

ACOUSTIC ANOMALIES IN DIGLYCINE-NITRATE

S. V. RODIN,† M. ZGONIK and M. COPIC,

*J. Stefan Institute and Department of Physics, University E. Kardelj, Ljubljana,
Yugoslavia*

and

N. I. KHASINEVICH

Radioengineering Institute, Minsk, USSR

(Received 28 April 1987, in final form 4 November 1987)

The behaviour of some elastic constants of diglycine nitrate across the ferroelectric phase transition were measured with Brillouin scattering. The results were compared with low frequency behaviour of one elastic constant. Results were analysed in the framework of Landau free energy expansion. Discrepancy was found between the relaxation time for the spontaneous polarization from dielectric measurements and our results.

1. INTRODUCTION

Diglycine nitrate, $(\text{NH}_2\text{CH}_2\text{COOH})_2\text{HNO}_3$, abbreviated DGN, undergoes a ferroelectric phase transition from monoclinic space group $\text{P2}_1/\text{a}$ to polar monoclinic group Pa at 206 K.^{1,2} The transition appears to be of second order and is of the order-disorder type. Ferroelectricity in DGN has been known for a long time and several physical properties of the crystal in the vicinity of the transition have been studied, including dielectric properties,^{3,4,5} pyroelectricity,⁴ electrostriction⁶ and piezooptic properties.⁷ In particular, studies of dielectric relaxation⁸ show a single relaxation time with critical slowing down around the transition. The relaxation time is of the order of 1 to 6×10^{-10} s.

The behaviour of elastic constants of DGN across the transition has been investigated by the electromechanical resonance method.^{3,9} In the present work we have studied the high frequency elastic properties by means of Brillouin scattering and compared the results with measurements of electrostriction and low frequency behaviour of elastic constants as determined by the electromechanical resonance method. We have also measured thermal expansion along the three crystallographic axes.

2. EXPERIMENT

The samples were grown from aqueous solution³ and were of good optical quality. For Brillouin scattering, samples were cut with a diamond saw and polished with alcohol. Two samples were used for measurements, one cut in the

† Permanent address: Radioengineering Institute, Minsk, USSR.

directions (1, 0, 1), (1, 0, $\bar{1}$) and (0, 1, 0) and the other in the directions (1, 0, 0), (0, 1, 1) and (0, 1, $\bar{1}$), where the z axis is in the direction of spontaneous polarization P_s and the y axis is perpendicular to the mirror plane. The z direction makes an angle of 33° with the crystallographic c direction.

The sample was placed in a cryostat with temperature stability of about 0.2 K. Brillouin spectra were excited with an Ar⁺ ion laser operating at 514.5 nm and about 100 mW single mode power. The scattering angle was 90° . For spectral analysis, a triple-pass piezoelectrically scanned Fabry–Perot interferometer was used. The data were collected with a photon-counting photomultiplier and fed to a microcomputer, which was used both for data averaging and for analysis.

For the analysis of Brillouin shifts, the indices of refraction are also necessary. As only the data on birefringence⁷ are available from the literature, we have also measured the refractive indices by a combination of immersion and wedge methods, described previously.¹⁰ The measured values at room temperature are:

$$n_x = 1.586, n_y = 1.520 \quad \text{and} \quad n_z = 1.455.$$

The geometry of samples allowed us to measure the hypersound velocities in three directions with higher symmetry: one perpendicular to the crystal mirror plane (y), the other two lying in the mirror plane with one parallel to $P_s(z)$, and the other perpendicular to $P_s(x)$. Along the y direction the wave is purely longitudinal, while in the x and z directions the elastic waves are of mixed polarizations. (The two directions in the x – z plane with pure polarizations are arbitrarily oriented with respect to the crystallographic axes.) We measured the velocities of quasilongitudinal waves. From the measured velocities the following elastic constants can be calculated:

$$\rho v_x^2 = \frac{1}{2} [C_{11} + C_{55} + \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2}] = C_{11}^*, \quad (1)$$

$$\rho v_y^2 = C_{22} \quad (2)$$

and

$$\rho v_z^2 = \frac{1}{2} [C_{33} + C_{55} + \sqrt{(C_{33} - C_{55})^2 + 4C_{35}^2}] = C_{33}^*, \quad (3)$$

where C_{11}^* and C_{33}^* are effective quasilongitudinal elastic constants.

For any direction of propagation there also exist two transverse or quasi transverse waves. For example, in the x direction their velocities are given by

$$\rho v_{x(\text{quasitr.})}^2 = \frac{1}{2} [C_{11} + C_{55} - \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2}]$$

and

$$\rho v_{x(\text{tr.})}^2 = C_{66}.$$

These velocities are considerably smaller than those of the quasilongitudinal waves. The coupling of the transverse waves to the refractive index is usually also weaker, so they are considerably more difficult to observe than the longitudinal waves.

3. RESULTS AND DISCUSSION

The temperature dependence of the elastic constants C_{11}^* , C_{22} and C_{33}^* are presented in Figures 1 and 2. In the calculation of the elastic constants, the room

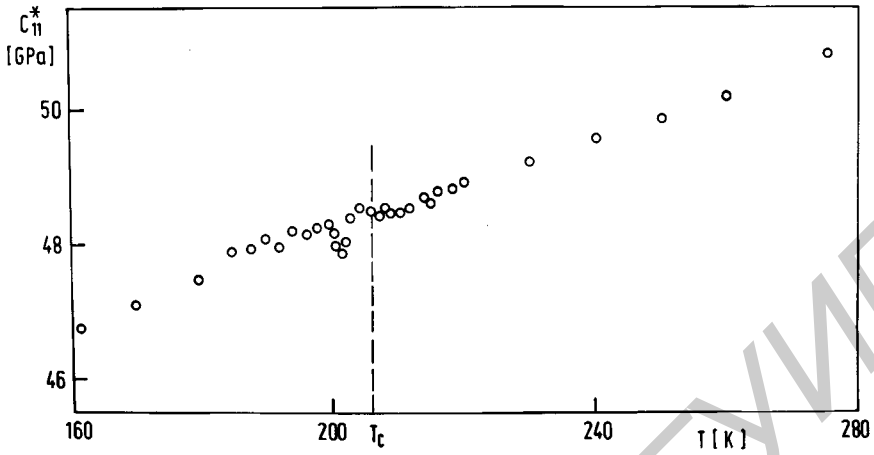


FIGURE 1 Dependence of the quasilongitudinal elastic constant C_{11}^* , defined in Equation (1), on temperature.

temperature values of the refractive indices were used. However, their temperature dependence is too small to significantly affect the evaluation of the elastic constants from the Brillouin shifts. The density of the crystal was calculated using the thermal expansion data⁹ presented in Figure 3. Comparison of Figures 1 and 2 with Figure 3 shows that the general temperature dependence of the elastic constants is in accordance with thermal expansion. The small anomalies just

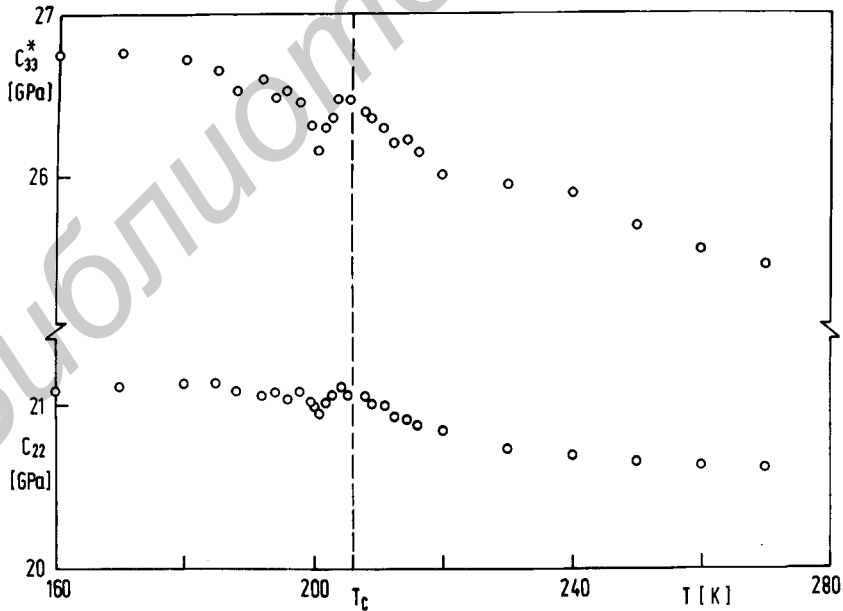


FIGURE 2 Dependence of the quasilongitudinal elastic constant C_{33}^* and longitudinal elastic constant C_{22} on temperature.

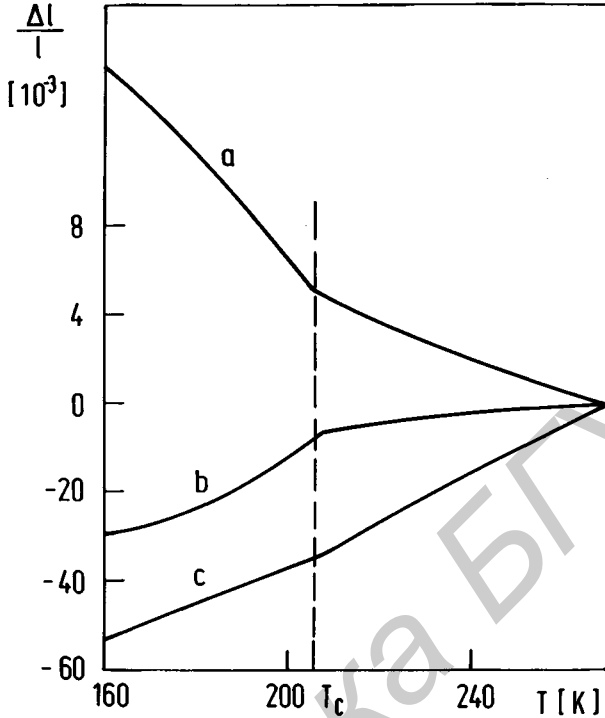


FIGURE 3 Linear thermal expansion in DGN in the direction of the crystallographic axes. Note scale change.

below the transition are the result of the electrostrictive coupling between the spontaneous polarization and the components of the strain tensor.

Elastic anomalies associated with structural phase transitions are best discussed within the framework of the Landau phenomenological theory. This is valid for equilibrium properties, but must be corrected when the characteristic frequency of the order parameter (soft mode frequency) is lower than the frequency of the measured acoustic wave.

The crystal possesses inversion symmetry above the transition and so there can be no bilinear coupling between the components of the strain tensor and polarization. Thus, the free energy can be written in the form (summation over repeated indices is assumed)

$$F = \frac{1}{2} \alpha P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6 + \frac{1}{2} C_{ij}^p X_i X_j + q_i P^2 X_i + r_{ij} P^2 X_i X_j + t_i P^4 X_i + c_{ijk} X_i X_j X_k \quad (4)$$

where the first three terms give the ferroelectric transition, the next one is the elastic contribution to the free energy, the fifth term describes electrostriction, the sixth and the seventh are the next order coupling between P and X , and the last term represents nonlinear elasticity. The last three terms are all of third order in P^2 . Strictly, one should include two components of polarization in the free

energy because it can point in any direction in the mirror plane; the final result for the changes in the elastic constants, however, is not essentially affected by using only the magnitude of the polarization P .

The constants C_{ij}^P describe the elastic response at constant polarization. One can use standard thermodynamic procedures to obtain the elastic constants at constant electric field, which one usually measures.¹⁰ At the ferroelectric transition the electrostrictive coupling gives rise to a step decrease in the elastic constants at zero electric field:

$$\Delta C_{ij} = -\frac{2q_i q_j}{\beta} \neq 0 \quad \text{for } i, j = 1, 2, 3, 5. \quad (5)$$

Monoclinic symmetry requires that q_4 and $q_6 = 0$

The sixth order terms give to the elastic constants an additional contribution so that the elastic constants at zero electric field are given by

$$C_{ij}^E = C_{ij}^P + \Delta C_{ij} + \frac{1}{3} c_{ijk} X_k^s + D_{ij} P_s^2 \quad (6)$$

where X_k^s and P^s denote the spontaneous values of strains and polarization, and D_{ij} is the symmetric part of the lengthy expression

$$2 \frac{q_i}{\beta} (r_{ij} S_{kl} q_l - t_j) + 2 \frac{q_i q_j}{\beta^2} (\gamma - t_k S_{kl} q_l) \quad (7)$$

in which S_{ij} is the inverse of C_{ij} . As the the spontaneous strains X_k^s are proportional to P_s^2 , Equations (6) and (7) show that all the sixth order terms in Equation (4)—via electrostriction—give a contribution to the elastic constants, which is proportional to P_s^2 . Experimentally it is quite difficult, if not impossible, to separate the different terms contributing to D_{ij} . Therefore it really does not matter which of the sixth order terms one keeps in the free energy. The nonlinear elastic contribution can be estimated to some extent by comparing the thermal expansion data and the temperature dependence of the elastic constants above the transition. The total effect of the ferroelectric transition on the static elastic constants is thus a step decrease at the transition, followed by a gradual increase due to the sixth order terms in free energy.

Brillouin scattering probes elastic properties in the frequency region of 10^{10} Hz. At such high frequencies, relaxation of the spontaneous polarization has to be taken into account. This modifies the step discontinuity, described by Equation (5):¹¹

$$\Delta C_{ij}(\omega) = \Delta C_{ij} \frac{1}{1 + i\omega\tau(T)} \quad (8)$$

where $\tau(T)$ in the vicinity of the transition depends critically on temperature: $\tau = c/(T - T_c)$. Dielectric relaxation measurements in DGN give for the constant c a value of approximately 2.5×10^{-10} sK.

At high frequencies, probed by Brillouin scattering, the expected elastic anomaly of the transition, described by Equations (5), (6), and (7), is thus a dip at a temperature slightly below the transition. The temperature shift of the dip depends on the constant c . The depth of the dip is smaller than the low frequency step in the elastic constant.

Previous measurements of low frequency (100 kHz) elastic constants by the electromechanical resonance method show step discontinuities. The step in C_{22} is close to ten times larger than the C_{22} anomaly in Figure 2. By comparing the low and high frequency anomalies it is possible to estimate the product $c\omega$. This product is roughly equal to the temperature shift of the minimum of the elastic constant from the transition temperature, that is, around (5 ± 1) K. In Brillouin scattering, C_{22} is measured at $\omega = 8 \times 10^{10} \text{ s}^{-1}$, so we get $c = (0.6 \pm 0.2) \times 10^{-10} \text{ sK}$. This value is significantly smaller than that obtained from dielectric measurements. At present, we can offer no explanation for this discrepancy, but further ultrasonic measurements are under way to obtain more information on this phase transition.

4. ACKNOWLEDGEMENT

One of the authors (S. Rodin) wishes to thank professor R. Blinc and other members of the Solid State Physics Department, J. Stefan Institute, for the opportunity to perform this work and for their kind hospitality during his stay there.

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