Tensorial Representation of f' for Nb in Lithium-niobate, $LiNbO_3$

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Using synchrotron radiation, the dependence of resonant phenomena (absorption, fluorescence and Raman scattering) on the angle between the polarisation plane of the incident radiation and the polar c-axis in ferroelectric Lithium-niobate, $LiNbO_3$, was studied in the vicinity of the Nb K-absorption edge. Applying the "optical theorem", the observed dipolar anisotropies can be explained in terms of the projection of the dipole momentum operator on the polarisation vector of the X-ray photons.

Keywords: Synchrotron radiation; X-ray absorption; Anomalous dispersion; Ferroelectricity; $LiNbO_3$.

The availability of polarized and tunable synchrotron radiation has stimulated experimental and theoretical studies on the X-ray absorption and inelastic scattering at core-electron binding energies [1–4]. For single crystals absorption-edge spectra have been found to depend on the orientation of the photon polarisation vector with respect to the crystal lattice. Consequently, the anomalous dispersion corrections f' and f'' for the edge-atom are approximated by general second rank tensors which are related to the local X-ray susceptibility $\varkappa(\boldsymbol{r})$ and must be compatible with the atom's site symmetry. Thus, in the vicinity of K- or L-absorption edges, anomalous dispersion becomes more than an atomic property, i.e. it also reflects the chemical and structural environment of the anomalous scatterer. Consequences and applications of this are reported elsewhere [5, 6].

The scattering of a photon of momentum $\boldsymbol{k}$ and of the polarisation $\boldsymbol{\varepsilon}$ by an atomic system is treated in terms of its absorption and the simultaneous emission of a different photon $(\boldsymbol{k}', \boldsymbol{\varepsilon}')$. The "optical theorem" relates the total scattering cross-section σ_{tot} to the imaginary part of the forward scattering amplitude $f(\boldsymbol{k}, \boldsymbol{k}')$:

$$\sigma_{\text{tot}} = \frac{4\pi}{\boldsymbol{k}} \operatorname{Im}(f(\boldsymbol{k}, \boldsymbol{k})). \tag{1}$$

The resonant part of σ_{tot} is in the dipole approximation proportional to

$$\sum |\boldsymbol{d}_{\text{on}} \cdot \boldsymbol{\varepsilon}|^2 \frac{\Gamma_n}{2} \left[(\omega - \omega_{\text{on}})^2 + \frac{\Gamma_n}{2} \right]^{-1}, \tag{2}$$

where $\boldsymbol{d}_{\text{on}}$ is the matrix element of the momentum operator $\boldsymbol{d} = \sum e\boldsymbol{x}$ corresponding to a transition $E_0 \mapsto E_n$. Γ_n is the level width, $h\omega$ the photon energy ($h\omega_{on} = E_0 - E_n$), and the sum extends over all states of energy E_n. Defining ϱ as the angle between $\boldsymbol{d}_{\text{on}}$ and $\boldsymbol{\varepsilon}$, the angular dependence of the linear absorption coefficient becomes evident by separating μ into two terms:

$$\mu = \mu_0 + \mu_n \cdot \cos^2 \varrho. \tag{3}$$

μ_0 is the isotropic component, while the second term, originating from (2), can be exploited in order to acquire information about the resonant dipole.

In ferroelectric Lithium-niobate, $LiNbO_3$, $\boldsymbol{a} = 5.147$ Å, $\boldsymbol{c} = 13.856$ Å, space group $\boldsymbol{R}3\boldsymbol{c}$ [7], the Nb atom in (0, 0, 0) – point symmetry 3 – has a polar oxygen environment, which results in a considerable dipole moment parallel to $\boldsymbol{c}$. A first investigation of the Nb K-edge anomalous dispersion corrections f', f'' in $LiNbO_3$ was undertaken by Bonse and Henning [8], who performed absorption and interferometric measurements at varying photon energies and $\boldsymbol{\varepsilon}$ parallel and perpendicular to $\boldsymbol{c}$, respectively. The significant polarisation dependence reported by them stimulated our investigation. A modified experiment was designed in order to study $\mu = \mu(\varrho)$ in more detail and under the "optical theorem" conditions $\boldsymbol{k} = \boldsymbol{k}'$, $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}'$.

Lithium-niobate wafers (of about 100 µm-thickness) were cut and polished parallel (type I) and normal (type II) to $\boldsymbol{c}$. Absorption measurements at varying energies were carried out on the Two-Axis-Diffractometer [9] at HASYLAB using a Ge-511 double-crystal monochromator. Crystal plates of both types were mounted perpendicular to and rotated around the X-ray beam in ϱ-steps of 5° or 10°, respec-

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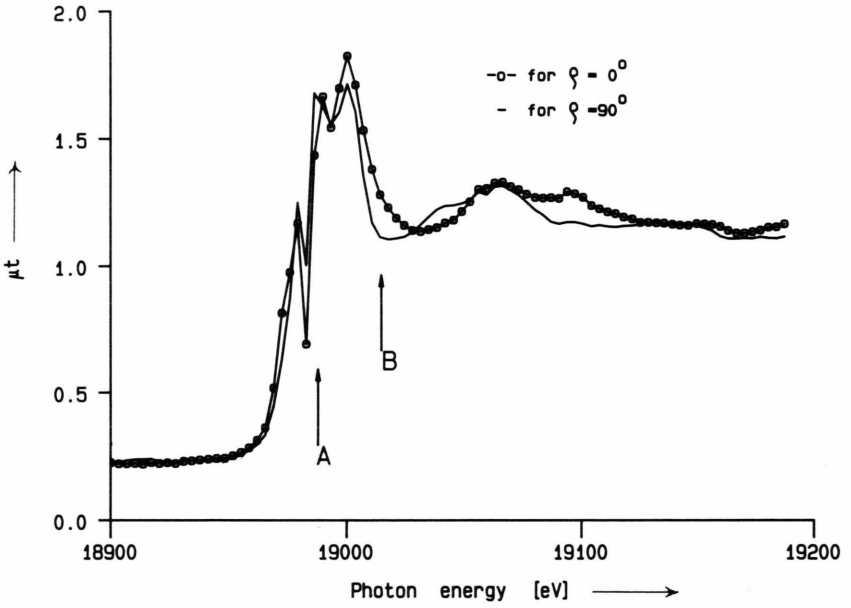

Fig. 1. Nb-K edge absorption spectrum of $LiNbO_3$ (type I sample): —○— c_0 parallel, —— c_0 perpendicular to the photon polarization vector.

ENC = 305311. Iso. u∗t = 1.1080 Dipol. u∗t = 0.1586 Count. SD. = 0.2663%
R2 = 1.3435% D.alpha = − 12.89
ENC = 305470. Iso. u∗t = 0.8261 Dipol. u∗t = 0.3277 Count. SD. = 0.3584%
R2 = 1.4337% D.alpha = 80.09

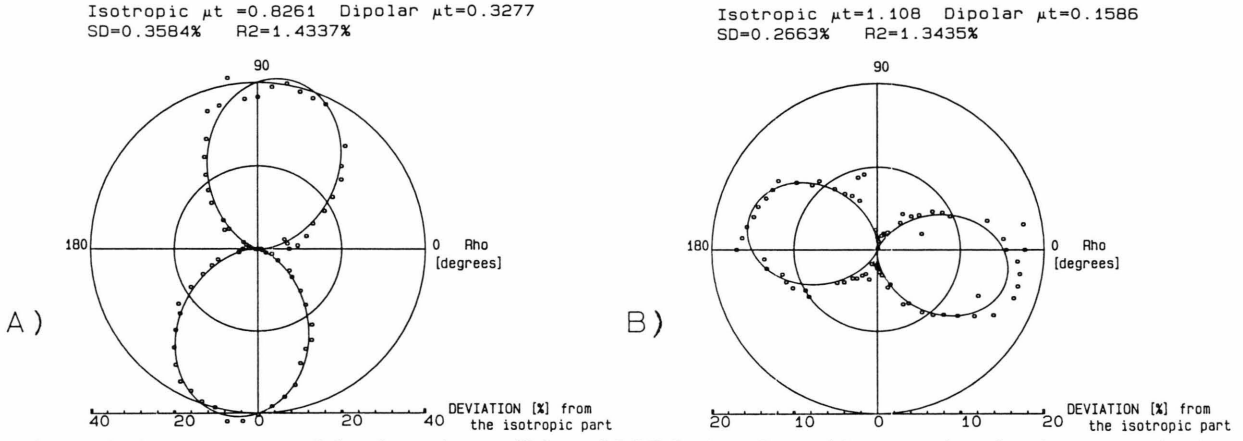

Fig. 2. Dipolar components of the absorption coefficient of $LiNbO_3$ (type I sample) measured at the photon energies A and B of Fig. 1 (SD = relative e.s.d. of the counting statistics, R 2 = agreement index of the fit).

tively. The horizontally polarized components of both the incident and the transmitted radiation were monitored by counting the photons vertically scattered by diamond powder coated Kapton-foils placed in front and behind the rotating sample. In addition, a Ge solid-state-detector in the horizontal plane (at $2\Theta = 140°$) served to record the Nb fluorescent radiation. After completion of a full ϱ-circle we altered the energy of the photons and repeated the procedure. The $\mu(\varrho, E)$-observations of each ϱ-scan were then evaluated in terms of (3) by fitting to the data a dipolar characteristic on top of an isotropic component. With mean statistical errors $\sigma(I)/I \approx 0.4\%$ we obtained agreement indices of at most 1.5%. At energies close to the Nb K-absorption edge (Fig. 1) a considerable dipolar component of the absorption coefficient was

observed for the type I samples. Moreover, several distinct resonances were indicated by the resolution of subsequent 90° rotations of the dipole axis (Figure 2). Simultaneously, for the unresolved K_α-fluorescence and the resonant Raman scattering the Ge-detector registered a complementary effect, which was large in the region of the absorption pre-peak. Since no such dipolar contribution could be detected for the transmission and fluorescence of the type-II samples (with c normal to ε), the necessity of treating f' and f'' as energy dependent and site symmetry compatible tensors is experimentally supported.

The observed anisotropies seem to be a sensitive indicator of the influence of the crystal chemical environment on an anomalously scattering atom. Further evidence is expected from our forthcoming experiments including the study of energy and polarisation dependent Bragg-diffraction.

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