

X-ray diffraction by a crystal in a permanent external electric field: general considerations

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The variations of X-ray diffraction intensities from a crystal in the presence of a permanent external electric field is modeled analytically using a first-order stationary perturbation theory. The change in a crystal, induced by an external electric field, is separated into two contributions. The first one is related to a pure polarization of an electron subsystem, while the second contribution can be reduced to the displacements of the rigid pseudoatoms from their equilibrium positions. It is shown that a change of the X-ray diffraction intensities mainly originates from the second contribution, while the influence of the pure polarization of a crystal electron subsystem is negligibly small. The quantities restored from an X-ray diffraction experiment in the presence of an external electric field were analyzed in detail in terms of a rigid pseudoatomic model of electron density and harmonic approximation for the atomic thermal motion. Explicit relationships are derived that link the properties of phonon spectra with *E*-field-induced variations of a structure factor, pseudoatomic displacements and piezoelectric strains. The displacements can be numerically estimated using a model of independent atomic motion if the Debye–Waller factors and pseudoatomic charges are known either from a previous single-crystal X-ray diffraction study or from density functional theory calculations. The above estimations can be used to develop an optimum strategy for a data collection that avoids the measurements of reflections insensitive to the electric-field-induced variations.

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1. Introduction

The interaction of a permanent external electric field (*E*-field) with a crystal generates a number of phenomena, which are of great interest for both technical applications and fundamental – theoretical and experimental – research. On a macroscopic scale, these phenomena are well known as dielectric polarization, piezoelectricity, ferroelectricity and pyroelectricity and can be described phenomenologically (Landau & Lifshits, 1977) or semi-empirically (Levine, 1969; Harrison, 1980). Experimental techniques for the measurement of dielectric, piezoelectric and pyroelectric moduli (Haussuehl, 1983) are well developed. However, such kinds of experiments do not provide any elucidation of the microscopic origin of the effects on an atomic scale.

X-ray diffraction looks a promising tool to investigate the response of a crystal to an external *E*-field at the microscopic level. However, owing to experimental reasons, the maximal strength of an external *E*-field that can be applied to a crystal (10 kV mm⁻¹) is several orders of magnitude smaller than the inner-crystal field. Therefore, the study of small *E*-field-induced changes in electron and nuclear subsystems is a big challenge for an X-ray diffraction experiment. Only a few

works dealing with this approach have been published so far. Fujimoto (1982) has studied structural changes in crystalline LiTaO₃ and LiNbO₃ using the modulation–demodulation technique and a conventional X-ray tube. A modified experimental set-up with a movable X-ray tube and a movable detector has been proposed by Aslanov *et al.* (1989). Synchrotron radiation has also been implemented in recent years. This type of study of electric-field-induced structural changes was initiated by Graafsma *et al.* (1993, 1998) and Reeuwijk *et al.* (2000*a,b*, 2001), who investigated KD₂PO₄ at the European Synchrotron Radiation Facility. Stahn *et al.* (1998, 2001) have investigated the change in a structure of GaAs/ZnSe compounds at HASYLAB. Davaasambuu *et al.* (2003) (HASYLAB) and Guillot *et al.* (2004) (LURE) have measured the changes in X-ray diffraction intensities of selected reflections for α -quartz in an *E*-field to analyze the reorganization of atoms within a unit cell. Unfortunately, the works mentioned above were not supported by any kind of microscopic theory explaining the physical meaning of the measured quantities.

Another important problem in the study of the electric-field-induced microscopic structural changes by means of X-ray diffraction consists in the expensive and time-

consuming character of the measurements. Because an external E -field is much smaller than an inner-crystal field, the induced changes of the structure factors are tiny as well. Therefore, synchrotron radiation is required to reduce the statistical error $\sigma = 2/N^{1/2}$ of the reflection intensity (N is the total number of photons registered by the detector) and to accumulate a number of photons sufficient to detect the effect. It is clear that the number of reflections, which can be measured in a reasonable synchrotron beamline time, is restricted. Therefore, an optimum strategy of data collection is required based on a proper selection of the most field sensitive structure factors.

The aim of this work is to analyze the response of a crystal to an external E -field on a microscopic level, to predict the corresponding change of diffraction intensities and to work out the optimum strategy for an X-ray diffraction experiment. Firstly, we apply a perturbation theory to describe the behavior of crystal electron and nuclear subsystems under a permanent external E -field. Then, the obtained results are used for the analysis of the corresponding change of the X-ray diffraction intensities. Finally, we present an optimal strategy for data collection and treatment.

2. The response of the crystal electrons to a permanent external electric field

Let us consider a crystal without an applied E -field. In the Born–Oppenheimer approximation, the non-relativistic wavefunctions of a crystal in the electronic ground state can be presented as a product of electron $|0\rangle$ and nuclear $|A\rangle$ wavefunctions. The ground-state one-electron density averaged over the thermal motion is given by the following expression (Maradudin *et al.*, 1971; Tsirelson & Ozerov, 1996):

$$\langle\rho(\mathbf{r})\rangle = \frac{\sum_A \exp(-\varepsilon_A/k_B T) \langle 0A | \hat{\rho}(\mathbf{r}) | 0A \rangle}{\sum_A \exp(-\varepsilon_A/k_B T)}. \quad (1)$$

Here $|0A\rangle$ is the many-particle wavefunction of the crystal corresponding to the electronic ground state and nuclear vibrational state with the energy ε_A , k_B is the Boltzmann constant and T is the absolute temperature, $\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$ is the operator of the electron density, $\delta(\mathbf{r})$ is the Dirac function, and vectors $\{\mathbf{r}_i\}$ indicate the positions of electrons in a crystal. The expression

$$\rho(\mathbf{r}, A) = \langle 0A | \hat{\rho}(\mathbf{r}) | 0A \rangle \quad (2)$$

represents a static ground-state electron density of a crystal at the fixed nuclear configuration.

The interaction of a crystal with a permanent external electric field \mathbf{E} is described by the Hamiltonian

$$\hat{W}^{(E)} = -e\mathbf{E} \sum_{m\mu} Z_\mu \mathbf{R}_{m\mu} + e\mathbf{E} \sum_i \mathbf{r}_i. \quad (3)$$

Here e and eZ_μ are the absolute values of the electron and nuclear charges, respectively, m marks all unit cells of a crystal, μ enumerates the nuclei within any unit cell and i runs over all electrons of the crystal. In terms of a stationary perturbation theory (Landau & Lifshits, 1977), the wavefunction of a crystal

in an external electric field can be presented as a superposition of unperturbed wavefunctions:

$$|0A(\mathbf{E})\rangle = \sum_n \sum_B c_{nB,0A}(\mathbf{E}) |nB\rangle, \quad (4)$$

n runs over the electronic states and B runs over corresponding nuclear vibrational states. The expansion coefficients $c_{nB,0A}(\mathbf{E})$ are (Sakurai, 1994)

$$c_{nB,0A}(\mathbf{E}) = \frac{\langle nB | \hat{W}_E | 0A \rangle}{\hbar\omega_{0A,nB}}, \quad (5)$$

where $\hbar\omega_{0A,nB} = \hbar\omega_{0A} - \hbar\omega_{nB}$ is the energy difference between the $0A$ and nB states.

Substituting (5) into (4) and then into (2) and considering the first power of the perturbation only, one can express the polarization of an electron and nuclear subsystems in an external E -field as

$$\Delta\rho(\mathbf{r}, A) = \sum_{nB} [\langle 0A | \hat{\rho}(\mathbf{r}) | nB \rangle \langle nB | \hat{W}_E | 0A \rangle + \langle 0A | \hat{W}_E | nB \rangle \langle nB | \hat{\rho}(\mathbf{r}) | 0A \rangle] (\hbar\omega_{0A,nB})^{-1}. \quad (6)$$

The meaning of this expression becomes clearer if one rewrites it in the following form:

$$\begin{aligned} \Delta\rho(\mathbf{r}, A) = & \sum_B [\langle 0A | \hat{\rho}(\mathbf{r}) | 0B \rangle \langle 0B | \hat{W}_E | 0A \rangle \\ & + \langle 0A | \hat{W}_E | 0B \rangle \langle 0B | \hat{\rho}(\mathbf{r}) | 0A \rangle] (\hbar\omega_{AB})^{-1} \\ & + \sum_{n \neq 0, B} [\langle 0A | \hat{\rho}(\mathbf{r}) | nB \rangle \langle nB | \hat{W}_E | 0A \rangle \\ & + \langle 0A | \hat{W}_E | nB \rangle \langle nB | \hat{\rho}(\mathbf{r}) | 0A \rangle] (\hbar\omega_{0A,nB})^{-1} \end{aligned} \quad (7)$$

($\hbar\omega_{AB} = \hbar\omega_A - \hbar\omega_B$ is the difference between the nuclear vibrational energy states). The first sum in (7) includes the ground-state electron wavefunction only. The other contains excited electronic states and describes the polarization of the electron subsystem of a crystal.

3. The response of the X-ray diffraction intensities to a permanent external electric field

The field-free differential effective cross section of an elastic X-ray photon scattering from the primary beam directed along \mathbf{k}_0 into the secondary beam with direction \mathbf{k}_1 (Tsirelson & Ozerov, 1996) is given by:

$$\frac{d\sigma}{d\Omega}(\mathbf{k}_0 \rightarrow \mathbf{k}_1) = p \frac{\sum_A \exp(-\varepsilon_A/k_B T) \sum_B |\langle 0B | \hat{F}(\mathbf{H}) | 0A \rangle|^2}{\sum_A \exp(-\varepsilon_A/k_B T)}. \quad (8)$$

Here p is the polarization factor describing the transition of an X-ray photon from one polarization state to another, $\mathbf{H} = \Delta\mathbf{k}/2\pi$ is a reciprocal-space vector and

$$\hat{F}(\mathbf{H}) = \sum_i \exp(2\pi i \mathbf{H} \mathbf{r}_i) \quad (9)$$

is the crystal structure-factor operator. The change in the matrix elements of a structure factor due to an E -field is

$$\langle 0A | \Delta \hat{\mathbf{F}}(\mathbf{E}) | 0B \rangle = \left[- \sum_{nC} \frac{\langle 0A | \hat{\mathbf{F}} | nC \rangle \langle nC | \hat{\mathbf{W}}^{(E)} | 0B \rangle}{\hbar \omega_{nC,0B}} + \sum_{nC} \frac{\langle 0A | \hat{\mathbf{W}}^{(E)} | nC \rangle \langle nC | \hat{\mathbf{F}} | 0B \rangle}{\hbar \omega_{0A,nC}} \right]. \quad (10)$$

Transforming (10) in the same way as has been done above for expression (6), we can separate it into two contributions: the first one depends on the ground-state electron wavefunction and includes the nuclear excitations only, while the second one accounts for the excitations of a crystal electron subsystem and describes the pure polarization of crystal electrons [see the second part of (7)]:

$$\langle 0A | \Delta \hat{\mathbf{F}}(\mathbf{E}) | 0B \rangle = \left[- \sum_C \frac{\langle 0A | \hat{\mathbf{F}} | 0C \rangle \langle 0C | \hat{\mathbf{W}}^{(E)} | 0B \rangle}{\hbar \omega_{CB}} + \sum_C \frac{\langle 0A | \hat{\mathbf{W}}^{(E)} | 0C \rangle \langle 0C | \hat{\mathbf{F}} | 0B \rangle}{\hbar \omega_{AC}} \right] + \left[- \sum_{n \neq 0, c} \frac{\langle 0A | \hat{\mathbf{F}} | nC \rangle \langle nC | \hat{\mathbf{W}}^{(E)} | 0B \rangle}{\hbar \omega_{nC,0B}} + \sum_{l \neq 0, c} \frac{\langle 0A | \hat{\mathbf{W}}^{(E)} | lC \rangle \langle lC | \hat{\mathbf{F}} | 0B \rangle}{\hbar \omega_{0A,lC}} \right]. \quad (11)$$

It is worth noting that, for the case of the fixed nuclear positions, the second two terms in (11) are reduced to the expression obtained in previous works by Buckingham (1964) and Tsirelson *et al.* (2003). These works deal with X-ray scattering by a free atom in a permanent external E -field. It has been shown there that the change of the atomic scattering factor and the scattering intensity in an electric field E of $\sim 5 \text{ kV mm}^{-1}$, which is normally applied in practice, is only $\sim 10^{-5}$. It is at least two orders of magnitude smaller than can be detected by X-ray diffraction (Davaasambuu, 2003). For the case of a crystal, the numerical estimation of the matrix elements in (11), related to pure electric polarization, is difficult. However, they can be directly compared to the matrix elements associated with the nuclear excitations [the first part of expression (11)]. Indeed, for non-conducting crystalline compounds, the minimum electron transition frequency, $\hbar \omega_{nC,0B}$, is defined by the width of an energy gap, which amounts to several electronvolts. At the same time, the difference between the nuclear vibrational states, $\hbar \omega_{CB}$, is about 10^{-2} eV . Subsequently, the denominators in the first part of (11) are roughly two orders lower than those in the second part. Therefore, the electron polarization of a crystal can be neglected and the matrix elements in (11) describing the change in the crystal structure factor due to an E -field can be written as

$$\langle 0A | \Delta \hat{\mathbf{F}}(\mathbf{E}) | 0B \rangle \approx - \sum_C \frac{\langle 0A | \hat{\mathbf{F}} | 0C \rangle \langle 0C | \hat{\mathbf{W}}^{(E)} | 0B \rangle}{\hbar \omega_{CB}} + \sum_C \frac{\langle 0A | \hat{\mathbf{W}}^{(E)} | 0C \rangle \langle 0C | \hat{\mathbf{F}} | 0B \rangle}{\hbar \omega_{AC}}. \quad (12)$$

Thus, the change in a nuclear vibrational state of a system due to an E -field yields the main contribution to the change in X-ray diffraction intensities.¹ To provide an opportunity to analyze this change in terms of electric-field-induced displacements of nuclear positions, we need to transform the corresponding matrix elements in (12) and take the sum over all the nuclear vibrational states. To do that, we have to introduce a structural crystal model for an electron density and assume a model for nuclear vibrations.

4. Modeling the electric-field-induced changes in a pseudoatomic approximation

Using the explicit form of the interaction Hamiltonian (3) and integrating over electronic coordinates $\{\mathbf{r}_i\}$, we can write the field-dependent matrix elements in (12) as

$$\langle 0A | \hat{\mathbf{W}}^{(E)} | 0B \rangle = -e \mathbf{E} \langle A | \sum_{m\mu} Z_\mu (\mathbf{R}_{m\mu}^{(0)} + \hat{\mathbf{u}}_{m\mu}) - \int \rho(\mathbf{r}, \{\mathbf{R}\}) \mathbf{r} \, d\mathbf{r} | B \rangle. \quad (13)$$

Here $\hat{\mathbf{u}}_{m\mu} = \hat{\mathbf{R}}_{m\mu} - \mathbf{R}_{m\mu}^{(0)}$ are the thermal displacements of nuclei from their equilibrium position $\mathbf{R}_{m\mu}^{(0)}$ without an external E -field. $\rho(\mathbf{r}, \{\mathbf{R}\})$ is the ground-state electron density of a crystal at the fixed nuclear positions $\{\mathbf{R}\}$. It is convenient to express the electron-density distribution of a crystal *via* a structural model in the form of a sum of rigid pseudoatomic densities, $\rho_\mu(\mathbf{r})$ (Stewart, 1976), centered at nuclear sites

$$\rho(\mathbf{r}) = \sum_{m\mu} \rho_\mu(\mathbf{r} - \hat{\mathbf{R}}_{m\mu}). \quad (14)$$

Then, the integral in (13) is transformed to

$$\int \rho(\mathbf{r}) \mathbf{r} \, d\mathbf{r} = \sum_{m\mu} \int \rho_\mu(\mathbf{r} - \mathbf{R}_{m\mu}) \mathbf{r} \, d\mathbf{r} \quad (15)$$

with

$$\int \rho_\mu(\mathbf{r} - \mathbf{R}_{m\mu}) \mathbf{r} \, d\mathbf{r} = \int \rho_\mu(\mathbf{r}) \mathbf{r} \, d\mathbf{r} + \mathbf{R}_{m\mu} \int \rho_\mu(\mathbf{r}) \, d\mathbf{r}. \quad (16)$$

The first term on the right-hand side of (16) defines the electron contribution to the dipole moment of the μ th pseudoatom: $\mathbf{P}_\mu = -e \int \rho_\mu(\mathbf{r}) \mathbf{r} \, d\mathbf{r}$. The second integral is related to a pseudoatomic charge

$$Q_\mu = e [Z_\mu - \int \rho_\mu(\mathbf{r}) \, d\mathbf{r}]. \quad (17)$$

With expressions (15)–(17), the matrix elements (13) take the form

$$\langle 0A | \hat{\mathbf{W}}^{(E)} | 0B \rangle = -\mathbf{E} \langle A | \sum_{m\mu} \mathbf{P}_\mu + \sum_{m\mu} Q_\mu (\mathbf{R}_{m\mu}^{(0)} + \hat{\mathbf{u}}_{m\mu}) | B \rangle. \quad (18)$$

The first term inside the brackets defines the electric field effect on pseudoatomic dipoles in a crystal. For rigid pseudoatoms, it is constant and does not contribute to the matrix elements (18) owing to the condition $\langle A | B \rangle = 0$.

The second term in (18) is responsible for E -field-induced pseudoatomic displacements. The operators of the nuclear displacements $\hat{\mathbf{u}}_{m\mu}$ in (18) can be presented as a sum of the

¹ The contribution, related to the pure polarization of a crystal electron density, deserves special consideration when the change in the nuclear system is forbidden by the crystal symmetry.

plane waves corresponding to the phonons in a crystal lattice (Reisland, 1973; Maradudin *et al.*, 1971):

$$\hat{\mathbf{u}}_{m\mu} = \left(\frac{\hbar}{2Nm_\mu}\right)^{1/2} \sum_{\alpha} \frac{1}{\omega_{\alpha}^{1/2}} \left[\mathbf{e}_{\mu\alpha} \exp(i\mathbf{q}_{\alpha} \mathbf{R}_m^{(0)}) \hat{\mathbf{b}}_{\alpha} + \mathbf{e}_{\mu\alpha}^* \exp(-i\mathbf{q}_{\alpha} \mathbf{R}_m^{(0)}) \hat{\mathbf{b}}_{\alpha}^{\dagger} \right]. \quad (19)$$

Here N is the total number of unit cells in the crystal, m_{μ} is the atomic mass of the μ th nucleus in the unit cell. $\mathbf{R}_m^{(0)}$ are the positions of unit cells within a crystal given by the respective Bravais-lattice vectors. α enumerates $3sN$ phonon modes, where s is the number of atoms per unit cell. \mathbf{q}_{α} and $\mathbf{e}_{\mu\alpha}$ are the wavevector and the polarization vector for the phonon mode α , and $\hat{\mathbf{b}}_{\alpha}$ and $\hat{\mathbf{b}}_{\alpha}^{\dagger}$ are the phonon creation and annihilation operators, respectively.

Introducing a notation $\sum_{m(E)} \exp(i\mathbf{q}_{\alpha} \mathbf{R}_m^{(0)}) = \Delta(\mathbf{q}_{\alpha})$ (Born & Huang, 1954) for the sum over all unit cells, which are immersed in an electric field, one can rewrite expression (18) as

$$\langle 0A | \hat{\mathbf{W}}^{(E)} | 0B \rangle = \sum_{\alpha} \mathbf{E} \langle A | \mathbf{G}_{\alpha} \hat{\mathbf{b}}_{\alpha} + \mathbf{G}_{\alpha}^* \hat{\mathbf{b}}_{\alpha}^{\dagger} | B \rangle, \quad (20)$$

where $\mathbf{G}_{\alpha} = -(\hbar/2N\omega_{\alpha})^{1/2} \Delta(\mathbf{q}_{\alpha}) \sum_{\mu} Q_{\mu} \mathbf{e}_{\mu\alpha} / m_{\mu}^{1/2}$.

In the harmonic approximation, the nuclear vibrational wavefunctions are presented as a product of the single-phonon wavefunctions, $|A\rangle = \prod_{\alpha} |A_{\alpha}\rangle$, where A_{α} are the occupation numbers of the phonon mode α . Using the properties of phonon creation and annihilation operators (Reisland, 1973), one can transform (20) into the expression

$$\begin{aligned} \langle 0A | \hat{\mathbf{W}}^{(E)} | 0B \rangle &= \sum_{\alpha} \mathbf{E} \left[\mathbf{G}_{\alpha} B_{\alpha}^{1/2} \langle A_{\alpha} | B_{\alpha} - 1 \rangle + \mathbf{G}_{\alpha}^* (B_{\alpha} + 1)^{1/2} \langle A_{\alpha} | B_{\alpha} + 1 \rangle \right] \prod_{\gamma \neq \alpha} \langle A_{\gamma} | B_{\gamma} \rangle. \end{aligned} \quad (21)$$

Within the pseudoatomic structural model (14) and the harmonic approximation, the matrix elements of a crystal structure factor in (12) can be transformed in a similar way:

$$\langle 0A | \hat{\mathbf{F}} | 0B \rangle = \sum_{m\mu} f_{\mu}(\mathbf{H}) \left[\prod_{\alpha} \langle A_{\alpha} | \hat{\mathbf{T}}_{m\mu\alpha}(\mathbf{H}) | B_{\alpha} \rangle \right] \exp(2\pi i \mathbf{H} \mathbf{R}_{m\mu}^{(0)}). \quad (22)$$

Here $f_{\mu}(\mathbf{H})$ is an atomic scattering factor and

$$\begin{aligned} \hat{\mathbf{T}}_{m\mu\alpha} &= \exp[iC_{\alpha m\mu} \hat{\mathbf{b}}_{\alpha} + iC_{\alpha m\mu}^* \hat{\mathbf{b}}_{\alpha}^{\dagger}] \\ C_{\alpha m\mu} &= \left(\frac{\hbar}{2Nm_{\mu}}\right)^{1/2} \frac{2\pi \mathbf{H} \mathbf{e}_{\mu\alpha}}{\omega_{\alpha}^{1/2}} \exp(i\mathbf{k}_{\alpha} \mathbf{R}_m^{(0)}). \end{aligned} \quad (23)$$

Substituting expressions (21) and (22) into (12), we get (see Appendix A)

$$\begin{aligned} \langle 0A | \Delta \hat{\mathbf{F}}(\mathbf{E}) | 0B \rangle &= \sum_{m\mu} f_{\mu}(\mathbf{H}) \left[\prod_{\alpha} \langle A_{\alpha} | \hat{\mathbf{T}}_{m\mu\alpha}(\mathbf{H}) | B_{\alpha} \rangle \right] \\ &\times \exp(2\pi i \mathbf{H} \mathbf{R}_{m\mu}^{(0)}) D_{m\mu}(\mathbf{E}). \end{aligned} \quad (24)$$

Here the function

$$D_{m\mu}(\mathbf{E}) = \sum_{\alpha} -i\mathbf{E} \left[\frac{C_{\alpha m\mu}^* \mathbf{G}_{\alpha} + C_{\alpha m\mu} \mathbf{G}_{\alpha}^*}{\hbar\omega_{\alpha}} \right] \quad (25)$$

describes the influence of an external electric field on an X-ray scattering intensities.

The X-ray diffraction intensity (8) is represented by the squared structure factor, averaged over the nuclear vibrational states. With account of (22) and (24), it provides the following expression for the electric-field-dependent effective X-ray cross section:

$$\begin{aligned} \frac{d\sigma_E}{d\Omega}(\mathbf{H}) &= p \sum_{m\mu} \sum_{nv} f_{\mu}(\mathbf{H}) T_{\mu}(\mathbf{H}) f_{\nu}^*(\mathbf{H}) T_{\nu}(\mathbf{H}) \\ &\times \exp[2\pi i \mathbf{H} (\mathbf{R}_{m\mu}^{(0)} - \mathbf{R}_{nv}^{(0)})] [1 + D_{m\mu}(\mathbf{E}) + D_{nv}^*(\mathbf{E})], \end{aligned} \quad (26)$$

where the temperature factor is expressed by the standard form $T_{\mu} = \exp(-M_{\mu})$ with

$$M_{\mu} \approx \frac{2\pi^2 k_B T}{Nm_{\mu}} \sum_{\alpha} \frac{|\mathbf{H} \mathbf{e}_{\mu\alpha}|^2}{\omega_{\alpha}^2}. \quad (27)$$

Considering the expression (26), one can conclude that the structure amplitude of a crystal in an external E -field $|F_E(\mathbf{H})|^2$ differs from that without a field by the following term:

$$[1 + D_{m\mu}(\mathbf{E}) + D_{nv}^*(\mathbf{E})] \approx \exp\{2\pi i \mathbf{H} [\Delta \mathbf{R}_{m\mu}(\mathbf{E}) - \Delta \mathbf{R}_{nv}(\mathbf{E})]\}. \quad (28)$$

Here the explicit form of E -field-induced displacements of nuclei from their equilibrium positions is

$$\begin{aligned} \Delta \mathbf{R}_{m\mu} &= \sum_{\alpha} \sum_{\nu} \frac{Q_{\nu}}{2N(m_{\mu} m_{\nu})^{1/2} \omega_{\alpha}^2} [(\mathbf{E} \mathbf{e}_{\nu\alpha}^*) \exp(i\mathbf{q}_{\alpha} \mathbf{R}_m) \Delta_{\alpha}^* \mathbf{e}_{\mu\alpha} \\ &+ (\mathbf{E} \mathbf{e}_{\nu\alpha}) \exp(-i\mathbf{q}_{\alpha} \mathbf{R}_m) \Delta_{\alpha} \mathbf{e}_{\mu\alpha}^*]. \end{aligned} \quad (29)$$

Expression (26) shows that the influence of the E -field on X-ray diffraction intensities is described by a static Debye-Waller factor. Note that the derived equations are valid only within a rigid pseudoatom approximation. Non-rigidity can be, in principle, taken into account by using the formalism described by March & Wilkins (1978).

5. The displacement of pseudoatoms related to the external and internal piezoelectricity

The pseudoatomic displacements, $\Delta \mathbf{R}_{m\mu}$, can be separated into two parts related to an external and internal piezoelectric effect, respectively. For this purpose, one takes into account that the lattice sums, Δ_{α} , in (29) significantly differ from zero only in the vicinity of the Brillouin zone center, *i.e.* for small \mathbf{q}_{α} (Born & Huang, 1954) and rapidly decrease to nearly zero with increasing \mathbf{q}_{α} . Expanding the exponents in (29) in Taylor series and keeping the terms in the first power of \mathbf{q}_{α} allows one to divide the displacements into two contributions:

$$\Delta \mathbf{R}_{m\mu} = \Delta \mathbf{R}_{\mu} + \Delta \mathbf{R}_{m\mu}^{(\text{ext})}. \quad (30)$$

The term

$$\Delta \mathbf{R}_\mu = \sum_\alpha \sum_v \frac{Q_v}{2N(m_\mu m_v)^{1/2} \omega_\alpha^2} [(\mathbf{Ee}_{v\alpha}^*) \Delta_\alpha^* \mathbf{e}_{\mu\alpha} + (\mathbf{Ee}_{v\alpha}) \Delta_\alpha \mathbf{e}_{\mu\alpha}^*] \quad (31)$$

depends on the position of an atom within a unit cell only, while the term

$$\Delta \mathbf{R}_{m\mu}^{(\text{ext})} = \sum_\alpha \sum_v \frac{Q_v i \mathbf{q}_\alpha \mathbf{R}_m}{2N(m_\mu m_v)^{1/2} \omega_\alpha^2} \times [(\mathbf{Ee}_{v\alpha}^*) \Delta_\alpha^* \mathbf{e}_{\mu\alpha} - (\mathbf{Ee}_{v\alpha}) \Delta_\alpha \mathbf{e}_{\mu\alpha}^*] \quad (32)$$

depends on the position of a unit cell within a crystal. Expression (31) depends on the bulk properties of a crystal. Indeed, the functional behavior of the lattice sum $\Delta(\mathbf{q}_\alpha)$ is completely defined by the number of atoms in the whole crystal, N , and the number of atoms, M , of that part of the crystal, which is directly affected by an external E -field. In a one-dimensional case, the set of permitted wavevectors is defined by $q_h = (2\pi/N)h$, where h is an integer number. The lattice sum has the value M in the center of the Brillouin zone, *i.e.* at $h = 0$, and drops to zero at $h = N/M$. In this case, $\sum_{q_\alpha} \Delta(q_\alpha) \approx 2(N/M)(M/2) = N$, where $M/2$ is the mean value of the lattice sum taken over the interval $[-N/M; N/M]$. The lattice sum is changing fast with a change of the wavevector in comparison with a change of the polarization vectors and phonon frequencies. Therefore, replacing the polarization vectors and phonon frequencies in (31) by their fixed values taken in the center of the Brillouin zone, we get:

$$\Delta \mathbf{R}_\mu = \sum_{\alpha(\mathbf{q}_\alpha=0)} \sum_v \frac{Q_v (\mathbf{Ee}_{v\alpha}) \mathbf{e}_{\mu\alpha}}{(m_\mu m_v)^{1/2} \omega_\alpha^2} \quad (33)$$

The displacement $\Delta \mathbf{R}_\mu$ does not depend on the number of unit cells within a crystal. Thus, expression (33) describes the internal (on atomic scale) structural changes induced by an external E -field.

The vectors $\Delta \mathbf{R}_{m\mu}^{(\text{ext})}$ are related to external strains and describe the macroscopic deformation induced by an external E -field (converse piezoelectric effect). These displacements are a linear function of the position of a unit cell within a crystal; therefore, the displacements of the same atoms in different unit cells are different. The acoustic vibrations give the major contribution to (32) due to the presence of the prefactor $\mathbf{q}_\alpha/\omega_\alpha^2$. That agrees with the fact that a macroscopic deformation (elastic strains) is directly related to the long-wavelength acoustic phonons (Born & Huang, 1954). The approximate expression for the polarization vectors of acoustic phonons near the Brillouin zone center (Maradudin *et al.*, 1971)

$$\mathbf{e}_{\mu\alpha} = m_\mu^{1/2} \mathbf{e}_\alpha^{(0)} \exp(i \mathbf{q}_\alpha \mathbf{R}_\mu) \approx m_\mu^{1/2} \mathbf{e}_\alpha^{(0)} (1 + i \mathbf{q}_\alpha \mathbf{R}_\mu) \quad (34)$$

allows one to express (32) in the form

$$\Delta \mathbf{R}_{m\mu}^{(1)} = \sum_\alpha \sum_v \frac{Q_v i \mathbf{q}_\alpha \mathbf{R}_m}{N \omega_\alpha^2} [(\mathbf{Ee}_\alpha^{(0)}) \mathbf{e}_\alpha^{(0)} \Delta_\alpha i \mathbf{q}_\alpha (\mathbf{R}_\mu - \mathbf{R}_v)], \quad (35)$$

where the vectors $\mathbf{e}_\alpha^{(0)}$ do not depend on the position of an atom within a unit cell. The lattice sum, Δ_α , is supposed to be a

real quantity, which is provided by the proper choice of the origin of a crystal lattice. The neutrality condition for a unit cell, $\sum_v Q_v = 0$, leads to the final expression for the external displacements:

$$\Delta \mathbf{R}_{m\mu}^{(\text{ext})} \equiv \Delta \mathbf{R}_m^{(\text{ext})} = - \sum_\alpha \frac{\tilde{\mathbf{q}}_\alpha \mathbf{R}_m}{c_\alpha^2} [(\mathbf{Ee}_\alpha^{(0)}) \mathbf{e}_\alpha^{(0)} (\tilde{\mathbf{q}}_\alpha \mathbf{P})], \quad (36)$$

where $\mathbf{P} = \sum_v Q_v \mathbf{R}_v$ is the dipole moment of a unit cell, $c_\alpha = \omega_\alpha/q_\alpha$ is the sound velocity corresponding to a specific acoustic phonon mode (longitudinal or transverse), $\tilde{\mathbf{q}}_\alpha$ is the unit vector, marking the direction of the wavevector, $\mathbf{q}_\alpha = q_\alpha \tilde{\mathbf{q}}_\alpha$.

Equation (36) can be expressed as

$$\Delta \mathbf{R}_{mi}^{(1)} = \sum_{k=1}^3 \sum_{j=1}^3 d_{kij} E_k R_{mj}, \quad (37)$$

where the third-rank tensor with the elements

$$d_{kij} = - \sum_\alpha \frac{\tilde{q}_{\alpha j}}{c_\alpha^2} e_{\alpha k}^{(0)} e_{\alpha i}^{(0)} \tilde{\mathbf{q}}_\alpha \mathbf{P} \quad (38)$$

gives the microscopic representation of piezoelectric moduli. The external atomic displacements (37) describe the macroscopic deformation or the change in crystal lattice parameters; they do not change the relative atomic positions.

6. The change of the diffraction intensities due to external and internal pseudoatomic displacements

Reduced to a single unit cell deformed by an external E -field, the diffracted intensity is

$$|F_E(\mathbf{H})|^2 = \sum_\mu \sum_v f_\mu(\mathbf{H}) f_v^*(\mathbf{H}) T_\mu(\mathbf{H}) T_v(\mathbf{H}) \exp[2\pi i \mathbf{H}(\mathbf{R}_\mu - \mathbf{R}_v)] \times [1 + 2\pi i \mathbf{H}(\Delta \mathbf{R}_\mu - \Delta \mathbf{R}_v)]. \quad (39)$$

Note that the reciprocal-lattice vectors \mathbf{H} differ from their field-free values and correspond now to the crystal lattice deformed by external piezoelectricity.

Considering the possibility of tuning the wavelength, the final expression for the structure factor in an external electric field takes the form

$$F_E(\mathbf{H}) = \sum_\mu [f_\mu(\mathbf{H}) + f'(\lambda) + i f''(\lambda)] T_\mu(\mathbf{H}) \exp(2\pi i \mathbf{H} \mathbf{R}_\mu) \times \exp[2\pi i \mathbf{H} \Delta \mathbf{R}_\mu(\mathbf{E})], \quad (40)$$

where $f'(\lambda)$, $f''(\lambda)$ are introduced to account for the anomalous X-ray scattering.

Expression (40) can be applied for the numerical estimation of the relative change in X-ray diffraction intensity and selection of reflections that are expected statistically to have significant changes in the diffraction intensities. This should be done under actual experimental conditions, such as the direction of an E -field relative to a crystal, the wavelength used for the data collection and others. To do that, we shall consider separately the influence of external and internal pseudoatomic displacements on the X-ray diffraction intensity.

The external pseudoatomic displacements, $\Delta\mathbf{R}_{m\mu}^{(\text{ext})}$, result in macroscopic changes of a crystal form and the lattice parameters while the relative positions of the atoms within a unit cell remain fixed. The main effect in the diffraction pattern is the change of the angular position of the diffraction peak (Graafsma *et al.*, 1993; Hansen *et al.*, 2004)

$$\Delta\theta = -\tan\theta d_{kij}H_iH_jE_k/H^2. \quad (41)$$

The components of the external E -field vector E_k and the reciprocal-lattice vector H_j are expressed in the Cartesian coordinate system associated with the crystallographic set-up (Nye, 2004).

External atomic displacements also change the length of a reciprocal-lattice vector H due to the deformation of a crystal lattice. Correspondingly, the value of the atomic scattering factor $f(H)$ is also changed: $\Delta f(H) \approx \partial f(H)/\partial H \Delta H$. The Δf magnitude can be estimated if the piezoelectric coefficients of the material under study are known. Fig. 1 shows the dependence of the shift in the atomic scattering factor for the Ga atom in α -GaPO₄, owing to the piezoelectric deformation, as a function of the length of the reciprocal vector. The piezoelectric coefficients for the right-handed modification of α -GaPO₄ were taken from Krispel *et al.* (1997). For the typical strength of an external E -field (5 kV mm⁻¹), the maximal variation of an atomic scattering factor is $\sim 10^{-4}$, *i.e.* one order of magnitude smaller than the measured effects. The atomic Debye–Waller factors change for the same reason. However, we have found that the corresponding variation in diffraction intensity for the model system α -GaPO₄ is of the order of 10^{-6} .

Expressions (39) can be used to derive relative changes of the X-ray diffraction intensities due to the internal atomic displacements, $\Delta\mathbf{R}_\mu$. These displacements (33) are complicated functions of the phonon spectrum and other microscopic parameters of the electronic subsystem of a crystal, which are strictly related to each other (Baroni *et al.*, 2001). To clarify their behavior, we rewrite (33) in the coordinate form, using the dynamical matrix of the crystal lattice D (Born & Huang, 1954):

$$\begin{aligned} \Delta\mathbf{R}_{\mu i} &= \sum_v Q_v \left[\sum_{\alpha(\mathbf{q}_\alpha=0)} \frac{e_{\mu\alpha i} e_{\nu\alpha j}}{(m_\mu m_\nu)^{1/2} \omega_\alpha^2} \right] E_j \\ &= \sum_v Q_v D_{ij}^{-1} E_j / (m_\mu m_\nu)^{1/2} \end{aligned} \quad (42)$$

($i = x, y, z$; the Einstein summation rule is assumed). The displacement tensor

$$a_{ij}(\mu) = \sum_v Q_v D_{ij}^{-1} / (m_\mu m_\nu)^{1/2} \quad (43)$$

allows one to re-write (42) in the form

$$\Delta\mathbf{R}_\mu = \hat{\mathbf{a}}(\mu)\mathbf{E}. \quad (44)$$

In general, the matrix (43) is non-diagonal; therefore, the atomic displacements (44) are non-parallel to an external E -field. Apart from the properties of the phonon spectra, the displacements $\Delta\mathbf{R}_\mu$ depend on both the pseudoatomic charge

of the given atom, which adiabatically follows the given nucleus, and the pseudoatomic charges of the rest of the atoms within the unit cell. The first mechanism is quantitatively described by the elements of the matrix $D_{\mu\mu}^{-1}$, while the second one is accounted for by those elements D_{ij}^{-1} of $D_{\mu\nu}^{-1}$ for which $\mu \neq \nu$. In other words, the displacements depend on both the immediate influence of the electric field on the pseudoatomic charge and displacements of the neighboring atoms. It is clear that the first mechanism depends on the value of pseudoatomic charge, while the second one depends on the kind and strength of the chemical bonding in a crystal. It is worth noting that, in previous works relating to the study of pseudoatomic displacements in α -SiO₂ (Davaasambuu *et al.*, 2003; Davaasambuu, 2003), it was assumed that the Si–O chemical bonds were rigid. Formulating this semi-empirical approach in terms of the presented theory, one can say that the displacements (42), associated with the non-diagonal elements of the dynamical matrix, dominate. The validity of such an assumption for a specific compound, in principle, can be verified by comparing the diagonal and non-diagonal contributions to the displacements.

To get the approximate values of the internal pseudoatomic displacements and corresponding relative changes of the diffraction intensities, we suppose that the pseudoatomic fragments vibrate independently from each other relative to their equilibrium positions. Although this approach contradicts the one assumed by Davaasambuu *et al.* (2003), it allows an estimate of the pseudoatomic displacements induced by an external E -field in a crystal to be easily performed and the results of the measurements to be predicted. Also, the model of independent atomic vibrations considered below can serve either as a starting point for a refinement or as a reference point to compare it with the final experimental results.

In the harmonic approximation, the effective potential energy is described by the following expression

$$\Phi = \Phi_0 + \frac{1}{2} \sum_{m\mu} \sum_{ij} \gamma_{ij}(\mu) u_{m\mu i} u_{m\mu j}. \quad (45)$$

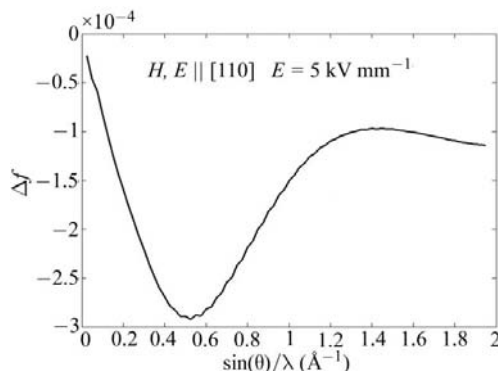


Figure 1
The change in the values of atomic scattering factors for the Ga atom in an α -GaPO₄ crystal due to the piezoelectric deformation of the crystal lattice.

This corresponds to the special form of the dynamical matrix, D , where cross elements between different atoms are zero and the rest do not depend on the phonon wavevector

$$D_{ij}^{\mu\nu} = \delta_{\mu\nu} \gamma_{ij}(\mu) / m_{\mu}. \quad (46)$$

The force constant matrix of the μ th atom satisfies the dynamic equation

$$\sum_j \gamma_{ij}(\mu) e_{\mu\omega j} = m_{\mu} \omega_{\alpha}^2 e_{\mu\omega i}. \quad (47)$$

Transforming this expression to the form

$$\frac{e_{\mu\omega i}}{\omega_{\alpha}^2} = m_{\mu} B_{ik}^{(\mu)} e_{\mu\omega k}, \quad (48)$$

where $B_{ik}^{(\mu)} = [\gamma_{ik}(\mu)]^{-1}$ and inserting (48) into (42) and using the orthogonality of polarization vectors, we arrive at an approximate expression for the pseudoatomic displacements:

$$\Delta R_{\mu i} = Q_{\mu} B_{ij}(\mu) E_j. \quad (49)$$

In terms of the same independent-atom approximation, the expression for the field-free temperature factor (27) takes the standard form

$$T_{\mu} = \exp[-2\pi^2 k_B T B_{ij}(\mu) H_i H_j] = \exp(-2\pi^2 U_{ij}^{(\mu)} H_i H_j), \quad (50)$$

where polarization vectors and phonon frequencies do not depend on the wavevector; U_{ij} are the elements of the field-free thermal displacement tensors in the Cartesian coordinate system.

The final simplified expression for the electric-field-dependent structure factor is

$$F_E(\mathbf{H}) = \sum_{\mu} f_{\mu}(\mathbf{H}) \exp(-2\pi^2 U_{ij}^{(\mu)} H_i H_j) \exp(2\pi i \mathbf{H} \mathbf{R}_{\mu}) \times \exp\left(2\pi i Q_{\mu} \frac{U_{ij}^{(\mu)}}{k_B T} H_i E_j\right). \quad (51)$$

For the displacements of the pseudoatoms induced by a permanent external E -field,

$$\Delta R_{\mu i} = Q_{\mu} \frac{U_{ij}^{(\mu)}}{k_B T} E_j. \quad (52)$$

The physical interpretation of expression (52) may be achieved by rewriting it in the form

$$k_B T [U_{ij}^{(\mu)}]^{-1} \Delta R_{\mu j} = Q_{\mu} E_i. \quad (53)$$

The right-hand side of (53), $Q_{\mu} E_i$, is the force acting on the μ th atom from an external E -field, while the quantities $k_B T [U_{ij}^{(\mu)}]^{-1}$ can be treated as the force constants for the effective harmonic atomic potential (Willis & Pryor, 1975). The longitudinal polarization only will be induced if the thermal atomic displacements are isotropic or the external E -field is parallel to one of the major axes of the thermal ellipsoid. Transverse effects are associated solely with the anisotropy of atomic thermal displacements.

The field-free parameters of the structural model, *i.e.* the components of the atomic thermal displacement tensor \mathbf{U} and the pseudoatomic charges, are usually taken from the results

Table 1

The elements of the thermal displacement tensor of α -GaPO₄ and the pseudoatomic charges, calculated by integrating of the electron density within the Bader atomic basins.

	Ga	P	O1	O2
U^{11} (10^{-2} \AA^2)	0.856 (4)	0.834 (5)	1.835 (17)	1.935 (18)
U^{22} (10^{-2} \AA^2)	0.706 (3)	0.615 (5)	1.347 (11)	1.237 (11)
U^{33} (10^{-2} \AA^2)	0.688 (2)	0.656 (5)	1.162 (10)	1.249 (12)
U^{12} (10^{-2} \AA^2)	$\frac{1}{2} U^{22}$	$\frac{1}{2} U^{22}$	1.084 (11)	1.089 (13)
U^{13} (10^{-2} \AA^2)	$\frac{1}{2} U^{23}$	$\frac{1}{2} U^{23}$	-0.395 (10)	-0.483 (11)
U^{23} (10^{-2} \AA^2)	-0.055 (1)	-0.041 (3)	-0.443 (8)	-0.445 (8)
Q (e)	1.62	3.15	-1.19	-1.19

of a precise X-ray diffraction experiment for $E = 0$ (Tsirelson & Ozerov, 1996; Coppens, 1997). For practical purposes, the model of the structure factor (51) should be reduced to the model for the relative change in the diffraction intensity

$$\frac{\Delta I_E}{I}(\mathbf{H}) = \frac{|F_E(\mathbf{H})|^2 - |F_{E=0}(\mathbf{H})|^2}{|F_{E=0}(\mathbf{H})|^2}. \quad (54)$$

7. Planning the X-ray diffraction experiment in the presence of an external electric field

Expressions (51) and (54) were applied to estimate the expected changes of diffraction intensities in α -GaPO₄ in an external E -field. The model parameters for this compound are given in Table 1. To determine the elements of the displacement tensor \mathbf{U} , we have measured intensities of 333 symmetry-independent reflections in the wavelength ranges $0.65 < \sin \theta / \lambda < 0.75 \text{ \AA}^{-1}$ (34 reflections), $0.95 < \sin \theta / \lambda < 1.05 \text{ \AA}^{-1}$ (27 reflections) and $1.28 < \sin \theta / \lambda < 1.33 \text{ \AA}^{-1}$ (272 reflections). The refinement of the atomic positional parameters and the elements of the \mathbf{U} tensor was carried out with *MOLDOS97* (Protas, 1997; Hansen & Coppens, 1978); it resulted in $R = 0.011$, $R_w = 0.013$ and goodness of fit $S = 0.99$. The obtained displacement parameters are in good agreement with results of the previous studies dealing with the X-ray diffraction study of α -GaPO₄ (Baumgartner *et al.* 1984; Litvin *et al.*, 1987).

The set of pseudoatomic charges, Q , presented in model (51) was derived by integration of the electron density over Bader's (1990) zero-flux atomic basins. The electron density of GaPO₄ was calculated using the 'full-potential augmented-plane-wave plus local orbitals' method as implemented in the *WIEN2k* program package (Blaha *et al.*, 2001).

The E -field-induced atomic displacements in α -GaPO₄ were evaluated according to (52) for the electric field $E = 1 \text{ kV mm}^{-1}$ oriented perpendicular to the (110) Miller plane; this corresponds to the twofold symmetry axis in the GaPO₄ crystal structure and crystallographic direction [110] (Table 2). These displacements were further used for the calculation of the structure factors (51) and the corresponding relative changes in the X-ray diffraction intensities (54). Fig. 2 shows the distribution of the $\Delta I/I$ values for all the reflections over a reciprocal space at $\lambda = 0.80 \text{ \AA}$. It turns out that the E -field-induced change in the majority of reflections in α -GaPO₄ is

Table 2

The displacements of the pseudoatoms (in the crystallographic coordinate system) induced by an external electric field in α -GaPO₄ calculated on the basis of the independent atomic vibration model ($E \parallel [110]$) $E = 1 \text{ kV mm}^{-1}$.

	$\Delta R^1 (10^{-5})$	$\Delta R^2 (10^{-5})$	$\Delta R^3 (10^{-5})$
Ga1	1.06	0.93	-0.03
Ga2	0.93	1.06	0.03
Ga3	1.18	1.18	0.00
P1	1.94	1.57	-0.04
P2	1.57	1.94	0.04
P3	2.31	2.31	0.00
O11	-1.87	-1.56	0.21
O12	-1.03	-0.82	-0.12
O13	-1.13	-1.66	-0.09
O14	-1.56	-1.87	-0.21
O15	-0.82	-1.03	0.12
O16	-1.65	-1.13	0.09
O21	-1.94	-1.49	0.23
O22	-0.89	-0.73	-0.10
O23	-1.18	-1.78	-0.13
O24	-1.49	-1.94	-0.23
O25	-0.73	-0.89	0.10
O26	-1.78	-1.18	0.13

$\Delta I/I < 0.1\%$. At the same time, some reflections show the relative change of 1.0–2.7%; only very few reflections exhibit the value of $\Delta I/I$ about 5%. It is remarkable that, by the proper choice of wavelength, one can exploit the anomalous dispersion for the enhancement of the sensitivity of the measured reflection to the structural changes induced by an external E -field. As an example, Fig. 3 shows the typical wavelength dependence of the relative intensity variation for reflection 5,3,10 calculated in the wavelength range $\lambda = 0.80\text{--}1.35 \text{ \AA}$.

Thus, only a few reflections in α -GaPO₄ exhibit a high sensitivity to a permanent external E -field, while the majority of reflections does not provide the information concerning E -field-induced effects. Examples of both types of these reflections for α -GaPO₄ are given in Table 3: such information allows us to make a choice of suitable candidates for the

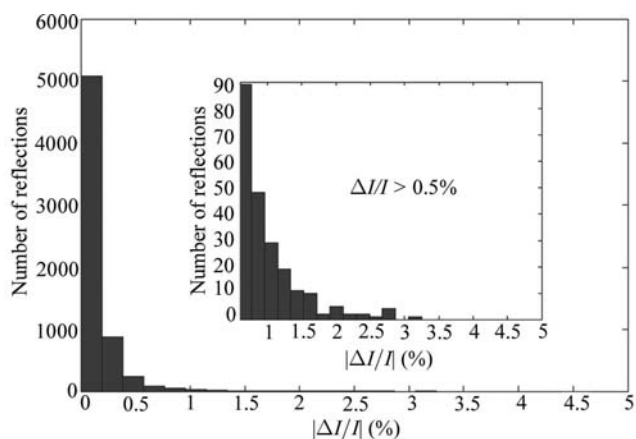


Figure 2
The distribution of the expected relative diffraction intensity variation in α -GaPO₄ over the reciprocal space at the wavelength $\lambda = 0.8 \text{ \AA}$ and electric field $E = 1 \text{ kV mm}^{-1}$

Table 3

A selection of reflections in α -GaPO₄ strongly and weakly affected by an external E -field ($E = 5 \text{ kV mm}^{-1}$) as predicted by a model of independent atomic vibrations.

N	(hkl)	$\Delta I/I (\%)$	$ F ^2$	$\lambda (\text{\AA})$
1	(880)	-5.64	0.0095	0.800
2	(5,3,19)	-3.09	0.0225	0.800
3	(607)	3.44	0.3380	1.210
4	(504)	-5.14	0.1711	1.210
5	(401)	-5.92	0.1304	1.215
6	(369)	2.10	0.1234	1.222
7	(8,0,12)	0.17	6.9077	0.800
8	(7,10,5)	0.10	14.7342	0.800
9	(8,10,5)	-0.06	32.4815	0.800
10	(1,5,17)	0.06	46.7512	0.800
11	(1,0,16)	0.01	835.6093	0.800

precise measurement and further data analysis. Note that a similar conclusion is valid for α -quartz.

As is evident from Table 3, the reflections sensitive to the structural changes, induced by an external E -field, are normally weak. This observation corresponds to the fact that the weak reflections are usually related to the fine features of the crystal structure, such as aspherical electron density and anharmonic atomic vibration. Reflection 880, whose scattering vector is perpendicular to the external E -field direction, can give especially valuable information, related to the pure transverse polarization caused by the anisotropy of the atomic thermal motion. Although the anisotropy of the thermal motion in GaPO₄ is relatively small, the sensitivity of this reflection is high because of its very low intensity.

Thus, proper experimental planning should include the following steps: (a) analysis of the diffraction intensity variation on the basis of the developed model (51); (b) the choice of reflections with a large diffraction intensity variation in the applied external E -field; (c) determination of the parameters of the model (44) using the collected reflections and analyzing the diffraction intensity variation with this model; (d) since the model of independent atomic vibration is an estimate for the atomic displacement and cannot be used as a final result, the new search for additional significant E -field-sensitive reflections and additional data collection might be done on the basis of the refined model parameters. The process can be repeated

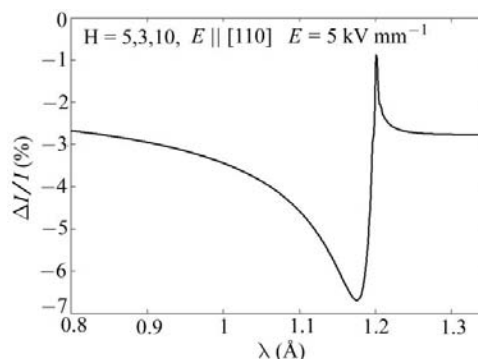


Figure 3
The wavelength dependence of the relative diffraction intensity variation for the 5,3,10 reflection.

iteratively until a reasonable number of reflections are collected.

The experimental study of α -GaPO₄ based on these pre-selected reflections will be described in a forthcoming paper (Gorfman *et al.*, 2005).

8. Conclusions

In the present paper, we present the quantum-mechanical description of the changes in X-ray diffraction intensities induced by a permanent external E -field. It is shown that the major changes are related to the displacement of pseudoatoms from their equilibrium ‘without-the-field’ positions. The pure electron polarization is shown to give approximately two orders lower contribution to the X-ray diffraction intensity and thus can be normally neglected. The structural E -field-induced deformations important for the X-ray data treatment are analyzed in the harmonic approximation and coupled with the properties of phonon spectra. The microscopic representation for the piezoelectric tensor elements is derived. The simplified model based on the supposition of independent atomic vibrations is considered and used for the estimation of pseudoatomic displacements and relative changes in X-ray diffraction intensities. We show that only a small part of the reflections exhibits reasonable sensitivity to the structural changes induced by an external E -field and a strategy for planning an X-ray diffraction experiment in the presence of an external electric field is suggested.

APPENDIX A

Derivation of X-ray scattering amplitude of a crystal in an external electric field

The following matrix elements are to be calculated for addition to the X-ray structure amplitude (12),

$$\langle 0A | \Delta \hat{F}(\mathbf{E}) | 0B \rangle = \left[- \sum_c \frac{\langle 0A | \hat{F} | 0C \rangle \langle 0C | \hat{W}^{(E)} | 0B \rangle}{\hbar \omega_{CB}} + \sum_c \frac{\langle 0A | \hat{W}^{(E)} | 0C \rangle \langle 0C | \hat{F} | 0B \rangle}{\hbar \omega_{AC}} \right]. \quad (55)$$

The matrix elements for the crystal structure amplitude between two nuclear states are given by the expression

$$\langle 0A | \hat{F} | 0B \rangle = \sum_{m\mu} f_\mu(\mathbf{H}) \left[\prod_\alpha \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha \rangle \right] \exp(2\pi i \mathbf{H} \mathbf{R}_{m\mu}^{(0)}) \quad (56)$$

and for the perturbation Hamiltonian

$$\langle 0A | \hat{W}^{(E)} | 0B \rangle = \sum_\alpha \mathbf{E} [\mathbf{G}_\alpha B_\alpha^{1/2} \langle A_\alpha | B_\alpha - 1 \rangle + \mathbf{G}_\alpha^* (B_\alpha + 1)^{1/2} \langle B_\alpha | B_\alpha + 1 \rangle] \prod_{\gamma \neq \alpha} \langle A_\gamma | B_\gamma \rangle. \quad (57)$$

Let us first derive the explicit form for the matrix elements (57) in the harmonic approximation. Substituting (56) and (57) into (55), one gets

$$\begin{aligned} & \sum_c \frac{\langle 0A | \hat{F} | 0C \rangle \langle 0C | \hat{W}^{(E)} | 0B \rangle}{\hbar \omega_{CB}} \\ &= \sum_{m\mu} f_\mu(\mathbf{H}) \exp(2\pi i \mathbf{H} \mathbf{R}_{m\mu}^{(0)}) \\ & \times \sum_\alpha \prod_{\gamma \neq \alpha} \langle A_\gamma | \hat{T}_{\gamma m\mu} | B_\gamma \rangle [-\mathbf{E} \mathbf{G}_\alpha B_\alpha^{1/2} \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha - 1 \rangle \\ & + \mathbf{E} \mathbf{G}_\alpha^* (B_\alpha + 1)^{1/2} \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha + 1 \rangle] (\hbar \omega_\alpha)^{-1} \end{aligned} \quad (58)$$

and

$$\begin{aligned} & \sum_c \frac{\langle 0A | \hat{W}^{(E)} | 0C \rangle \langle 0C | \hat{F} | 0B \rangle}{\hbar \omega_{AC}} \\ &= \sum_{m\mu} f_\mu(\mathbf{H}) \exp(2\pi i \mathbf{H} \mathbf{R}_{m\mu}^{(0)}) \\ & \times \sum_\alpha \prod_{\gamma \neq \alpha} \langle A_\gamma | \hat{T}_{\gamma m\mu} | B_\gamma \rangle [-\mathbf{E} \mathbf{G}_\alpha (A_\alpha + 1)^{1/2} \langle A_\alpha + 1 | \hat{M}_{\alpha m\mu} | B_\alpha \rangle \\ & + \mathbf{E} \mathbf{G}_\alpha^* A_\alpha^{1/2} \langle A_\alpha - 1 | \hat{M}_{\alpha m\mu} | B_\alpha \rangle] (\hbar \omega_\alpha)^{1/2}. \end{aligned} \quad (59)$$

Here we took into account that the energy denominators in (55) can be expressed through the phonon frequencies as $\hbar \omega_{AB} = \sum_\alpha (A_\alpha - B_\alpha) \hbar \omega_\alpha$, where A_α, B_α are the number of phonons in the given state, described by the nuclear harmonic wavefunctions $|A\rangle$ and $|B\rangle$. The expression in the square brackets of (59) can be transformed and merged with (58) by using the explicit form for the matrix elements (Maradudin *et al.*, 1971):

$$\begin{aligned} \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha \rangle &= \frac{\exp(\frac{1}{2} |C_{\alpha m\mu}|^2)}{(A_\alpha! B_\alpha!)^{1/2}} (iC_{\alpha m\mu})^{B_\alpha - A_\alpha} \\ & \times \sum_{k=0}^{\infty} (-1)^k |C_{\alpha m\mu}|^{2k} \frac{(B_\alpha + k)!}{k! (B_\alpha - A_\alpha + k)!} \end{aligned} \quad (60)$$

and the following recurrent relationships that follow from (60):

$$\begin{aligned} (A_\alpha + 1)^{1/2} \langle A_\alpha + 1 | \hat{T}_{\alpha m\mu} | B_\alpha \rangle &= B_\alpha^{1/2} \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha - 1 \rangle \\ & + (iC_{\alpha m\mu}^*) \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha \rangle \\ A_\alpha^{1/2} \langle A_\alpha - 1 | \hat{T}_{\alpha m\mu} | B_\alpha \rangle &= (B_\alpha + 1)^{1/2} \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha + 1 \rangle \\ & + (-iC_{\alpha m\mu}) \langle A_\alpha | \hat{T}_{\alpha m\mu} | B_\alpha \rangle. \end{aligned} \quad (61)$$

Substitution of (61) into (59) and then (59) and (58) into (55) gives

$$\begin{aligned} \langle 0A | \Delta \hat{F}(\mathbf{E}) | 0B \rangle &= \sum_{m\mu} f_\mu(\mathbf{H}) \left[\prod_\alpha \langle A_\alpha | \hat{T}_{\alpha m\mu}(\mathbf{H}) | B_\alpha \rangle \right] \\ & \times \exp(2\pi i \mathbf{H} \mathbf{R}_{m\mu}^{(0)}) D_{m\mu}(\mathbf{E}), \end{aligned} \quad (62)$$

where

$$D_{m\mu}(\mathbf{E}) = \sum_\alpha -i \mathbf{E} \left[\frac{C_{\alpha m\mu}^* \mathbf{G}_\alpha + C_{\alpha m\mu} \mathbf{G}_\alpha^*}{\hbar \omega_\alpha} \right]. \quad (63)$$

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