New Experimental Methods for Perturbation Crystallography.
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Chapter 1

Introduction

1.1 Piezoelectricity

Every day millions of people on earth, and the few who are (supposed to be) in earth’s orbit, make use of crystalline materials for their physical properties, like conduction, magnetism, luminescence and piezoelectricity.

The latter property, accidentally discovered by Pierre and Jacques Curie in 1880, may show in certain crystals as an electrical polarisation upon application of a mechanical stress (i.e. the direct piezoelectric effect) whereas the converse piezoelectric effect results in formation of strain by the application of an electric field. The piezoelectric effect remained a peculiarity and was only a matter of academic interest until it was put to use in World War I in submarine echo-location devices\(^1\). In the 1950s a commercialisation of the effect became available in the charge-amplifier technology. Nowadays, the piezoelectric effect is used in more general applications like buzzers, microphones and gas lighters. They can also be found in high-tech applications, for example in all sorts of sensors (e.g. acceleration, force and pressure), micro actuators, gyroscopes, frequency-controlling devices, micro motors and micro pumps.

Although piezoelectric materials are widely used in technological applications, the underlying processes are mainly understood at the macroscopic level. At this level, the piezoelectric effect is mathematically described as a third-rank tensor\(^3\). The determination of the piezoelectric constants, i.e. third-rank tensor elements, was performed mechanically by means of the direct piezoelectric effect. However, new possibilities in studying piezoelectricity became available by the development of the X-ray diffraction modulation method\(^4\). With this tool, the converse effect can be used for the (re)determination of the piezoelectric constants\(^5\) and to study this effect at the microscopic, i.e. atomic, level. Meanwhile, phenomenological studies\(^2\) on piezoelectricity were derived on the basis
of the unperturbed crystal structure, deducing some of the piezoelectric effects, whereas first-principle studies are only recently becoming available\textsuperscript{[5-9]}. However, still no prediction of the amplitude of the piezoelectric constants can be made.

Over the years, a number of X-ray diffraction studies on the electric-field-induced structural changes by external electric fields have been performed\textsuperscript{[10-14]}. These studies have shown that, for example, ion displacement and electron redistribution are fundamental aspects of piezoelectricity, and are considered to play an important role in this effect. Since in general the structural changes, and consequently the changes in the diffracted intensity, are small, good counting statistics are needed. This implied that long data-collection times were needed to measure these small changes in integrated intensities, which were performed at a conventional X-ray source, such as an X-ray tube or rotating anode. Therefore, the experiments were limited to a few selected reflections and the deduced structural changes had to be based on preconceived models.

A larger flux became accessible by the development of synchrotron sources, allowing a significant decrease in the data-collection time. This opened the possibility to perform more complete diffraction studies in a reasonable time, within weeks rather than months. Furthermore, the brilliance\textsuperscript{-} was dramatically increased with the development of the third generation synchrotron sources. New developments in X-ray optics allow that the increased brilliance is conserved to a great extent during beam conditioning and results in a much higher photon flux on the sample. This opens the way to study either series of iso-structural compounds or compounds under different conditions, such as temperature, strength and frequency of the applied electric field, to obtain better understanding of the origin of piezoelectricity on the atomic level. In a range of experiments, the dynamic range and count-rate capability of the detector has now become a limiting factor. This is especially true for perturbation studies where in general one has strong reflections since large and almost perfect crystals are used. Furthermore, since large samples are used, often containing heavy elements, a relatively high photon energy is needed in order to reduce absorption effects.

1.2 Subject of Thesis

The subject of the thesis was to develop new methods allowing faster data-collection on a third generation synchrotron source (European Synchrotron Radiation Facility, ESRF), with the goal to improve the understanding of the piezoelectric effect at the atomic level by measuring the changes in integrated intensities.

It should be noted that the methods described in this thesis can be used not only for electric field experiments but also for any other experiment where a modulation of a perturbation is applied, such as irradiation by laser light or magnetic fields. The methods are very powerful in perturbation studies where the measurement of only one single-crystal reflection suffices to understand a particular physical property.

\textsuperscript{1} Brilliance of an X-ray source is the delivered photon beam in photons s\textsuperscript{-}1 mm\textsuperscript{2} mrad\textsuperscript{-2} per 0.19 band width.
1.3 Outline

This thesis is organised as follows. In Chapter 2 the theory of piezoelectricity and its relation to X-ray diffraction is discussed, followed by the theory of X-ray sources with an emphasis on the synchrotron source of the ESRF. The conventional modulation method will be discussed in Chapter 3, together with the sample preparation, development of software and the experimental stations. Furthermore, experimental results obtained with this method for the piezoelectric constants of LiNbO₃, AgGaS₂, KDP and DKDP crystals are presented. The subject of Chapter 4 is the development of a new detector system which is a combination of a Ge-detector and a (digital) lock-in amplifier. With this detection system the temperature dependence of the piezoelectric constant of KTiOPO₄ was determined and first results for changes in integrated intensities for a DKDP crystal are given. In Chapter 5 the broad-energy X-ray band method is introduced. This method is based upon the principle of a thick Ewald shell instead of a thin Ewald sphere, which allows obtaining the integrated intensity in a single measurement without the necessity to perform time-consuming scans. The theory, experimental set-up and results for two different techniques for creating a broad-energy X-ray band are presented. The first technique uses a bent-Laue monochromator whereas the second one uses a bent multi-layer. First results obtained for both techniques with Si, AgGaS₂ and LiNbO₃ samples are given. Finally, Chapter 6 will discuss the application of the broad-energy X-ray band to a LiNbO₃ crystal in an electric field. The measured changes in integrated intensities for several reflections were used in combination with a newly developed refinement procedure in order to obtain the structural changes induced by the applied electric field.

References
