ULTRASONIC INVESTIGATION OF FERROELECTRIC TRIGLYCINE SULPHATE AND DEUTERATED TRIGLYCINE SULPHATE*

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Ferroelectric single crystal solutions of Triglycine Sulphate (TGS) and Deuterated Triglycine Sulphate (DTGS) have been investigated by means of ultrasonic waves.

It has been shown that the relaxation time constant for the relaxation of a long range order to equilibrium in a TGS—DTGS crystal solution linearly increases with the increase of the average molecular mass of the investigated crystal.

It has also been shown that a phonon-polarization coupling constant decreases with the increasing Curie temperature of the crystal.

The presented experimental results are within the error of measurements in a good agreement with the theoretical formulae obtained for a model of uniaxial ferroelectrics that contains polar molecules with a temperature independent electric dipole. Our experimental results are also in a very good qualitative agreement with the experimental results obtained previously for isomorphous crystals of TGSe, TGS, and TGFBe.

ИССЛЕДОВАНИЕ СЕГНЕТОЭЛЕКТРИЧЕСТВА ОБЫЧНОГО И ДЕЙТЕРИРОВАННОГО СУЛЬФАТОВ ТРИГЛИЦИНА С ПОМОЩЬЮ УЛЬТРАЗВУКА

В работе приведены результаты исследований сегнетоэлектрического раствора монокристаллов обычного и дейтерированного сульфатов триглицина. Показано, что постоянная времени релаксации для релаксации от дальнего порядка к равновесию в упомянутых растворах кристаллов линейно увеличивается с ростом среднего молекулярного веса исследуемого кристалла. Показано также, что постоянная фонон-поляризационной связи уменьшается с уменьшением точки Кюри кристалла. Полученные экспериментальные результаты в пределах ошибок измерений находятся в хорошем согласии с теоретическими формулами, полученными в модели одноосного сегнетоэлектрика, содержащего полярные молекулы, которые обладают электрическим дипольным моментом, не зависящим от температуры. Приведенные экспериментальные результаты находятся также в хорошем согласии с экспериментальными данными, полученными раньше для изоморфных кристаллов солей триглицина селеновой, серной и фтороберилиевой кислот.

I. INTRODUCTION

The present paper will be dealing with the ultrasonic investigation of a single crystal solution of Triglycine Sulphate (TGS) and Deuterated Triglycine Sulphate (DTGS).

Pure TGS is a ferroelectric crystal that exhibits a second order (order—disorder) phase transition at the Curie temperature $\Theta_c = 322.76$ K and its chemical formula is as follows:

$$(NH_3^+CH_2COO^-)(NH_3^+CH_2COOH)_2SO_4^{2-}. \qquad (1)$$

Parkenson [1], Březina, and Smutný [2] demonstrated that from the seventeen hydrogen atoms in TGS eleven are active hydrogen atoms, i.e. those in amino and carboxyl radicals and the ionized sulphur acid, which can be exchanged with deuterium by recrystallization of TGS dissolved in D_2O. Thus DTGS having the chemical formula

$$(ND_3^+CH_2COO^-)(ND_3^+CH_2COOD)_2SO_4^{2-} \qquad (2)$$

will be understood as a 100 % deuterated TGS.

TGS and DTGS crystals are isomorphous. They have identical chemical bonds and the same structure of the lattice. The only difference between crystals with different concentrations of deuterium is the difference in the mass of some points in the crystal lattice. From this point of view the investigation of TGS—DTGS crystal solutions can bring unique information useful in the elucidating of microscopic properties of ferroelectric materials.

II. EXPERIMENTAL PROCEDURE AND RESULTS

We have been investigating crystal solid solutions of TGS—DTGS with concentrations 0 %, 69.5 %, and 88.1 %, where the concentration is understood as the ratio

$$n = N^{(D)}/N, \qquad (3)$$

where $N^{(D)}$ is the number of moles of the 100 % deuterated component and N is the total number of moles of the binary system TGS—DTGS. We had one sample with $n = 69.5$ % and another with $n = 88.1$ % only. The samples were prepared by the procedure described in [2]. They were cut in planes perpendicular to the X, Y, and Z directions so that their dimensions L_x, L_y, and L_z were about 1.2 cm. The samples were optically polished so that their Z-surfaces were flat and parallel. The crystals were investigated by quasi-longitudinal ultrasonic waves propagating the Z-direction and having a frequency in the range 10 MHz—200 MHz.

First we measured room temperature values of velocity and attenuation accurately and then we measured the relative change of velocity and attenuation with a change of temperature.

The room temperature value of quasi-longitudinal ultrasonic waves propagating in the Z-direction of a single crystal of a TGS—DTGS solid solution does not depend on concentration and is $(4.07 \pm 0.1) \times 10^3$ ms^{-1}. The error 2.5 % in velocity measurement can be considered as very high since it can be measured with a much higher accuracy also in our laboratory. The error in this case was estimated from the reproducibility of velocity measured in more than 10 different samples of pure TGS and most probably its high value is due to errors in the crystallographic orientation of the samples. Nevertheless, we can conclude that the room temperature elastic properties of TGS—DTGS do not depend on concentration within an accuracy of 2.5 %. It means that the parabolic part of the potential energy of ions in the crystal lattice of TGS—DTGS within the observed accuracy is not affected by concentration.

A slight decrease of velocity with the temperature increasing to the Curie point Θ_{nc} was observed. Then the Curie temperature velocity increases rapidly from the value $v_{n\infty}$ to the value $v_{n\infty}$. Using these values the attenuation constant

$$A_n^{(P)} = \frac{v_{n\infty}^2 - v_{n0}^2}{2v_{n\infty}^3} \qquad (4)$$

was calculated. The attenuation constant $A_n^{(P)}$ can be also calculated using the temperature dependence of the ultrasonic attenuation coefficient $\alpha_n^{(P)}$, which expresses the exponential decrease of wave energy per unit length due to its scattering through the interaction with polarization. The attenuation coefficient can be written as [3—11]:

$$\alpha_n^{(P)} = A_n^{(P)} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \qquad (5)$$

where

$$\tau_n = b_n(\Theta_{nc} - \Theta)^{-1} \qquad (6)$$

and b_n is the relaxation time constant, Θ_{nc} is the Curie temperature, Θ is temperature, ω is the angular frequency of the ultrasonic wave, and the index n denotes the concentration of the sample.

The maximum value of $\alpha_n^{(P)}$ occurs at a temperature for which $\tau_n = \omega^{-1}$ and it is

$$[\alpha_m^{(P)}]_{max} = A_n^{(P)} \omega/2. \qquad (7)$$

Analyzing relation (5) we can show that in the temperature region where $\omega \tau_n \ll 1$, $\alpha_n^{(P)}$ depends linearly on the squared frequency. Fig. 1 shows the dependence of the ultrasonic attenuation coefficient on the squared frequency for quasi-longitudinal ultrasonic waves propagating in the Z-direction of TGS—DTGS crystal solutions at room temperature.

Analyzing the experimental results presented in Fig. 1 and then the results obtained from the investigation of the temperature dependence of attenuation, it was shown that the total attenuation coefficient can be expressed as

$$\alpha_n^{(T)} = \alpha_n^{(A)} + \alpha_n^{(P)},$$ (8)

where $\alpha_n^{(P)}$ represents losses due to polarization and $\alpha_n^{(A)}$ represents "other" losses.
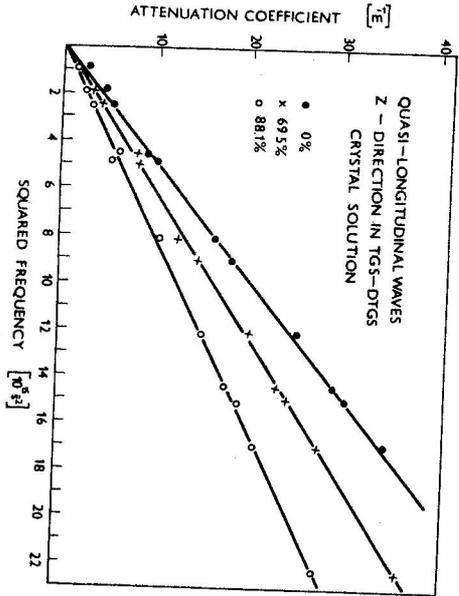

Fig. 1. Squared frequency dependence of the attenuation coefficient of quasi-longitudinal ultrasonic waves propagating in the Z-direction of a single crystal solution of TGS—DTGS

where $A_n^{(A)}$ is constant and f is the frequency of the ultrasonic wave.

The results of our experiments are summarized in Table 1.

Analyzing the results in Table 1 we can see that there is a large discrepancy between the values $A_n^{(A)}$ calculated using relation (4) and $A_n^{(P)}$ calculated using the calculation of b_n. Thus we have two different values $A_n^{(P)}$ which can be used in the calculation of the product of $A_n^{(P)} b_n$, which is experimentally determined from the temperature dependence of $\alpha_n^{(P)}$ in the region where $\omega\tau_n \ll 1$. Using $A_n^{(A)}$ estimated from $[\alpha_n^{(P)}]_{max}$ we get for $n = 0$ %, $b_0 = 2.4\times10^{-10}$ Ks and using $A_0^{(P)}$ estimated from the measurement of the velocity dispersion, we get $b_0 = 0.7\times10^{-10}$ Ks. These two values can be compared with the experimental values of $A_0^{(P)}$, b_0, and $A_0^{(P)} b_0$ published previously by various authors. Table 2 shows these values and one can see that the values b_0 referred to by various authors are

The room temperature value of $\alpha_n^{(A)}$ is negligibly small in comparison with $\alpha_n^{(A)}$, mechanism [4]. It can be seen from Fig. 1 that $\alpha_n^{(A)}$ is given as

$$\alpha_n^{(A)} = A_n^{(A)} f^2,$$ (9)

Thus Fig. 1 shows $\alpha_n^{(A)}$, which in this case represents losses due to the Akiezer

Table 1

n [%]	$A_n^{(A)}$ [10^{-20} m^{-1} s^2]	v_{n0} [10^3 ms^{-1}]	$(v_{n\infty}^2 - v_{n0}^2)/2v_{n\infty}^3$ [10^6 m^{-1} s]	$2\omega^{-1}[\alpha_n^{(P)}]_{max}$ [10^6 m^{-1} s]	$A_n^{(P)} b_m$ [10^{16} m^{-1} s^2 K]
0	21	3.92	16±2	5 ±0.05	12±2
69.5	16	3.8	8±1	2.2±0.04	16±1.5
88.1	12.5	3.776	5±1	1.5±0.03	13±1.5

Constant $A_n^{(A)} = \alpha_n^{(A)} f^{-2}$; ultrasonic wave phase velocity v_{n0} in the low frequency limit; attenuation constant $(v_{n\infty}^2 - v_{n0}^2)/2v_{n\infty}^3$; attenuation constant $2\omega^{-1}[\alpha_n^{(P)}]_{max}$; and the product $A_n^{(P)} b_n$ as a function of concentration n in TGS—DTGS crystal solutions obtained using quasi-longitudinal ultrasonic waves propagating in the Z-direction of the investigated sample.

Table 2

METHODS	Θ_{oc} [K]	b_0 [10^{-10} K]	$A_0^{(P)}$ [10^{-7} m^{-1} s]	$A_0^{(P)} b_0$ [10^{-17} m^{-1} s^2 K]	REFERENCE
BRILLOUIN	322.66	0.37	—	—	12
SCATTERING	—	0.29	—	—	13
ULTRASONIC	322.25	2.25	215	485	3
METHODS	—	0.4	870	350	4
	322.76	—	—	165	6
DIELECTRIC	322.31	0.55	—	165	14
METHODS	—	0.73	—	—	15

Data on the Curie temperature Θ_{oc}, the relaxation time constant b_0, the attenuation constant $A_0^{(P)}$, and the product $A_0^{(P)} b_0$ reported for a single crystal of TGS by various authors.

scattered from 0.3 to 2.3×10^{-10} Ks. The values $b_0 = (0.3\pm0.1)\times10^{-10}$ Ks are estimated using the Brillouin scattering, while the values $b_0 = (0.6\pm0.2)\times10^{-10}$ Ks were obtained using dielectric or ultrasonic methods. The value 2.25×10^{-10} Ks referred to in [3] is in agreement with our calculation where we use $A_0^{(P)}$ estimated from $[\alpha_0^{(P)}]_{max}$. These values were evaluated using the experimental data taken at temperatures for which $\Theta_{oc} \geq \Theta > \Theta_{oc} - 1$ K. It is quite probable that in the very close vicinity of the Curie point the attenuation of ultrasonic waves due to a relaxation of a long range order to equilibrium is replaced by a fluctuation mechanism [18] and therefore experimental data taken from this interval cannot be used in the evaluation of $A_0^{(P)}$ and b_0 in the Landau—Khalatnikov theory [17].

The relaxation time constant b_0 measured by the Brillouin scattering differs from that measured by dielectric or ultrasonic methods. This difference might be due to the dependence of the relaxation time on frequency.

Thus in our calculations the constant $A_n^{(P)}$ estimated from the dispersion of velocity was used. Table 3 presents experimental results for b_n, $A_n^{(P)} = (v_{n\infty}^2 - v_{n0}^2)/2v_{n\infty}^3$, the Curie temperature $\Theta_{n\infty}$, and the average molecular weight in atomic

Our experimental values of the Curie temperature Θ_{nc}, the average molecular mass M_n, the relaxation time constant b_n, and the attenuation constant $A_n^{(P)}$, obtained when TGS—DTGS single crystal solutions have been investigated by quasi-longitudinal ultrasonic waves propagating in the Z-direction of the investigated sample.

Table 3

n [%]	Θ_{nc} [K]	M_n [a m u]	b_n [10^{-10} Ks]	$A_n^{(P)}$ [10^{-6} m^{-1} s]
0	322.76	323	0.7 ± 0.2	16 ± 3
69.5	329.66	330.6	2 ± 0.4	8 ± 1.5
88.1	332.66	332.6	2.6 ± 0.5	5 ± 1

mass units, obtained when TGS—DTGS crystal solutions were investigated using quasi-longitudinal ultrasonic waves propagating in the Z-direction of the samples having concentrations 0%, 69.6%, and 88.1%.

Results in Table 3 show that the relaxation time constant b_n is directly proportional to the average molecular weight M_{no} while $A_n^{(P)}$ decreases with the increasing Curie temperature of the investigated crystal. These dependences are graphically demonstrated in Fig. 2 and Fig. 3. A pronounced change of the relaxation time constant and attenuation constant with the change of the average mass of the molecule of the crystal can be described using a simple model of uniaxial ferroelectrics having an order-disorder phase transition. In the following section a discussion of the model [10] and its applicability to our experimental results will be presented.
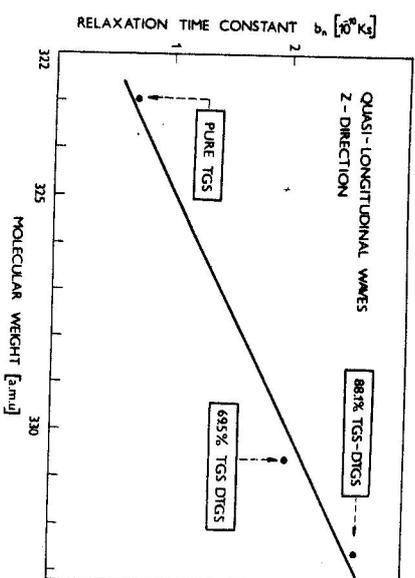

Fig. 2. Dependence of the relaxation time constant for the relaxation of a long range order to equilibrium on the average molecular mass of a single crystal solution of TGS—DTGS

III. THEORETICAL DISCUSSION

A uniaxial ferroelectric crystal that exhibits an order—disorder phase transition can be described using a model based on the following assumptions [10], [16]:
— A ferroelectric material contains polar molecules having a temperature independent permanent dipole p.
— Spontaneous polarization in the material occurs through the alignment of the dipoles in some appropriate direction, which at zero K is the direction of the ferroelectric axis.
— At temperatures higher than zero K dipoles may be oriented in two opposite directions and the long-range order parameter can be expressed as $L = (\mu_p - \mu_a)/\mu$, where μ_p is the concentration of dipoles parallel to the ferroelectric axis, μ_a is the concentration of dipoles antiparallel to the ferroelectric axis, while μ is the total concentration of the dipoles [16].
— The positive part of the dipole has the effective mass M^+, while its negative part has the effective mass M^-.
— The ultrasonic wave does not change the value of the permanent dipole of the molecule; however, it excites rotational vibrations of the molecules around an axis perpendicular to the ferroelectric one.
— Employing these assumptions it can be shown [10] that the ultrasonic attenuation of ultrasonic waves, polarized perpendicularly to the ferroelectric axis of the considered model can be written as

$$\alpha^{(P)} = \frac{\mu R^2}{v}\left[1 + \frac{M^+ M^-}{(M^+ a^+ - M^- a^-)^2}\right]^{-1}(\Theta_c - \Theta)^{-1}\frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \qquad (10)$$

where

$$\tau = \beta[M^+ (a^+)^2 + M^- (a^-)^2](\Theta_c - \Theta)^{-1}, \qquad (11)$$

while R and β are temperature independent constants, v is the ultrasonic wave phase velocity, a^+ and a^- are the distances of the mass centre of the positive and the negative part of the polar molecule from the axis of rotation, respectively, $a = a^+ + a^-$, and μ is the concentration of polar molecules in the crystal.

We can see according to relation (11) that the relaxation time is a linear function of the momentum of inertia of the polar molecule calculated with respect to the axis of rotation. This is in very good agreement with the experimental results shown in Fig. 2, provided that the distances a^+ and a^- do not change with the change of M^-.

The phonon-polarization coupling constant in our case is represented by $A^{(P)} v \mu^{-1}$. It can be phenomenologically shown [10] that crystals with a higher value of the coupling constant have a lower transition temperature and vice versa. This conclusion is quite reasonable, since in crystals with a higher value of the phono-polarization coupling thermal vibration of a lower energy are necessary to destroy spontaneous polarization, while in crystals with a low value of the

phonon-polarization coupling spontaneous polarization can be cancelled only through thermal vibration of a high energy.

Realizing that the mass density of a TGS–DTGS crystal solution depends on the concentration n as $\varrho_n = \varrho_0(1 + \gamma n)$, where $\varrho_0 = 1680$ kg m^{-3} and $\gamma = 762 \times 10^{-6}$, we can show that the concentration of polar molecules μ does not change remarkably with n and therefore the results in Fig. 3 demonstrate qualitatively a decrease of the coupling constant with the Curie temperature.
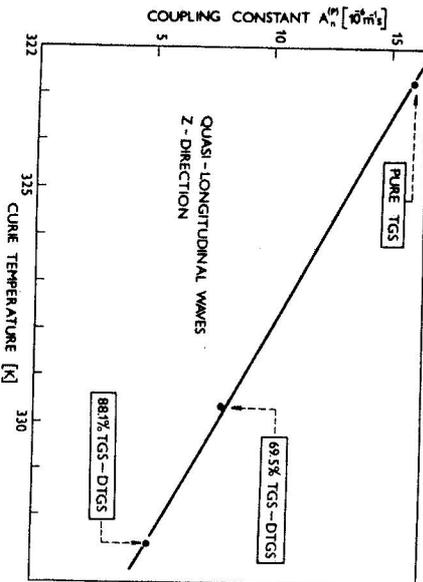
Fig. 3. Dependence of the coupling constant $A_n^{(p)}$ on the Curie temperature of a single crystal solution of TGS–DTGS

IV. CONCLUSIONS

We can draw the following conclusions from our experimental results:

1) The relaxation time of a long range order to equilibrium in the order-disorder type crystals is proportional to the average of the effective momentum of inertia of the polar molecules contained in the crystal.

2) The phonon-polarization coupling constant decreases with the increasing Curie temperature of the crystal.

3) The relative distance of the mass centre of the positive part and the negative part of the polar molecule from its rotational axis in TGS–DTGS crystals do not change with the change of the effective mass M^-.

4) Our experimental results have been estimated with accuracy of 20 % and within this error they do agree with theoretical conclusions.

5) Our conclusions should be applicable not only to TGS–DTGS crystals but also to all isomorphous crystals of TGS-type. In order to prove it we use data reported for TGSe, TGS, and TGFBe crystals in paper [4].

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Fig. 4 shows the dependence of the relaxation time constant on molecular weight and Fig. 5 shows the dependence of the phonon-polarization coupling $A^{(p)}v\mu^{-1}$ on the Curie temperature for TGFBe, TGS, and TGSe isomorphous crystals. Results presented in Figs. 4 and 5 are in agreement with our conclusions. The results obtained in [4] have not been discussed with respect to relations (10) and (11), and they do inspire confidence in our conclusions.
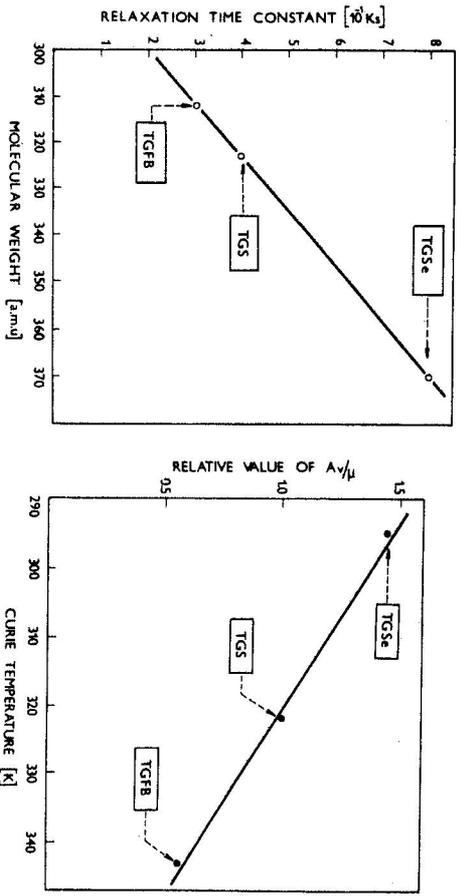
Fig. 4. Dependence of the relaxation time constant for the relaxation of long range order to equilibrium on the molecular mass of isomorphous crystals of the TGS-type

Fig. 5. Dependence of the relative value of the coupling constant on the Curie temperature in isomorphous crystals of the TGS-type

REFERENCES

[1] Parkerson, C. R.: NOLC Technical Memo, 42 (1960), 42.
[2] Březina, B., Smutný, F.: Czech. J. Phys. B 18 (1968), 393.
[3] O'Brien, E. J., Litovitz, T. A.: J. Appl. Phys. 35 (1964), 180.
[4] Minaeva, K. A., Levanyuk, A. P., Strukov, B. A., Kopcik, V. A.: Fiz. Tverd. Tela 9 (1967), 1220.
[5] Minaeva, K. A., Strukov, B. A., Varnsdorff, K.: Soviet. Phys. Cryst. 10 (1969), 1665.
[6] Baják, I. L.: Fyz. čas. SAV 2 (1971), 90.
[7] Beerman, H. P., Ferroelectrics 8 (1974), 653.
[8] Kay, M. I., Kleinberg, R.: Ferroelectrics 5 (1973), 45.
[9] Kay, M. I.: Ferroelectrics 17 (1977), 415.
[10] Baják, I. L.: to be published.
[11] Landau, L. D., Ž. exp. Teor. Fiz. 7 (1937), 19.
[12] Luspin, Y., Hauret, G.: Ferroelectrics 15 (1977), 43.

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[13] Gammon, R. W., Cummins, Z.: Phys. Rev. Lett. *17* (1966), 193.
[14] Luther, G.: Phys. Stat. Sol. *20* (1973), 227.
[15] Hill, R. M., Ichiki, S. K.: Phys. Rev. *132* (1963), 1603.
[16] Burfoot, J. C.: *Ferroelectrics.* D. van Nostrand Company, LTD. London 1967.
[17] Rehwald, W.: Advances in Phys. *22* (1973), 721.
[18] Nattermann, Th.: Phys. Stat. Sol. B *85* (1978), 291.