low temperature and high frequency.
Our aim of the experiment was to develop the beamline capabilities by introducing a time resolved experimental technique, for the first time, at the beam line P09 and to test the intrinsic ferroelectric behaviour of magnetite by monitoring intensities of selected Bragg peaks under periodically applied external electric field. Time-resolved in-electric field measurements so far have been done only on piezoelectric crystals [8]. At P09, as a part of the proposed work, we have developed a time resolved diffraction technique as shown in the figure 2. Detailed description of the set up can be found elsewhere [8].

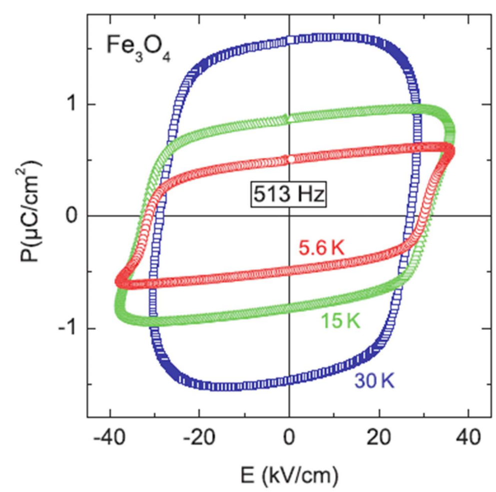

Figure 1: *Ferroelectric polarization P of Fe_3O_4 as a function of external electric field E at 513 Hz and three temperatures [7].*

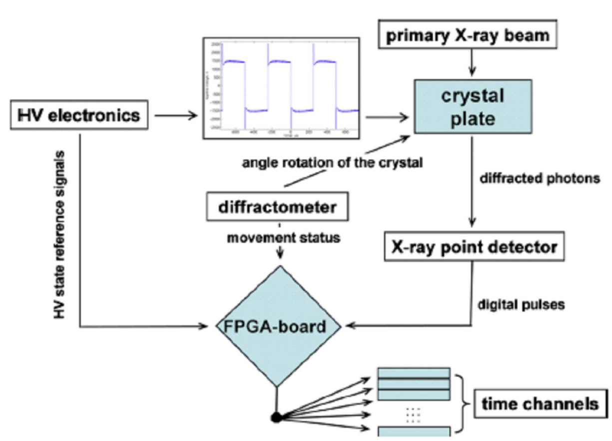

Figure 2: *Flow chart of the novel DAQ system [8]. HV electronics (left upper corner) generates the HV along with the digital pulses synchronized with the change in the HV polarities. The analog HV is directly delivered to the crystal. The digital signals, the current movement status of the diffractometer axes and the signals from the scintillating counter are processed by the field programmable gate array board .*

To obtain the conclusive of a ferroelectricity in Magnetite, we have tested if the alternating polarities of the field are able to switch steadily between the polar structures related by inversion- symmetry. The obtained result is shown in the figure 2. The variation of Bragg intensities upon the inversion of a polar structure is numerically equal to the contrast between Friedel pairs (hkl and $\overline{hkl}$). This method has been successfully implemented on $DyMn_2O_5$ crystal (not affected by residual conductivity) to investigate the polar atomic displacement [9]. In order to obtain the significant contrast between the Friedel pairs, we have chosen the energy which is above the Fe K-absorbtion edge of a anamalous scattering (E= 8.550keV) at which there occurring significant absorption, corresponding to a large imaginary part of the form factor, and applied ac voltage pulses up to 1 kV/150μm with the frequency 1kHz, in order to observe the switching effect. Since the measurement had to be performed at low temperature[7] the periodic voltage is applied with the very short pulses with zero voltage in between in order to avoid the heating of the sample. The preliminary calculations based on the recently refined polar structure of magnetite [4] and taking into account the presence of 24 charge ordered domains, suggested that opposite polarities of applied electric field would change the intensities of selected relatively strong Bragg peaks by several percent. The observed effect is qualitatively consistant with theory, but about 30 times smaller than expected. However the calculations assume that the polarities of all domains are switched, whereas with the electric field applied only those domains with direction of the polarization close to the direction of the applied voltage should be expected to switch. Nevertheless figure 3 constitutes microscopic proof of ferroic behaviour. But the unambiguous proof would require testing several reflections against available structure models, which has yet to be achieved.

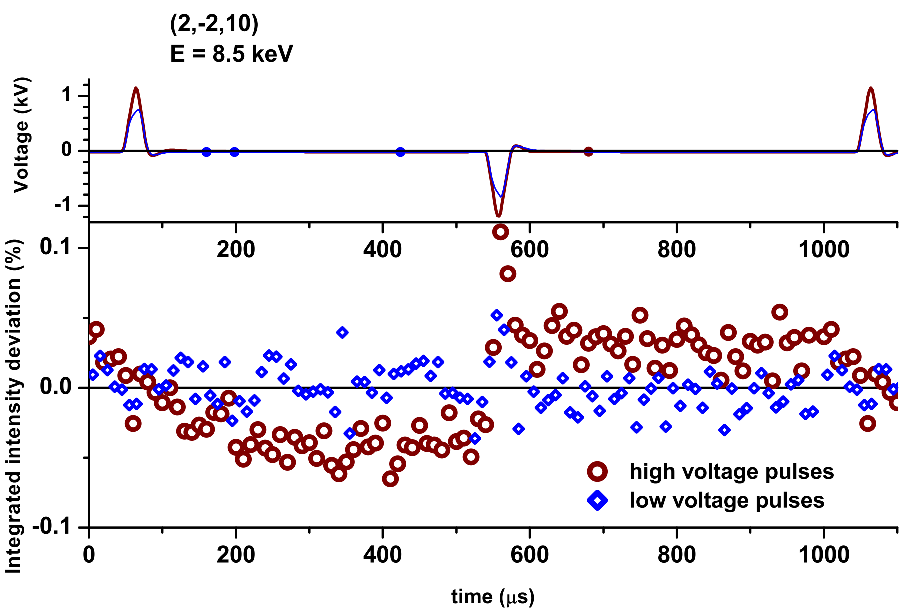

Figure 3: *The change in the intensity of Bragg reflection (2 -2 10) observed by an application of periodic high (1kV) and low (700V) voltage pulses with fast switches between opposite polarities*

References

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