

Studies of electric field induced structural and electron-density modifications by X-ray diffraction

Niels K. Hansen,* Pierre Fertey and Régis Guillot‡

Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, UMR-CNRS-7036, Faculté des Sciences, Université Henri Poincaré – Nancy I, BP 239, F-54506 Vandoeuvre-lès-Nancy CEDEX, France. Correspondence e-mail: niels.hansen@lcm3b.uhp-nancy.fr

Received 2 February 2004

Accepted 9 July 2004

During the last two decades, a number of X-ray diffraction studies on the response of a crystal to an applied electric field have been carried out. In a few cases, the electron-density polarizations could be determined. The analysis of the induced variations of the structural properties on an atomic scale are of prime importance in order to acquire a better understanding of physical properties like the piezoelectric and dielectric properties of crystals. This article reviews the experimental technique used and the modelling methods of the Bragg scattering variations induced by the field. Some noteworthy results are presented that illustrate the possibility of detecting subtle structural changes, for example as small as 0.1° in bond angles arising from applying a strong field, $10\text{--}40\text{ kV cm}^{-1}$, as well as the pitfalls of such an approach for clarifying the relevance of the structural properties in physical mechanisms.

© 2004 International Union of Crystallography
Printed in Great Britain – all rights reserved

1. Introduction

From accurate X-ray diffraction data measured out to large momentum transfers ($\sin \theta/\lambda = 1\text{ \AA}^{-1}$), a detailed description of atomic structure, thermal vibrations and electron-density distributions can be obtained. Beyond classical experiments, where basic structural properties can be described, their variation as a function of external perturbations is of prime interest. By now experiments at different temperatures or hydrostatic pressures can be done almost routinely. Nowadays, more ‘exotic’ perturbations are applied; laser irradiation or electric fields, as illustrated by a number of contributions at this workshop, all with the purpose of reaching a more profound understanding of the physical properties of crystals or, at least, of the correlations between structural and physical properties.

We will focus on structural changes induced by an applied electric field. When a crystal sample is subjected to an electric field, the Bragg scattering is affected: the expansion/contraction of the crystal lattice affects the Bragg angles and, in the best cases, the atomic structure and the electron-density polarization can be determined from intensity variations. This information helps our understanding of dielectric and piezoelectric properties of crystals.

Pioneering work was carried out by Puget & Godefroy (1975) and Fujimoto (1980, 1982). At present, three teams are working systematically on developing the experimental techniques and applying them to semiconductors and standard piezo- and ferroelectric crystals: H. Graafsma (ESRF), U. Pietsch (University of Potsdam and HASYLAB), and our

group in Nancy (N. K. Hansen, P. Fertey, P. Allé, R. Guillot & C. Lecomte) with the collaboration of colleagues from LURE and the French CRG at ESRF.

In this review, we shall first recall basic properties of electric field induced effects in crystals. We will then discuss the actual experimental techniques employed and their limitations/improvements in order to solve one of the major drawbacks: the long measuring times necessary to acquire a sufficient amount of experimental data. The following part will focus on computational problems in relation to the data analysis, especially if one considers how to treat the weak Bragg intensity variations induced by the applied electric field. Specific results will be presented to illustrate the state of the art. Finally, we will give a rapid survey of the fundamental difficulties encountered in a theoretical approach when attempting to relate the polarizations observed at an atomic scale to macroscopic electric properties of materials. Theoreticians have shown that even the spontaneous polarization of a crystal is not a simple ground-state electron-density property, and the same problem will evidently be encountered when interpreting experimental results from X-ray diffraction.

2. General considerations

The effects of an electric field on a non- (or weakly) conducting single crystal may be considered on three different scales: macroscopic, microscopic and atomic.

In text books, the dielectric theory is based on the idea that a macroscopic polarization of the medium is induced or modified when an electric field is applied. The manifestation of the polarization is the appearance of a surface charge, which can be measured as a current flow if the crystal is placed

‡ Present address: Institut de Chimie Moléculaire et des Matériaux, FR 1577, Université de Paris 11, 91405 Orsay CEDEX, France.

between electrodes. Very often this polarization is described using the ideas of a ‘molecular’ solid, where each ‘molecule’ possesses its own dipole moment.

On a microscopic scale (nm– μ m), phenomena like impurity migrations, domain structure and dynamics of domain walls (especially in ferroelectric crystals) have to be considered. An experimental technique that can bring valuable help is X-ray topography (*e.g.* Sebastian *et al.*, 1988, 1992).

Using classical single-crystal X-ray diffraction, effects at a truly atomic level can be studied. The effects of an electric field in solids are atomic displacements, charge transfer among atoms or ions, and bond polarization. These phenomena must in some way be related to the overall macroscopic polarization, P , of a crystal. One might imagine that the polarization can then be calculated from the knowledge of the deformed atomic structure (*i.e.* atomic positions) and the electron-density distribution, but this approach is too simple-minded as we will discuss later.

The polarization of a material is an interesting property in itself, but the way it varies as a function of external constraints is even more revealing. Considering the linear response of a material, several basic properties can be deduced. These are described by:

$$\text{a pyro-electric behaviour} \quad dP/dT \quad (1)$$

$$\text{a dielectric polarizability} \quad dP/dE \quad (2)$$

$$\text{a piezo-electric behaviour} \quad dP/d\underline{\underline{\tau}}, \quad (3)$$

where the actions exerted on the sample are dT , dE and $d\underline{\underline{\tau}}$, a temperature change, an applied electric field and an applied non-hydrostatic mechanical stress, respectively. It should be remembered that in (1) and (3) the derivatives are only non-vanishing in certain non-centrosymmetric crystal classes (Nye, 1957). Information on the structural response can be obtained by measuring the diffraction pattern under non-ambient conditions. As has already been stressed, accurate diffraction experiments may nowadays be carried out quite routinely at different temperatures, but less so when changing the applied electric field or mechanical stress.

Piezoelectric materials benefit from the converse effect, which is described by the same constants as the direct one (Nye, 1957):

$$d\underline{\underline{\varepsilon}}/dE = dP/d\underline{\underline{\tau}} \quad (4)$$

or in the Einstein notation

$$d\varepsilon_{jk}/dE_i = dP_i/d\tau_{jk}, \quad (5)$$

where ε_{jk} and τ_{jk} are the strain and stress tensor elements, respectively, and P_i are the components of the polarization in an axis system linked to the crystal. If the strain is homogeneous throughout the sample, it will manifest itself by a change in the crystal lattice parameters, thus small Bragg-angle variations will be observed. In the case of an inhomogeneous strain, the intrinsic widths of the diffraction profiles will be enlarged when the electric field is applied.

Equation (4) implies that we may determine the piezo-electric constants from different diffraction experiments but it

does not mean that the same final state may be obtained, either from applying an electric field or from a mechanical stress. In both cases, the final state depends on the piezo-electric properties but in the former it also depends on the dielectric polarizability whereas it depends on the elastic constants in the latter, and these two properties are not related in any simple way.

From here on, we will limit ourselves to the effects of an electric field on the Bragg scattering.

The converse piezoelectric effect leads to changes in the Bragg angles from which the piezoelectric tensor can be determined. Furthermore, the dielectric polarizability mainly leads to variations of the Bragg intensities due to relative displacements of the atoms within the unit cell and to polarization of the valence-electron density. These two effects are sometimes referred to as external and internal strain, respectively. For a diffraction experiment, this is a convenient classification which however does not imply a ‘cause-and-effect relationship’ between the two phenomena, especially not in the sense that the second is a consequence of the first as has been stated by Paturle *et al.* (1991). This would mean that an electric field only induces internal strain in piezoelectric crystals; this would completely neglect a direct effect of the electric field on the interatomic distances through a direct polarization of a structure composed of more or less strongly charged atoms or molecules.

An intuitive way of understanding the relationship between the internal and external strain is to consider a crystal as composed of bonds, each carrying an electric ‘dipole moment’. For a polar bond, the dipole moment will depend on its length. Therefore, for a crystal under stress, the dipole moments of all of the bonds will change. The stress-induced polarization will be the sum of all bond moments. For a centrosymmetric structure, their sum will cancel. For a non-centrosymmetric sample, this may not be the case and the strength of the total induced moment will depend not only on the polarizability of the individual bonds but also on their relative orientation within the crystal. For the converse piezoelectric effect, an electric field will modify the bond distances of polar bonds. However, in the linear regime, the net effect for bonds related by a centre of symmetry will be cancelled by opposite contributions, and therefore will not, to first order, have an effect on the macroscopic (external) strain.

The above description is of course oversimplified. Within the same spirit, one must also take into account valence- and conformation-angle changes. However, the general reasoning is the same.

It should be stressed that the diffraction experiment distinguishes the two phenomena in a natural way, but it does not explain their interdependency. For this, appropriate theories must be developed.

3. Experimental techniques

Puget & Godefroy (1975) were the first to publish an extensive study of the effect of an electric field on a crystal of rutile (TiO_2) by diffraction of X-rays. Their efforts were only

partially successful, to a large part because they only had access to a sealed-tube X-ray source with limitations on the intensity of the incident beam and working at quite a long wavelength (Cr $K\alpha$, 2.29 Å). However, the general outline of their technique has inspired most of the more recent work: an alternating electric field in the form of a square wave is applied to a crystal plate while the reflection profiles (rocking curves) are recorded in a step-scan mode. The periodic reversal of the direction of the field is the key point to avoid irreversible effects that may mask the response of the crystal. In this so-called field switching (or modulation–demodulation) technique, for each orientation of the crystal, the pulses from a point detector are counted in separate channels synchronized with the particular field strengths. In the experiment by Puget & Godefroy (1975), the field was alternately applied in one direction and the opposite. Our group and others have inserted a zero field level between the extreme levels, as shown in Fig. 1 where a four-stage square wave is represented as well as typical time duration of a particular field strength (Guillot *et al.*, 2002).

For a given orientation of the sample, the basic period of the field wave is repeated a large number of times in order to improve the signal-to-noise ratio. The diffraction profiles obtained for the different field strengths are therefore measured quasimultaneously, which means that most systematic errors, such as rapid or long-term incident intensity variations, scaling and absorption by the sample, will cancel when analysing intensity variations. This presents a second advantage of the switching method over a static field application.

Each rocking curve is remeasured several times in order to verify the reproducibility of the Bragg-angle shifts and intensity variations. As a consequence, measuring times become very long – typically several hours per reflection when conducting the experiment at a synchrotron beamline. In order to improve on this, different techniques have been tried. van Reeuwijk, Vonk, Puig-Molina & Graafsma (2000) used a two-dimensional detector. The field modulation was synchronized with a mechanical chopper system in such a way that the diffracted intensities corresponding to a single field value are detected. A new experiment has to be performed in order to analyse the response of the crystal for the other field strengths. With this method, one loses the advantage of the quasimultaneous detection for the different field values but increases considerably the number of measured reflections within a given time. Cousins (1988) proposed the use of an energy-dispersive Laue technique, allowing the simultaneous measurements of a reflection and its harmonics. However, only a few results have been reported (Hamichi *et al.*, 1994; Addison *et al.*, 1995).

Some groups have also used a multiple diffraction technique, which is inherently very sensitive to subtle changes in lattice geometry of single crystals when submitted to external perturbations (Avanci *et al.*, 1998). Multiple diffraction arises when an incident beam simultaneously satisfies the Bragg law for more than one set of lattice planes within the crystal (Chang, 1984). This versatile method has been successfully

used to obtain piezoelectric tensors (Avanci *et al.*, 1998, 2000; dos Santos *et al.*, 2001; Almeida *et al.*, 2003).

4. Modelling of Bragg intensity modulations

Once the electric field induced intensity variations have been measured accurately, the data interpretation needs some kind of modelling. If only a small number of reflections have been measured, the best that can be done is to compare the observed intensity changes with a calculation based on a preconceived idea of what is going on. This cannot exclude that other possibilities exist. When a larger number of data are available, one may determine parameter variations describing the induced changes in structure and electron density with much fewer assumptions. Suitable approaches are least-squares refinements. For these, the derivatives of the intensity variations with respect to the parameters in the model must be calculated. They can be obtained from successive structure-factor calculations for different values of the parameters [method used in the study of KDP (van Reeuwijk, Puig-Molina & Graafsma, 2000, 2001), see §6].

We have also adopted the least-squares method, building it into a standard computer program. The observed quantity against which a model is optimized is

$$\eta(hkl) = I_{\text{Bragg}}(hkl, E)/I_{\text{Bragg}}(hkl, E = 0). \quad (6)$$

A standard refinement program can easily be changed for this purpose. A starting model corresponding to the field-free situation is needed and also a hypothesis about the relation between the X-ray structure factor and the Bragg intensity. For the kinematical approximation, we simply consider that the intensities are proportional to the square of the structure-factor amplitudes. In that case, we may write that the derivative of η with respect to a parameter p is

$$d\eta(hkl)/dp = 2dF(hkl)/dp/F(hkl, E = 0). \quad (7)$$

From these equations, we can construct the least-squares-method normal equations, and solve them iteratively like in any structural refinement.

For this purpose, we have introduced the necessary modifications in the program *MOLLY-N* (Guillot & Hansen, 2003), in which a few other general options have been included. This version of the program can refine a full multipole model, including a Gram–Charlier expansion for the Debye–Waller factors, against the structure-factor moduli, their squares or the intensity changes (η).

In the case of a plate-shaped perfect crystal, a different expression for the intensity is used:

$$I_{\text{Bragg}}(hkl) \propto F(hkl)^{n(hkl)}, \quad (8)$$

where we calculate the exponent $n(hkl)$ from

$$n(hkl) = [F(hkl)/I_{\text{Bragg}}(hkl)][dI_{\text{Bragg}}(hkl)/dF(hkl)]. \quad (9)$$

For the dependence of the integrated intensity on the structure factor, we use the expressions proposed by Thorkildsen & Larsen (1999). This allows the asymmetrical Bragg and Laue cases to be treated.

The electron-density model in *MOLLY-N* has been augmented by ‘bond charges’. The aim is not to have a better model than the multipole model but to have a phenomenologically more intuitive model when refining against intensity variations, where we have relatively few independent reflections at our disposal. At present, the bond-charge distribution is located at the connecting line between two atoms and has a cylindrical symmetry. It is described by four free parameters: number of electrons, position along the bond, and radial extents parallel and perpendicular to the bond. In a ‘full’ charge-density model, atomic lone-pair densities should still be described by a multipole expansion, but it may be limited to the quadrupole level.

5. Examples of measurements of piezoelectric coefficients

The relationship between the applied electric field and the Bragg angles has been discussed by Barsch (1976) and by Graafsma (1992). For example, the relation given below illustrates the case of a Bragg-angle shift $\Delta\theta_{00l}$ induced by an expansion of the $00l$ lattice planes when the field is applied along the c^* axis:

$$\Delta\theta_{00l} = \tan(\theta_{00l})d_{33}E + \Delta\theta_{\text{Rot}}, \quad (10)$$

where θ_{00l} is the Bragg angle without field, d_{33} is a piezoelectric constant and E is the magnitude of the electric field. For the observed angular change, there may also be a contribution from an overall rotation of the sample, $\Delta\theta_{\text{Rot}}$.

Fig. 2 shows an example of what we have observed for an LiNbO_3 single-crystal plate cut perpendicular to the trigonal axis, when we apply a field of 25.5 kV cm^{-1} (Guillot, 2002). This is in good agreement with previous studies of this compound, *e.g.* Fujimoto (1982).

Using the field-switching technique as described above, the piezoelectric constants have also been determined for the molecular crystals of 3-methyl-*p*-nitropyridine-*N*-oxide (Paturle *et al.*, 1991), 2-methyl-4-nitroaniline (Graafsma *et al.*, 1992), the chalcopyrite AgGaS_2 (Graafsma *et al.*, 1993), KTiOPO_4 (Graafsma *et al.*, 1997) and for α -quartz, AlPO_4 and GaPO_4 (Guillot *et al.*, 2004).

Ferroelectric hysteresis in CsTiOAsO_4 has been examined by determining the Bragg-angle shift as a function of the electric field strength (Bolt *et al.*, 1997).

All of these experiments have been carried out using synchrotron radiation. This is almost mandatory, since a good angular resolution is needed in the measurement of the rocking curve; for high-angle reflections in a compound like LiNbO_3 , the change in the Bragg angle is of the order of 0.005° with a field of about 30 kV cm^{-1} . This is hardly measurable on a standard laboratory sealed-tube X-ray diffractometer.

Some piezoelectric tensors have also been measured by X-ray multiple diffraction methods: for example in organic (Avanci *et al.*, 1998, 2000) or semiorganic (Almeida *et al.*, 2003) crystals with non-linear optical effects and in ferroelectric materials like KDP (KH_2PO_4) (dos Santos *et al.*, 2001).

Determining the value of the piezoelectric constants by means of diffraction techniques and comparing them to known values can serve as an internal calibration of the magnitude of the electric field and as an assessment of its homogeneity within the scattering volume.

6. Structural and electron-density polarizations

Most of the diffraction studies on crystals under electric fields aim at determining how the field affects structure and electron density. In their work on TiO_2 , Puget & Godefroy (1975) set out to examine the polarizability and ionicity of the Ti–O bond. From the analysis of the intensity variations of the 002, 200 and 220 reflections as a function of the field strength, they concluded that the ionicity had an upper bound of 0.78. They were not able to make deductions concerning an atomic rearrangement since, having few data points, they could not separate the effects of structure deformations and the electronic polarizations.

The work by Fujimoto (1982) on LiNbO_3 seemed more promising. He both determined structural modifications and estimated that the polarization of the bonding electrons in the Nb–O bond is quite important. However, no other groups working on LiNbO_3 have been able to reproduce his results. In particular, our team has found that the field-induced intensity modulations vary randomly with time when the measurements are repeated over several hours (Guillot, 2002). This has also been observed by Addison *et al.* (1995) and Heunen (2000).

To our mind, a most spectacular study concerns the electric field induced structural changes in KDP (KH_2PO_4) and DKDP (van Reeuwijk, Puig-Molina & Graafsma, 2000, 2001). An expected divergence of the piezoelectric constant d_{36} as the temperature approaches the phase transition from above is observed for both of these materials. The field-induced structural variations concern especially the PO_4 tetrahedron and a partial ordering of the H atoms bridging the phosphate groups.

U. Pietsch and collaborators have been studying electric field effects on zincblende-type semiconductors in order to elucidate the effect on the bonding electron density: the first article was on GaAs (Pietsch *et al.*, 1985), the most recent in this line of work is Pietsch *et al.* (2001). In order to circumvent the problems due to the high degree of perfection of the crystals of these compounds, the experiments concentrated on the measurements of the pseudoforbidden or weak low-order reflections, thus minimizing the effect of primary extinction.

Some elegant but difficult experiments were carried out on GaAs and ZnSe (Stahn *et al.*, 2001): the measurements were conducted at several wavelengths close to the absorption edges, thus changing the anomalous-scattering amplitudes. This way, an increased sensitivity to different phenomena (structure deformation, charge transfer or bond polarization) is attained. The conclusion was that, even for the low-order reflection 222, the major effect on the Bragg intensity was due to ionic displacements. Stahn *et al.* (1999) have also demonstrated by a three-beam experiment that it is possible to detect

electric field induced changes of 1° in triple-phase relationships.

Our last example will illustrate some of the difficulties that are met in this type of work. When carrying out the experiments, one must constantly ask the question: are the observed intensity changes really due to atomic structural modifications typical of the compound studied or are they sample dependent, being determined by effects like purity, degree of crystal perfection and sample preparation?

Using the field-switching technique, U. Pietsch and his collaborators (Davaasambuu *et al.*, 2003) and our group in Nancy (Guillot *et al.*, 2004) have studied, independently of each other, the response of low quartz and the isotypical GaPO₄ to electric fields. Both groups find similar values of the piezoelectric constant d_{11} : 2.4 and 4.5 pm V⁻¹ for SiO₂ and GaPO₄, respectively. There is therefore no doubt either about the field strength or about the homogeneity of the induced strain in these studies. The general approach of the two groups for studying the structural modifications was different, especially in the number of collected crystallographically independent data. Davaasambuu *et al.* (2003) measured six crystallographically independent high-order reflections under various experimental conditions (different field strengths, 10–80 kV cm⁻¹, and temperatures) against which they have tested a model of rigid rotating tetrahedra (SiO₄, GaO₄ and PO₄). The major effect was then a minute change of the bridging angle of the tetrahedra of about 0.05 and 0.10° for quartz and GaPO₄, respectively, when the field was 30 kV cm⁻¹. High-order reflections were chosen in order to have a high sensitivity to structural changes and also to justify the use of kinematical scattering theory.

Our approach was different. We did not systematically test the linearity of the effects against the field. Sets of 20 and 64

crystallographically independent reflections at high angles were measured with an electric field of 30 kV cm⁻¹ for quartz and GaPO₄, respectively. Intensity changes as strong as 4% were observed. We were therefore able to perform an unconstrained refinement of the coordinates of all of the atoms in the strained structure. We have found internal deformations of the tetrahedra that amounted to as much as 0.4° in valence-angle changes. This is qualitatively in agreement with the deformation of the PO₄ tetrahedron observed in the studies of KDP (van Reeuwijk, Puig-Molina & Graafsma, 2000, 2001). Imposing rigid tetrahedra constraints in our refinements deteriorates significantly the quality of the fit.

For quartz, we have also measured the induced intensity changes for 14 independent reflections having $\sin \theta/\lambda < 0.6 \text{ \AA}^{-1}$. We have tried to refine these data using a bond-charge model, but it is premature to report on these results yet. Since the quartz crystals are close to perfect, one of the main difficulties in the data analysis is how to treat adequately primary and secondary extinction for the strong low-order reflections. This correction is of less importance, though not quite negligible, for the high-order data.

In this context, it becomes crucial that groups working in this field collaborate in order to improve and validate the techniques employed. We have therefore just started a collaboration with the group led by U. Pietsch in order to examine carefully what is the exact cause of the disagreement encountered on the quartz-type compounds.

7. Polarization

A complete study of the crystal structure and electron-density distribution allows us to calculate the dipole moment of the unit cell.

A fundamental problem is that there is no unique way to choose the cell and that the dipole moment does depend on this choice. A second problem arises when the cell polarization is compared with the macroscopic polarization. The macroscopic polarization manifests itself as a surface charge but the cell

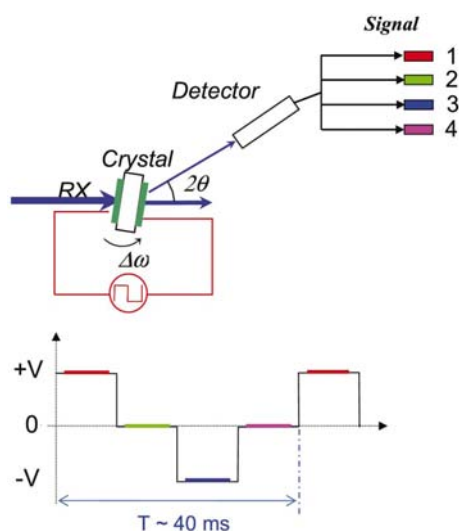


Figure 1

Experimental set-up for the field-switching method. The pulses from the detector are counted by the four detectors each synchronized with the high voltage applied to the sample crystal. The time period of the crenel-shaped high voltage is only indicative. The counting time is in general chosen to be shorter than the duration of one field value in order to avoid transient behaviour on the measured intensities.

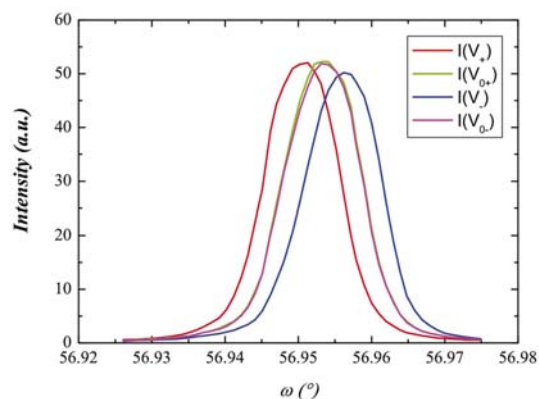


Figure 2

LiNbO₃ 0,0,36 reflection profiles measured using the field-switching method. The field strengths were ± 25.5 (red and blue curves) and 0 (violet and green) kV cm⁻¹. The abscissa gives the scan angle ω in degrees.

polarization is deduced from the analysis of the density in a crystal considered as infinite. In addition, the surface distribution can be changed without the bulk density being affected.

The first problem disappears when we look at perturbations of the crystal not leading to discontinuous modifications because in that case the derivative of the unit-cell moment will be independent of the initial choice of the cell. However, the question about surface effects remains when we want to compare the cell polarization with macroscopic quantities.

For example, the electric field induced polarization may be estimated from the structural changes (van Reeuwijk, Vonk, Puig-Molina & Graafsma, 2000; Guillot *et al.*, 2004), but it can also be calculated from known dielectric constants: surprisingly close values have been found.

The problem is not only experimental. Theoreticians are facing two difficulties.

The first one is that the Hamiltonian, for a crystal in a uniform electric field, is non-periodic. One attempt to circumvent this is to use a supercell approach in which the 'applied' electrostatic potential takes a saw-tooth shape. This has been employed by Stahn *et al.* (2001) on GaAs and by Kochin *et al.* (2004) on low quartz, both in collaboration with K. Schwarz and P. Blaha from Vienna. This theoretical approach indicates that the major effect of the field is a modification of the atomic coordinates. Because of the limited size of the supercells, *i.e.* the regions in which the applied field can be considered homogeneous, it is difficult to be very specific about the exact nature of the deformations in the real case.

The second problem is how to calculate the polarization by quantum-mechanical methods. It has been stated that the polarization is not only a property of the ground-state one-electron density (King-Smith & Vanderbilt, 1993; Resta, 1994, 2000) but that electronic current densities must also be accounted for: the macroscopic polarization of a crystalline dielectric is best defined as a Berry's phase of the electronic Bloch functions. This Berry's phase treatment has been extended in the case of the presence of finite electric fields (see Souza *et al.* 2002, and references therein). Discussing this point further is beyond the scope of this review.

8. Concluding remarks and perspectives

We have reviewed a number of the most conclusive single-crystal X-ray diffraction studies reporting structural changes induced by external electric fields and have covered most of the work in this speciality. We have presented the different experimental methods used as well as inherent drawbacks of the methods, the pitfalls of data treatment or interpretation of the data.

Most of the recent experiments have been carried out at synchrotron sources but, in the case of quartz, we measured some Bragg intensity changes on a standard diffractometer with a sealed-tube X-ray source; this was only possible for some of the strongest reflections and, even so, the measuring times were longer by about one order of magnitude. By

optimizing the set-up, this situation could be improved upon.

It appears that the different techniques used provide successful microscopic measurements of the piezoelectric tensor whatever the stability of the observed induced variations of the Bragg scattering intensity. Furthermore, induced structural effects at the atomic scale are now accessible without too many or restrictive preconceived ideas about what is happening. Nevertheless, we do not expect that electric field experiments will become a routine technique since we are working under extreme conditions: the applied electric field, with which we need to work in order to get measurable changes, is hardly one order of magnitude below dielectric breakdown (the field at which the sample becomes electrically conducting). Under these conditions, certain compounds do not give reproducible results.

Many questions may be asked, but because of the long measuring times, the most relevant ones must be carefully selected in order to get significant results. In this context, a collaboration between the few groups working in this area is of prime importance in order to unambiguously understand the induced effects observed or clarify the origin of the different behaviours. The experiments on quartz and some of its isotopes are very promising. Compounds with centrosymmetric structures, therefore not showing a piezoelectric effect, should also be studied. An interesting choice would be to repeat and extend the study on rutile by Puget & Godefroy (1975) because this compound has very strong and anisotropic dielectric constants (two orders of magnitude larger than quartz). Complete studies of the electron density response to electric fields in these compounds would be very useful for testing the reliability of the theoretical approaches being developed at present. The situation is rather similar to the one some 25 years ago when charge-density studies served for testing Hartree–Fock molecular calculations and band-structure calculations on simple crystalline solids using density functional theory.

We are grateful to Dr H. Graafsma and Professor U. Pietsch for many interesting discussions, and Professor C. Lecomte, director of the LCM3B, for his interest and support. The measurements carried out by the group in Nancy on quartz were carried out at LURE in collaboration with E. Elkaïm, and on GaPO₄ at the French beamline BM2 at the ESRF in collaboration with Drs N. Boudet and J.-F. Bézar; without their help, this work would never have succeeded.

References

- Addison, G. T., Cousins, C. S. G., Flood, S. M., Hamichi, M., Meads, R. E., Miners, F. & Sheldon, B. J. (1995). *Nucl. Instrum. Methods Phys. Res. B* **97**, 543–546.
- Almeida, J. M. A., Miranda, M. A. R., Remédios, C. M. R., Melo, F. E. A., Freire, P. T. C., Sasaki, J. M., Cardoso, L. P., dos Santos, A. O. & Kycia, S. (2003). *J. Appl. Cryst.* **36**, 1348–1351.
- Avanci, L. H., Cardoso, L. P., Girdwood, S. E., Pugh, D., Sherwood, J. N. & Roberts, K. J. (1998). *Phys. Rev. Lett.* **81**, 5426–5429.

- Avanci, L. H., Cardoso, L. P., Sasaki, J. M., Girdwood, S. E., Roberts, K. J., Pugh, D. & Sherwood, J. N. (2000). *Phys. Rev. B*, **61**, 6507–6514.
- Barsch, G. R. (1976). *Acta Cryst.* **A32**, 575–586.
- Bolt, R., Albertsson, J., Svensson, G., Ståhl, K. & Hanson, J. C. (1997). *J. Appl. Cryst.* **30**, 383–387.
- Chang, S. L. (1984). In *Multiple Diffraction of X-rays in Crystals. Springer Series in Solid State Science*, Vol. 50. Berlin: Springer Verlag.
- Cousins, C. S. G. (1988). *J. Appl. Cryst.* **21**, 496–503.
- Davaasambuu, J., Pucher, A., Kochin, V. & Pietsch, U. (2003). *Europhys. Lett.* **62**, 834–840.
- Fujimoto, I. (1980). *Jpn. J. Appl. Phys.* **19**, 345–348.
- Fujimoto, I. (1982). *Acta Cryst.* **A38**, 337–345.
- Graafsma, H. (1992). *J. Appl. Cryst.* **25**, 372–376.
- Graafsma, H., Coppens, P., Majewski, J. & Cahen, D. (1993). *J. Solid. State Chem.* **105**, 520–527.
- Graafsma, H., Heunen, G. W. J. C., Dahaoui, S., El Haouzi, A., Hansen, N. K. & Marnier, G. (1997). *Acta Cryst.* **B53**, 565–567.
- Graafsma, H., Paturle, A., Wu, L., Sheu, H.-S., Majewski, J., Poorthuis, G. & Coppens, P. (1992). *Acta Cryst.* **A48**, 113–120.
- Guillot, R. (2002). PhD thesis, Université Henri Poincaré – Nancy I, France.
- Guillot, R., Allé, P., Fertey, P., Hansen, N. K. & Elkaïm, E. (2002). *J. Appl. Cryst.* **35**, 360–363.
- Guillot, R., Fertey, P., Hansen, N. K., Allé, P., Lecomte, C. & Elkaïm, E. (2004). In preparation.
- Guillot, R. & Hansen, N. K. (2003). *DIFMOL*. Internal computer programs of LCM3B, Université Henri Poincaré – Nancy I, France.
- Hamichi, M., Cousins, C. S. G., Meads, R. E., Sheldon, B. J., Teat, S. J. & Thomas, P. A. (1994). *J. Appl. Phys.* **76**, 188–193.
- Heunen, G. W. J. C. (2000). PhD thesis, University of Amsterdam, The Netherlands.
- King-Smith, R. D. & Vanderbilt, D. (1993). *Phys. Rev. B*, **48**, 4442–4455.
- Kochin, V., Davaasambuu, J., Pietsch, U., Schwarz, K. & Blaha, P. (2004). Proceedings of the Sagamore XIV meeting, Broome, Australia, *J. Phys. Chem. Solids*. In the press.
- Nye, J. F. (1957). *Physical Properties of Crystals*. Oxford: Clarendon Press. Reprinted 1985 and 2000.
- Paturle, A., Graafsma, H., Sheu, H.-S., Coppens, P. & Becker, P. (1991). *Phys. Rev. B*, **43**, 14683–14691.
- Pietsch, U., Mahlberg, J. & Unger, K. (1985). *Phys. Status Solidi B*, **131**, 67–73.
- Pietsch, U., Stahn, J., Davaasambuu, J. & Pucher, A. (2001). *J. Phys. Chem. Solids*, **62**, 2129–2133.
- Puget, R. & Godefroy, L. (1975). *J. Appl. Cryst.* **8**, 297–303.
- Reeuwijk, S. J. van, Puig-Molina, A. & Graafsma, H. (2000). *Phys. Rev. B*, **62**, 6192–6197.
- Reeuwijk, S. J. van, Puig-Molina, A. & Graafsma, H. (2001). *Phys. Rev. B*, **64**, 6192–6197.
- Reeuwijk, S. J. van, Vonk, V., Puig-Molina, A. & Graafsma, H. (2000). *J. Appl. Cryst.* **33**, 1422–1429.
- Resta, R. (1994). *Rev. Mod. Phys.* **66**, 899–915.
- Resta, R. (2000). *J. Phys. Condens. Matter*, **12**, R107–R143.
- Santos, A. O. dos, Gelamo, R. V., Li, B. B., Cardoso, L. P., Miranda, M. A. R., Nogueira, M. A. M., Remédios, C. M. R., Melo, F. E. A., Sasaki, J. M., Avanci, L. H. & Morelhaio, S. L. (2001). *Mater. Res.* **4**, 43–46.
- Sebastian, M. T., Klapper, H. & Bolt, R. J. (1992). *J. Appl. Cryst.* **25**, 274–280.
- Sebastian, M. T., Zarka, A. & Capelle, B. (1988). *J. Appl. Cryst.* **21**, 326–329.
- Souza, I., Íñiguez, J. & Vanderbilt, D. (2002). *Phys. Rev. Lett.* **89**, 117602/1–4.
- Stahn, J., Pietsch, U., Blaha, P. & Schwarz, K. (2001). *Phys. Rev. B*, **63**, 165205/1–10.
- Stahn, J., Pucher, A., Pietsch, U., Zellner, J. & Weckert, E. (1999). *Acta Cryst.* **A55**, 1034–1037.
- Thorkildsen, G. & Larsen, H. B. (1999). *Acta Cryst.* **A55**, 1–13.