Fluids 19, 1924 (1976).
[9]H. L. Berk, T. D. Rognlien, and J. J. Stewart, Comments Plasma Phys. Controlled Fusion 3, 95 (1977).

[10]L. Chen, Phys. Lett. 47A, 229 (1974).
[11]A. Hasegawa and K. Mima, Phys. Rev. Lett. 39, 205 (1977).

Direct Detection of Electric-Field–Induced Microscopic Structural Changes in LiNbO₃ by Modulation X-Ray Diffraction

Isao Fujimoto

Broadcasting Science Research Laboratories of Nippon Hoso Kyokai, Setagaya-ku, Tokyo 157, Japan
(Received 12 January 1978)

An alternating electric field was applied to the (001) faces of a LiNbO₃ single crytal wafer, and the modulated fractions of the (00h)-diffracted intensities of x rays were measured by the synchronized detection. The displacements of Nb and Li ions relative to the oxygen framework were found to be 4.5×10^{-4} and 9.8×10^{-4} Å for the applied field of 51.5 kV/cm, respectively. The modulated fractions observed for the lower-indexed reflections give direct evidence for the redistribution of valence electrons which causes the electro-optic effect.

Lithium niobate has been known to possess interesting and useful properties such as acoustic, electro-optic, and nonlinear optical properties, and extensive studies on it have been carried out.[1] The electric-field–induced structural changes such as ion displacements and electron redistribution are fundamental and considered to play an important role in those phenomena, and direct detection of such microscopic structural changes by x-ray diffraction study is significant. However there have been no such investigations probably because the change in the diffracted intensities of x rays caused by such structural changes is considered to be too small to detect by the conventional method. In the present study, a modulation method[2] was newly developed for the x-ray diffraction measurement, and detection of the electric-field–induced structural changes was attempted.

When an alternating electric field is applied to the crystal, the diffracted intensities of x rays varies depending on the two alternating states and the small intensity difference between the two states can be obtained by the synchronized detection. The long-term drift of the measurement system such as those of the intensities of the incident x-ray beam and of the electronic instruments can be eliminated so as to allow us to measure the small intensity variation with high accuracy by taking the measurement time sufficiently long. The experimental setup is shown schematically in Fig. 1. Sample crystals used were cut from the single-domain poled boule and

polished to the thickness of 0.2 mm with 10×10 mm² face normal to the c axis. They were examined by x-ray topograph and found to have a sufficiently good quality without grain boundaries or residual strains. Ag $K\alpha_1$ radiation from the high-power x-ray generator (60 kV, 500 mA max) was used and the sample crystal was rotated around the Bragg peak position to obtain the integrated intensities and the modulated fraction was measured. The measurements were repeated many times until a sufficient accuracy was attained; this process, including data processing, was automatically controlled with use of a microcomputer. Aluminum was evaporated as electrodes on the two c faces and the electric field was applied along c axis normal to those faces. Alternating square wave with frequency of 19 Hz was employed to avoid the inhomogeneity of the
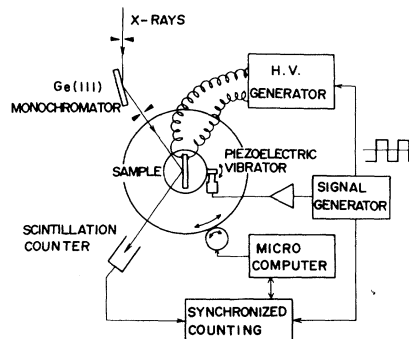

FIG. 1. Schematic view of the experimental setup.

field in the crystal due to the space charge which is often encountered with dc applied field.[3] To verify the homogeneity of the electric field in the crystal, the shift of the Bragg peak position $\Delta\theta_B$ associated with the variation of the lattice constant due to piezoelectricity was measured for $(00h)$ in a reflection geometry and $(h0\bar{h}0)$ in a transmission geometry, and found to satisfy the relation

$$\Delta\theta_B = -(\Delta d/d)\tan\theta_B, \tag{1}$$

which corresponds to the differential of Bragg's law, $2d\sin\theta_B = \lambda$, where d is the spacing of the diffracting planes, θ_B is the Bragg angle, and λ is the wavelength of x rays. From the variation of the lattice constants $\Delta c/c$ and $\Delta a/a$ deduced from the relation (1), the value of the piezoelectric constants d_{33} and d_{31} were obtained to be 8.4 $\times 10^{-12}$ C N^{-1} and -0.77×10^{-12} C N^{-1} respectively. These values are in reasonable agreement with those reported before by the measurement of the resonant and antiresonant frequencies of vibrational modes, i.e., $d_{33} = 6\times10^{-12}$ C N^{-1}, $d_{31} = -1\times10^{-12}$ C N^{-1} by Warner, Onoe, and Coquin[4] and $d_{33} = 16.2\times10^{-12}$ C N^{-1}, $d_{31} = -0.86\times10^{-12}$ C N^{-1} by Yamada, Niizeki, and Toyoda.[5] It should be noted that the values of d_{33} obtained for the two opposite faces agreed within the experimental error. It was concluded from these observations that the electric field in the crystal was practically homogeneous. The shift of the Bragg peak position associated with the variation of the lattice constant resulted in the reduction of accuracy, to some extent, in the measurement of the modulated fraction of the integrated intensities. In order to compensate for this shift, the sample was rotated in the angle $\Delta\theta_B$ given in the Eq. (1) by using piezoelectric apparatus synchronized to the applied field as shown in Fig. 1.

The modulated fractions of the integrated intensities measured for the $(00h)$ reflections are shown in Fig. 2 which are defined as

$$\Delta I/I = 2(I_+ - I_-)/(I_+ + I_-), \tag{2}$$

where I_+ and I_- represent the intensities with the external field parallel and antiparallel to the spontaneous polarization, respectively. As can be seen from Fig. 2, the modulated fractions, though very small, show remarkable variation with reflection indices, which indicates external-field–induced structural changes. In the analysis of the results, the dynamical formula was used for the integrated intensities because the intensities of $(00h)$ reflections measured relatively to
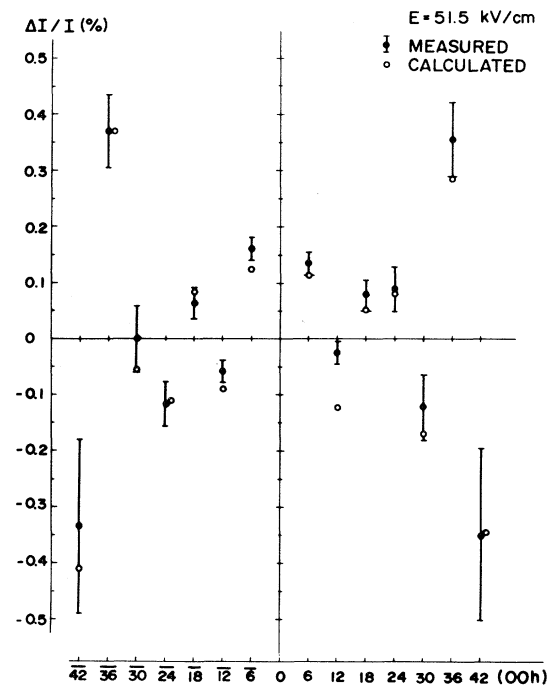

FIG. 2. Modulated fractions of the integrated intensities for $(00h)$ reflections ($h = \pm6$, ±12, $\cdots$, ±42). Positive sign of $\Delta I/I$ corresponds to the increase of the intensities with the direction of the applied field parallel to that of spontaneous polarization.

(333) reflection of a silicon perfect crystal were close to those expected from the dynamical theory.

For the analysis of the structural changes, accurate structure data with no external field are required, and those determined by Abrahams and co-workers[6] by both the x-ray and neutron methods seem to be the most thorough; there the positional coordinates (taking one of the oxygen layer as $z = 0$) and the temperature factor were given as follows:

$$z(\text{Nb}) = 0.1019, \quad z(\text{Li}) = 0.3848, \quad B(\text{Nb}) = 0.50 \text{ Å}^2,$$

$$B(\text{O}) = 0.43 \text{ Å}^2, \quad B(\text{Li}) = 0.94 \text{ Å}^2. \tag{3}$$

However the observed ratios of the integrated intensities of the two opposite faces were found to be significantly different from those calculated from the model of Abrahams and co-workers using the equation[7]

$$I(00h)/I(00\bar{h}) = |F(00h)|^2/|F(00\bar{h})|^2, \tag{4}$$

where $F(00h)$ is the structure factor and the anomalous dispersion correction $\Delta f''(\text{Nb}) = 2.86$ for Ag $K\alpha_1$ was used.[8] For example, the values of

$I(0\,0\,36)/I(0\,0\,\overline{36})$ and $I(0\,0\,42)/I(0\,0\,\overline{42})$ are calculated to be 1.92 and 0.51 respectively, whereas the observed values were 1.40 and 0.67. To fit the observed ratios the model of Abrahams and co-workers together with $\Delta f''(\text{Nb})$ were refined by the least-squares analysis and newly obtained data are

$$z(\text{Nb}) = 0.1035 \pm 0.0003, \quad z(\text{Li}) = 0.3830 \pm 0.0020, \quad B(\text{Nb}) = 0.35 \pm 0.10 \text{ Å}^2,$$

$$B(\text{O}) = 0.57 \pm 0.10 \text{ Å}^2, \quad B(\text{Li}) = 0.70 \pm 0.30 \text{ Å}^2, \quad \Delta f''(\text{Nb}) = 2.87 \pm 0.05. \tag{5}$$

The value of $z(\text{Nb})$ is close to the neutron data and the temperature factor to those obtained with dispersion correction in the work of Abrahams and co-workers. By taking this model as the structure before the external field was applied, the observed variation of the modulated fractions with reflection indices was almost accounted for by assuming the displacement of ions of opposite sign in the opposite direction along the c axis except for lower-indexed reflections. The amount of ionic displacements of Nb and Li ions relative to the oxygen framework were obtained by the least-squares analysis to be

$$u(\text{Nb}) = (4.5 \pm 0.4) \times 10^{-4} \text{ Å},$$

$$u(\text{Li}) = (9.8 \pm 2.0) \times 10^{-4} \text{ Å}, \tag{6}$$

at the applied field of 51.5 kV/cm.

According to the simple dielectric theory the ionic polarization densities P_i is given to be

$$P_i = (6/V)[Q(\text{Nb})u(\text{Nb}) + Q(\text{Li})u(\text{Li})], \tag{7}$$

where $Q(\text{Nb})$ and $Q(\text{Li})$ are the charge, $u(\text{Nb})$ and $u(\text{Li})$ are the ionic displacements for the Nb and Li ions, respectively, and V is the volume of the hexagonal unit cell. On the other hand, the difference $\Delta\kappa$ between the static and optical dielectric constants which may be ascribed to the ionic polarizabilities is 25.3 in LiNbO_3,[9] from which the ionic polarization densities of 1.1×10^{-3} C m^{-2} was obtained at 51.5 kV/cm. From (6) and (7) and the value of polarization densities obtained above, $Q(\text{Nb})$ was calculated to be 6.0, where $Q(\text{Li})$ was assumed to be 1.0 because the Li-O bond can be considered to be almost purely ionic. Kahn and Leyendecker[10] showed in the electronic-energy-band calculation of SrTiO_3 which has a typical structure composed of a network of oxygen octahedra homologous to LiNbO_3, that substantial covalency between O anions and Ti cations was to be expected. Peterson $et\ al.$[11] obtained the net charge of Nb to 1.6 by the study of the ^7Li nuclear magnetic resonance in LiNbO_3 and concluded the Nb ion was predominantly covalently bonded. The difference between the charge of Nb determined by Peterson, Bridenbaugh, and

Green[11] and $Q(\text{Nb})$ obtained above could be reduced if we take into account in the evaluation of the polarization densities the contribution of the deformation of valence electrons associated with ionic displacements. Many authors[1,12,13] have tried to explain the origin of the electro-optic and nonlinear optical effects by considering the change in electronic band structure associated with the deformation of valence electrons brought about by the ionic displacements. A direct evidence of such deformation of valence electrons is given in Fig. 2: There can be seen the remarkable difference between the measured values of $\Delta I/I$ and the calculated values taking only the ionic displacements into account for lower-indexed reflections especially for $(0\,0\,12)$ reflection. This difference could be attributed to the deformation of valence electrons because the lower-indexed reflections are more sensitive to the valence-electron distribution that the higher-indexed reflections which arises predominantly from the inner, more tightly bound electrons. The redistribution of valence electrons counteract the effect of ionic displacements on the modulated fraction of the intensities for $(0\,0\,12)$ reflections, but the detailed analysis including the deformation of overlap of $\text{O}(2p)\text{-Nb}(4d)$ orbitals remains to be studied and the extended work will be reported elsewhere.

The newly developed x-ray diffraction method with modulation technique was proved to be useful for the study of dynamical behavior of crystals, and the present observation may provide a substantial contribution to the microscopic understanding of the properties of dielectric substances such as the electro-optic effect.

[1] I. P. Kaminow and W. D. Johnston, Jr., Phys. Rev. 160, 519 (1967); M. DiDomenico, Jr., and S. H. Wemple, J. Appl. Phys. 40, 720 (1969); J. Jerphagnon, Phys. Rev. B 2, 1091 (1970); B. F. Levine, Phys. Rev. B 7, 2600 (1973).

[2]M. Cardona, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Suppl. 11.

[3]H. Motegi, J. Phys. Soc. Jpn. 32, 202 (1972).

[4]A. W. Warner, M. Onoe, and G. A. Coquin, J. Acoust. Soc. Am. 42, 1223 (1967).

[5]T. Yamada, N. Niizeki, and H. Toyoda, Jpn. J. Appl. Phys. 6, 151 (1967).

[6]S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, J. Phys. Chem. Solids 27, 997 (1966); S. C. Abrahams, W. C. Hamilton, and J. M. Reddy, J. Phys. Chem. Solids 27, 1013 (1966).

[7]H. Cole and N. R. Stemple, J. Appl. Phys. 33, 2227 (1962).

[8]*International Tables for X-ray Crystallography*, edited by J. A. Ibers and W. C. Hamilton (Kynoch, Birmingham, 1974), Vol. IV, p. 149.

[9]*Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and A. H. Hellwege (Springer, Heidelberg, 1969), Group III, Vol. 3, p. 89.

[10]A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).

[11]G. E. Peterson, P. M. Bridenbaugh, and P. Green, J. Chem. Phys. 46, 4009 (1967).

[12]J. R. Brews, Phys. Rev. Lett. 18, 662 (1967).

[13]J. David Zook and T. N. Casselman, Phys. Rev. Lett. 17, 960 (1967), and Surf. Sci. 37, 244 (1973).

Coupling between Orientational and Translational Order in a Liquid Crystal

Khoon-Cheng Lim and John T. Ho
Department of Physics and Astronomy, State University of New York at Buffalo, Amherst, New York 14260
(Received 23 December 1977)

A high-resolution measurement of the optical birefringence has been made in 4-cyano-4'-octyloxybiphenyl to study in detail the orientational order parameter near the nematic–smectic-A transition. There is no measureable discontinuity in the birefringence, but there is an abrupt change in its temperature coefficient at the transition. Contrary to the general impression obtained from published results, the behavior of the orientational order parameter does not follow the predictions of mean-field molecular and phenomenological theories, with or without fluctuations.

The current controversy over the nature of the nematic–smectic-A (NA) transition in liquid crystals calls for additional reliable data on relevant physical properties. One phenomenon that has received relatively little attention is the behavior of the orientational order parameter S near the NA transition. Both mean-field molecular[1,2] and phenomenological[3] theories predict a strong coupling between the orientational and the translational order. Specifically, the theories predict S to vary with temperature as represented in Fig. 1. If the NA transition is first order, S undergoes a step discontinuity at the transition temperature T_{NA}. If the transition is second order, S is continuous but its temperature coefficient decreases abruptly on heating at T_{NA}. The effect of fluctuations, however, has been neglected in these predictions. It is therefore somewhat surprising that, on the basis of existing data on S, real systems do appear to behave as depicted in Fig. 1(a) or Fig. 1(b).[4-7] This apparent agreement is disturbing because other experiments near the NA transition have clearly demonstrated the importance of critical fluctuations. In order to lead to a conclusive comparision with theory, an ex-

periment has to have sufficient resolution in both S and the temperature, and should include an independent determination of T_{NA}. Such an experiment may also help resolve the question of whether a second-order NA transition can exist in a
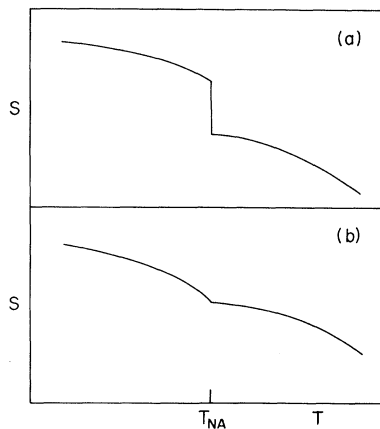

FIG. 1. Temperature dependence of orientational order parameter S near (a) a first-order and (b) a second-order NA transition as predicted by mean-field theories.