Ultrasonic Studies of Ferroelectric Phase Transition in Gly-H_3PO_3 Crystals

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Z. Naturforsch. **52a**, 778–782 (1997); received October 4, 1997

The temperature behaviour of the longitudinal and transverse ultrasound wave velocities and attenuation in the region of the ferroelectric phase transition ($T_C = 225$ K) of the glycine phosphite (Gly-H_3PO_3) crystals is studied. The obtained results are considered within the framework of phenomenological theory.

Key words: Ferroelectricity, Phase Transition, Ultrasonic Velocity, Attenuation.

Introduction

Crystals of glycine phosphite Gly-H_3PO_3 (abbreviated as GPI) belong to the low-symmetry representatives of hydrogen-bonded crystals. At room temperature the unit cell of this compound is monoclinic (space group $P2_1/a$) and contains four formula units [1]. The crystal structure is characterised by the presence of infinite chains of hydrogen-bonded phosphite anions that are directed along the crystallographic c-axis. Two kinds of symmetrical hydrogen bonds with a double potential well for protons exist in this crystal, and ordering of protons could be expected below room temperature. DSC and dielectric measurements [2] have revealed a ferroelectric phase transition at $T_C = 225$ K. Although the proton ordering is expected along the c-axis, the dielectric investigations showed the appearance of spontaneous polarization below T_C along the b-axis with the Curie-Weiss type anomaly of the corresponding dielectric permittivity in the vicinity of this phase transition. In this sense, GPI differs from betaine phosphite (BPI) in which the ferroelectricity is connected with ordering of protons along ferroelectric axis [3]. Thus, the mechanism of the ferroelectric phase transition in GPI crystals is not yet completely clear. In the present paper we report the results of ultrasonic studies of the paraferroelectric phase transition in GPI crystals.

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Experimental and Results

The high quality crystals of GPI were grown from saturated water solution of stoichiometric quantities of glycine and phosphorous acid by the slow evaporation method at 301 K. We use the following crystallographic orientation in the paraphase: $a > b > c^*$. The specimens with typical dimensions of about $5 \times 5 \times 5$ mm^3 were prepared for studying ultrasonic waves (USW) propagating along the X, Y, and Z axis, where $X \parallel a$, $Y \parallel b$ and $Z \perp b\,a$.

The acoustic waves were excited by a $LiNbO_3$ transducer with resonance frequency $f = 10$ MHz and bandwidth $\Delta f = 0.1$ MHz. The velocities changes of the transverse and longitudinal USW were measured by the continuous wave-echo overlap method [4] with an accuracy of the order of 10^{-4}–10^{-5}. The accuracy of the absolute velocity determination was about 1%. Ultrasonic attenuation was determined from the decay rate of echo pulses with an accuracy of about 10%. The rate of temperature changes was about 0.1 K/min.

Figure 1 shows the temperature dependence of the velocities of the pure longitudinal $V_2(\boldsymbol{q} \parallel Y, \boldsymbol{e} \parallel Y)$ and quasilongitudinal $V_1(\boldsymbol{q} \parallel X, \boldsymbol{e} \parallel X)$ and $V_3(\boldsymbol{q} \parallel Z, \boldsymbol{e} \parallel Z)$ USW in GPI crystals (here $\boldsymbol{q}$ is the USW vector, $\boldsymbol{e}$ is its polarization). The three curves exhibit a similar evolution consisting of a practically jump-like decreasing of the USW velocities in the vicinity of the phase transition from the paraelectric to the ferroelectric phase. The relative changes of the USW velocities $\Delta V_i/V_i$ here amount to 1.13, 1.62 and 1.89% for the X-, Y-, and Z-direction, respectively. A small jump at $T = T_C$ is observed also for the quasitransverse USW

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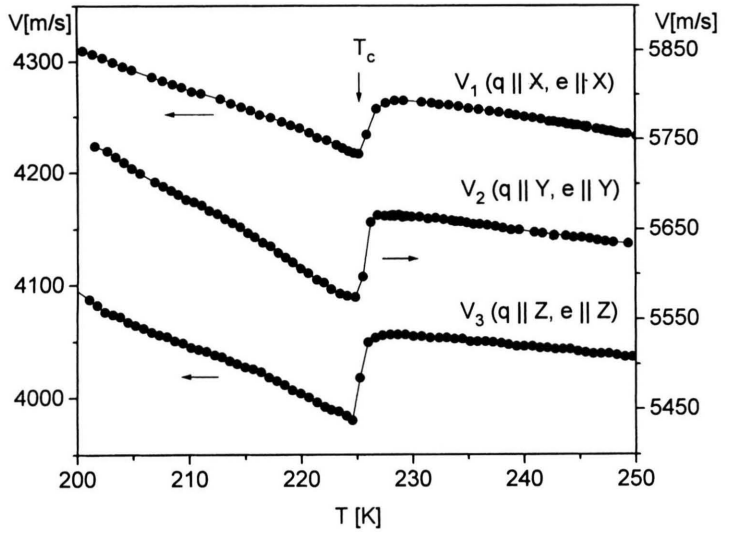

Fig. 1. The temperature dependence of the pure longitudinal V_2 and quasi-longitudinal V_1 and V_3 USW velocities of GPI crystals.

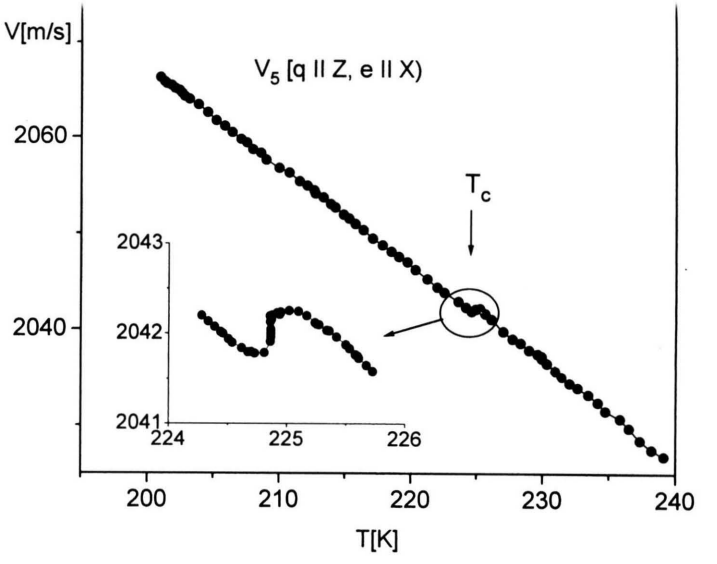

Fig. 2. The temperature dependence of the quasitransverse V_5 USW velocity of GPI crystals.

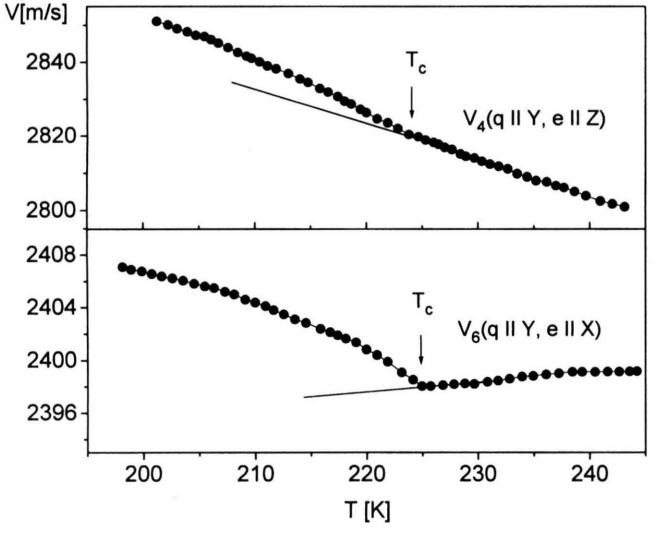

Fig. 3. The temperature dependence of the pure transverse V_4 and V_6 USW velocities of GPI crystals.

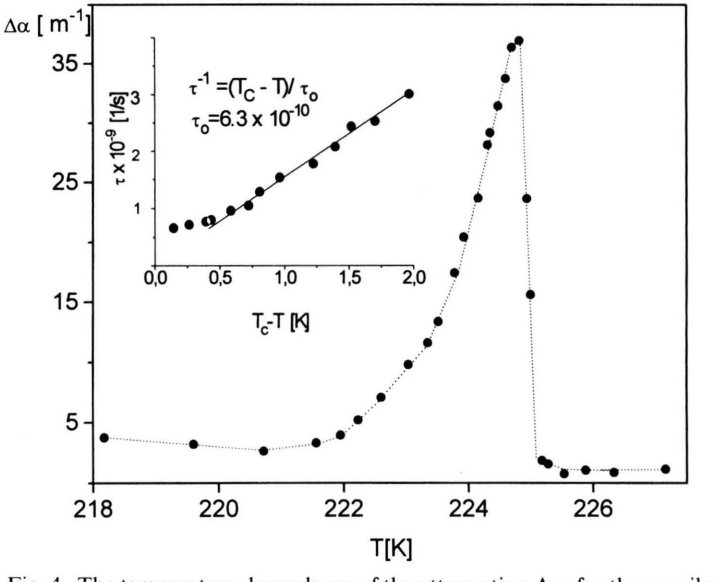

Fig. 4. The temperature dependence of the attenuation $\Delta\alpha_3$ for the quasilongitudinal USW V_3. The insert shows the temperature dependence of the inverse relaxation time τ^{-1}.

$V_5(\boldsymbol{q} \parallel Z, \boldsymbol{e} \parallel X)$ $(\Delta V_5/V_5 = 0.03\%)$ (Fig. 2), while for the pure transverse USW velocities $V_4(\boldsymbol{q} \parallel Y, \boldsymbol{e} \parallel Z)$ and $V_6(\boldsymbol{q} \parallel Y, \boldsymbol{e} \parallel X)$ only the visible kinks on their temperature dependences are seen (Figure 3). The decrease of the velocities of the longitudinal and quasilongitudinal USW at T_C is accompanied by a clear increase of the corresponding attenuation coefficients. The temperature dependence of the attenuation changes $\Delta\alpha_3$ for the quasilongitudinal USW V_3 is reported in the Figure 4. In the region of the phase transition from para- to ferroelectric $\Delta\alpha$ shows an anomalous asymmetric peak, i.e. the attenuation increases in a jump-like way at $T = T_C$ and then gradually decreases.

Discussion

Although there are no data about the crystal symmetry below T_C, the dielectric studies of the phase transition in GPI crystals [2] clearly shows that the low-temperature phase is ferroelectric with a spontaneous polarization along the two-fold axis. This means that the phase transition at T_C is associated with the polar soft mode condensed in the centre of the Brillouin zone. A simple group-theory consideration shows that the space group of the ferroelectric phase is $P2_1$ and the soft mode transforms according to the irreducible representation A_u of the $P2_1/a$ space group (see Table 1). The component of spontaneous polarization P_Y has the same transformation properties, so it can be used as the order parameter of the Landau theory. Using Cristofel's equation we have obtained the following relations between USW velocities and elastic constants C_{ij}:

$$2\varrho V_1^2 = C_{11} + C_{55} + [(C_{11} - C_{55})^2 + 4C_{15}^2]^{1/2}, \quad (1a)$$

$$\varrho V_2^2 = C_{22}, \quad (1b)$$

$$2\varrho V_3^2 = C_{33} + C_{55} + [(C_{33} - C_{55})^2 + 4C_{35}^2]^{1/2}, \quad (1c)$$

$$2\varrho V_4^2 = C_{44} + C_{66} - [(C_{44} - C_{66})^2 + 4C_{46}^2]^{1/2}, \quad (1d)$$

$$2\varrho V_5^2 = C_{11} + C_{55} - [(C_{11} - C_{55})^2 + 4C_{15}^2]^{1/2}, \quad (1e)$$

$$2\varrho V_6^2 = C_{44} + C_{66} + [(C_{44} - C_{66})^2 + 4C_{46}^2]^{1/2}, \quad (1f)$$

Table 1. The irreducible representation of the $P2_1/a$ space group in the centre of the Brillouin zone.

	$\{E\|000\}$	$\{C_{2Y}\|0\,\frac{1}{2}\,0\}$	$\{\sigma_Y\|00\,\frac{1}{2}\}$	$\{I\|0\,\frac{1}{2}\,\frac{1}{2}\}$	Base
A_g	1	1	1	1	XX, YY, ZZ, XZ
B_g	1	−1	−1	1	XY, YZ
A_u	1	1	−1	−1	Y
B_u	1	−1	1	1	X, Z

where ϱ is the crystal density. The contributions to the elastic constants, caused by the phase transition, may easily be obtained from the free energy expansion with coupling terms which correspond to anharmonic interaction between the strains $U_1 - U_6$ and the order parameter $P \equiv P_Y$. The free energy can be written as

$$\begin{aligned} F_{P,U} = {} & \frac{1}{2}\omega_P^2 P^2 + \frac{1}{4} B P^4 + \sum_{i=1}^{3} a_i P^2 U_i \\ & + a_5 P^2 U_5 + \frac{1}{2}\sum_{i,j=1}^{3} b_{ij} P^2 U_i U_j \\ & + \frac{1}{2}\sum_{j=4}^{6} b_{ij} P^2 U_j^2 + \sum_{i=1}^{3} b_{i5} P^2 U_i U_5 \\ & + b_{46} P^2 U_4 U_6, \end{aligned} \quad (2)$$

where $\omega_P^2 = A(T - T_C)$ is the soft mode frequency. The changes of the complex elastic constants in the region of phase transition can be determined using the relation [5]

$$\Delta C_{ij}^* = \frac{\partial^2 F}{\partial U_i \partial U_j} - \frac{1}{1 + i\Omega\tau} \frac{\partial^2 F}{\partial P \partial U_i} \left(\frac{\partial^2 F}{\partial P^2}\right)^{-1} \frac{\partial^2 F}{\partial P \partial U_j}, \quad (3)$$

where $\Omega = 2\pi f$ is the USW frequency and τ the soft-mode relaxation time. The first term of (3) corresponds to the contribution to the real part only, while the second one reveals the relaxation mechanism of the Landau-Khalatnikov type. Using (2) and (3) we obtain

$$\Delta C_{ij}^* = b_{ij} P_O^2 - 4 a_i a_j P_O^2 / [\omega_P^2 (1 + i\Omega\tau)], \quad i, j = 1, 2, 3, 5, \quad (4a)$$

$$\Delta C_{44}^* = b_{44} P_O^2, \quad \Delta C_{66}^* = b_{66} P_O^2,$$

$$\Delta C_{46}^* = b_{46} P_O^2, \quad (4b)$$

where $P_O^2 = A(T_C - T)/B$ is the equilibrium value of the spontaneous polarization. Comparing the experimental results presented in Figs. 1–4 with (1a–1f) and (4a–4b), and assuming that $\Omega\tau \ll 1$, one can see a good qualitative agreement of the experiment with the phenomenonological theory. Particularly, as it follows from (1a–1c), (1e) and (4a), the USW velocities V_1, V_2, V_3 and V_5 should exhibit a sudden decrease at T_C since they contain the contributions of the real part of the elastic constants which undergo the negative jumps ($\Delta C_{ij} = -2a_i a_j/B$, where $i, j = 1, 2, 3, 5$) at the phase transition from the para- to ferroelectric phase. The changes in those USW velocities below T_C are caused by the contribution of the first term of (4a), which appears as a result of the fourth-order anharmonic interaction between the order parameter and the

deformation (P^2U^2-type coupling). This type of anharmonicity gives a contribution to the real part only, leading to quadratic dependences of V_i on the equilibrium value of spontaneous polarization at $T > T_C$. At the same time the third-order anharmonic interaction between strain and soft mode (P^2U-type coupling) produces also a contribution to the imaginary part of the elastic constant ($\mathrm{Im}\,\Delta C_{ij} = 2 a_i a_j \Omega \tau / B$), which leads to the anomaly of the attenuation. Taking into account the relation [6]

$$\Delta\alpha_3 = (\Delta V_3 / V_3^2)\,\Omega^2 \tau\,, \tag{5}$$

and using the experimental values of the negative velocity jump ΔV_3 (Fig. 1) and attenuation $\Delta\alpha_3$ (Fig. 3), we have determined the soft mode relaxation time τ. The temperature dependence of the inverse relaxation time τ^{-1} in the ferroelectic phase is presented in the insert of Figure 3. In the temperature region T_C-2 ÷ T_C-0.3 K it can be linearly fitted as $\tau^{-1} = (T_C - T)/\tau_0$, where $\tau_0 = (6.3 \pm 0.5) \times 10^{-10}$ K s. The obtained value of τ_0 is close to the one determined from the dielectric measurements ($\tau_0 = (4.2 \pm 0.5) \times 10^{-10}$ K s [7]). Thus, we see that the condition $\Omega \tau \ll 1$ mentioned above is valid.

The anomalous temperature changes in the pure transverse USW V_4 and V_6 below T_C are caused by the fourth-order anharmonicity only. The changes of the relevant elastic constants ΔC_{44}, ΔC_{66} and ΔC_{46} are proportional to P_0^2, see (4b), which gives only the kinks on the $V_4(T)$ and $V_6(T)$ temperature dependences at $T = T_C$ (Fig. 3), while the anomalous attenuation is absent here.

Although the elastic anomalies in GPI crystals are generally in a good agreement with the phenomenological theory there is one mechanism which should suppress the Landau-Khalatnikov contribution for longitudinal USW which propagate along the ferroelectric axis. According to [8, 9], since the USW changes in this case the spontaneous polarization and consequently changes the macroscopic electric field due to the long-range dipole-dipole interactions, the polarization susceptibility lose the critical increase near T_C. Thus, the anomalies of the longitudinal USW velocity V_2 should be suppressed. On the other hand, it is known that the acoustic anomalies can be preserved in the polydomain specimen of the proper ferroelectric crystal if the USW length $\lambda \gg d$, where d is the domain size along the polar axis. Particularly, a similar situation took place in CDP [10] and DCDP [11] crystals, for which the acoustic softening near T_C was observed only for polydomain specimens, while the acoustic anomalies clearly disappeared after their monodomenization. For this aim we performed ultrasonic measurements on single domain specimens of GPI crystal, applying an external monodomenization electric field along ferroelectric axis. However, the monodomenization procedure practically does not change the character of the anomaly in the $V_2(T)$ dependence near T_C. Such an extraordinary behaviour of the elastic properties in GPI crystals can be explained if assuming a pseudoproper character of the ferroelectric phase transition. In this case we have to take into account the existence of another soft mode (associated with the primary order parameter η) of the same symmetry as P_Y but with different microscopic origin. An indirect confirmation of the pseudoproper ferroelectricity is the relatively small value of the spontaneous polarization in GPI crystals (0.5 μC) with respect to other classical ferroelectrics. It can occur that the contribution of this soft mode to the total polarization is small, while it is significant for the elastic properties. In this case the long-range dipol-dipol interactions will suppress only the polarization contribution the elastic properties which, as we assumed above, can be much smaller than the contribution of the primary order parameter. Since the transformation properties of the order parameter η and polarization P_Y are the same, the phenomenological description of the elastic anomalies in the framework of the pseudoproper ferroelectric model is identical to the one presented above. Both cases are different only in the microscopic origin of the primary order parameters. It should be noted that the proton ordering along the c-direction can not be used as the primary order parameter for the pseudoproper ferroelectric model in GPI crystals because it provides a symmetry change which differs from the one observed experimentally.

Conclusion

We have investigated the temperature dependences of the longitudinal and transverse USW velocities of GPI crystals in the region of the phase transition from the para- to the ferroelectric phase. The pure longitudinal V_2, quasilongitudinal V_1 and V_3 and quasitransverse V_5 USW exhibit a similar temperature behaviour consisting of a practically jump-like decreasing of the velocities in the vicinity of T_C, while for the pure transverse USW velocities V_4 and V_6 only kinks of their

temperature dependences are observed. The phase transition from the para- to the ferroelectric phase is accompanied also by an anomaly of the ultrasound attenuation for longitudinal and quasilongitudinal USWs. Generally, the obtained results are in good qualitative agreement with the phenomenological theory. However, the experimental investigations on the single domain specimens have not revealed the suppress of the Landau-Khalatnikov contribution the velocity of the longitudinal USW V_2 which propagates along the ferroelectric axis. We assume that this extraordinary behaviour of USW velocity V_2 is connected with the pseudoproper character of the ferroelectric phase transition in GPI crystals.

Acknowledgement

This work was supported by the KBN 2016/W/IFD/1997.

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