DIELECTRIC DISPERSION IN FERROELECTRIC TRIGLYCINE SULPHATE (TGS)

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The dielectric constant ε of Triglycine Sulphate was measured in a frequency range from several kHz to 23 kMHz. A dispersion band for ε was found in the 10 kMHz region. The observed dispersion is attributed to domain wall resonance.

Introduction

The dielectric constant of TGS was measured by Lurio and Stern (1960), Nakamuro and Furuichi (1960), Nishioka and Takeuchi (1960) and many others. However, no dispersion for the dielectric constant was found. In the case of a ferroelectric multidomain crystal at least two different dispersion bands should appear, the one due to domain wall motion (usually in the microwave region) and the other — in infrared — due to ionic polarization within the elementary cell. Domain wall resonance in ferroelectric crystals, as an analog to the same phenomenon in ferromagnetics, was first suggested by Kittel (1951). One can expect a similar effect to occur in a TGS multidomain crystal. First of all it was necessary to extend the microwave measurements of ε to frequencies higher than 9 kMHz. This was done by the present author (1961). Starting from simple equations describing the domain wall motion, it was possible to calculate the resonance frequencies which depend on the direction of the domain wall displacement, on the wall thickness and its effective mass per cm^2.

1. Measurements of the dielectric constant of TGS

The dielectric constant of TGS was measured within a broad frequency band from several kHz up to 23 kMHz. Three different measuring devices were applied according to the frequency of the measuring field. From 1 kHz to about 1 MHz a high frequency standard bridge was used. In the range from several MHz to about 100 MHz a resonance circuit

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supplied by an external oscillator was used (Fig. 1). The resonance circuit was formed of a copper box and the RF driving power was introduced through the coupling loop shown in Fig. 1. The measuring voltage was kept at a low level of several volt/cm, because the dielectric constant of TGS strongly depends on the measuring field strength. In the microwave region, dielectric loss in TGS is so high that is was not possible to determine its dielectric
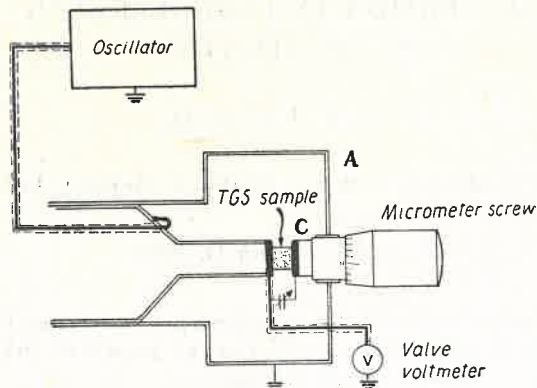

Fig. 1. Resonance circuit applied in the region from 10—100 MHz

constant by the usual method *i.e.* by placing the TGS probe sample in a rectangular waveguide. On the other hand, the high dielectric loss enables to make use of a method in which a large, optically polished TGS crystal is tightly attached to the open end of a waveguide (Fig. 2). In this method, the crystal is treated as infinite; thus, the back-
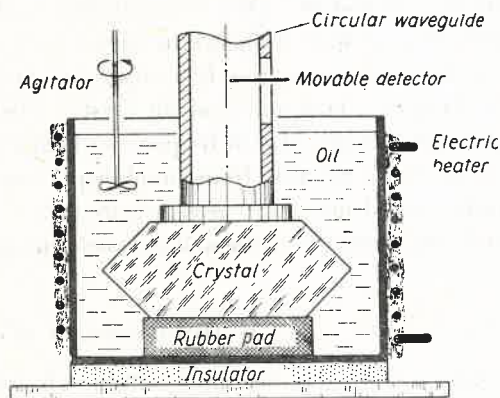

Fig. 2. Setup for measuring the dielectric constant of TGS in the microwave band

ward scattered microwave radiation from its further surfaces is neglected. The waveguide with the crystal at its end was immersed in an oil bath; thus, the ε *versus* temperature dependence could be determined. The applied circular waveguide operated in the TE_{11} mode. The direction of the electric field of the wave was made parallel to the ferro-

electric axis of the crystal. The dielectric constant of the crystal can be calculated using the following formula (Westphal, 1950):

$$\frac{\varepsilon}{\varepsilon_0} = \frac{1}{1 + \left(\frac{\lambda_g}{\lambda_c}\right)^2} \left[\left(\frac{\lambda_g}{\lambda_c}\right)^2 + \left(\frac{E_{max}}{E_{min}}\right)^2 \right],$$

where: ε_0 — free space dielectric constant, λ_g — wavelength within the waveguide, λ_c — cutt-off wavelength, $\dfrac{E_{max}}{E_{min}}$ — standing wave ratio (SWR).

The SWR was determined by means of a travelling diode detector with a square law response. In this case we have:

$$\frac{E_{min}}{E_{max}} = \frac{\sin\theta}{(2 - \cos^2\theta)^{1/2}}, \qquad \theta = \frac{\pi \Delta x}{\lambda_g},$$
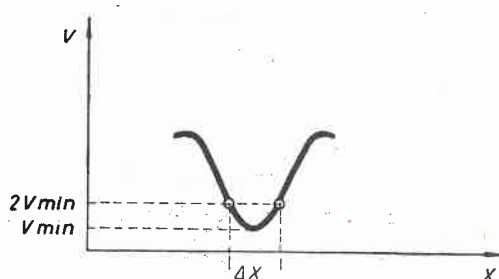

Fig. 3. Illustration of the microwave power display measured with a travelling detector

where θ is the angular displacement of the travelling detector, and Δx the distance between points in which the microwave power is twice the value at minimum (Fig. 3). If $\dfrac{\pi \Delta x}{\lambda_g}$ is small, then

$$\frac{E_{min}}{E_{max}} \cong \frac{\pi \Delta x}{\lambda_g}.$$

The obtained results are presented in Table I, where λ_0 denotes the free space wavelength.

TABLE I

Dielectric constant of TGS as function of frequency ν of the measuring field

ν	1 kHz	1 MHz	100 MHz	X band 8.5 kMHz	Y band 23.9 kMHz	K band 23 kMHz
λ_0 (cm)	—	—	—	3.52	2.162	1.3
λ_g (cm)	—	—	—	6	3.57	2
ε	44	30	26	25	19.5	15.5

The dispersion shown in Fig. 4 was also verified by measuring the temperature dependence of the dielectric constant of TGS when passing through the Curie Point. A pronounced decrease of the peak value of ε is clearly visible in Fig. 5. More details concerning measure-
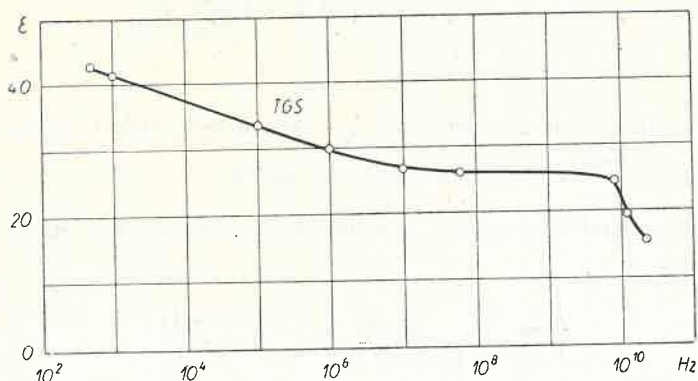

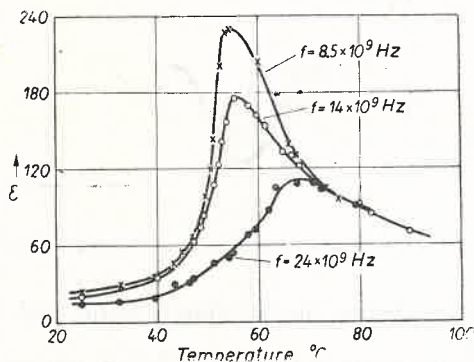Fig. 4. Dielectric constant of TGS *versus* frequency of the measuring field

Fig. 5. Dielectric constant of TGS measured in three different microwave bands as function of temperature

ments of the dielectric constant of TGS can be found in the Technical Report No. 163 by this author (1961).

2. Domain wall resonance

Let us now consider the equation of motion of a domain wall in the form (Kittel, 1951):

$$\varrho\ddot{x}+r\dot{x}+qx = 2P_sE, \tag{1}$$

where ϱ is the effective mass per cm² of the domain wall, E-the high frequency measuring field, and P_s-the spontaneous polarization of the crystal. The domain structure of TGS is antiparallel. The elastic constant q can be estimated if we take the simple model of domain wall displacement shown in Fig. 6. In the static case we have:

$$qx = 2P_sE,$$
$$P = \chi_0E, \tag{2}$$

where χ_0 is the static susceptibility arising from polarization due to domain wall motion. If the applied electric field E causes the wall to move by a distance of x, then the increase in charge per unit surface of the crystal is:
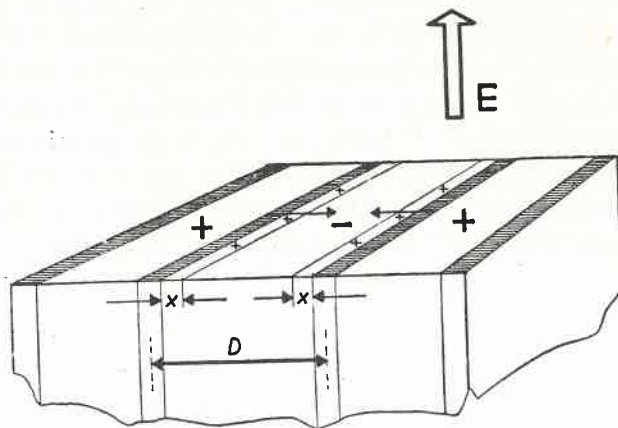
$$\Delta Q = \frac{2P_s x}{D},$$

Fig. 6. Illustration of domain wall displacement for antiparallel multidomain structure

wher $1/D$ is the number of domains per unit length. We have:

$$qx = 2P_s \frac{P}{\chi_0} = \frac{4P_s^2 x}{\chi_0 \cdot D}.$$

Finally:

$$q = \frac{4P_s^2}{\chi_0 D}. \tag{3}$$

Neglecting r in equation (1) one obtains the resonance frequency of the wall as:

$$\omega_r = \sqrt{\frac{q}{\varrho}} \quad \text{or} \quad \nu_r = \frac{P_s}{\pi \sqrt{\varrho \chi_0 D}}. \tag{4}$$

Thus, the resonance frequency depends on several parameters, some of which are already known from experiments (P_s, χ_0, D). The most troublesome question is the calculation of the effective mass of the domain wall.

1. The spontaneous polarization P_s of TGS measured by different authors varies from 2 to 2.8 $\mu C/cm^2$. We will take a value of 2.5 $\mu C/cm^2$ (= 7.5.10^3 e.s.u.).

2. The dielectric constant of TGS measured at room temperature is about 44. Hoshino et al. (1958), however, on the basis of thermodynamic theory, suggested that this dielectric constant should be larger by 50%. According to their suggestion, what one measures is not the dielectric constant of the free crystal because the antiparallel domain structure causes the sample to be clamped. As shown by Pietrzak and Kaczmarek (1962), this is true in the case of $BaTiO_3$ but not in TGS. Measurements of ε at coercive field yield a decrease of only 3.5%, which indicates that the electromechanical coupling coefficient of

TGS is very small. It is thus reasonable to attribute the measured ε value to domain wall motion. We have in this case:

$$\chi_0 = \frac{\varepsilon - 1}{4\pi} = 3.43.$$

3. Domain structure in TGS was investigated by many authors, most recently by Petroff (1969). The cigar shaped domains have domain walls almost parallel to the ferroelectric b-axis. The cross-section of the domain is usually elliptical in form, and the average width varies from 10^{-3} cm to a few mm or even cm. A stable domain structure consists of rather small domains. Here, we will take for our calculations an average domain width D of 10^{-3} cm.

4. The effective mass per cm² of the domain wall has not been calculated as yet. Some estimations of ϱ were given by Fatuzzo (1961), who investigated the switching process in TGS. We shall now proceed to some simple considerations permitting a determination of ϱ.

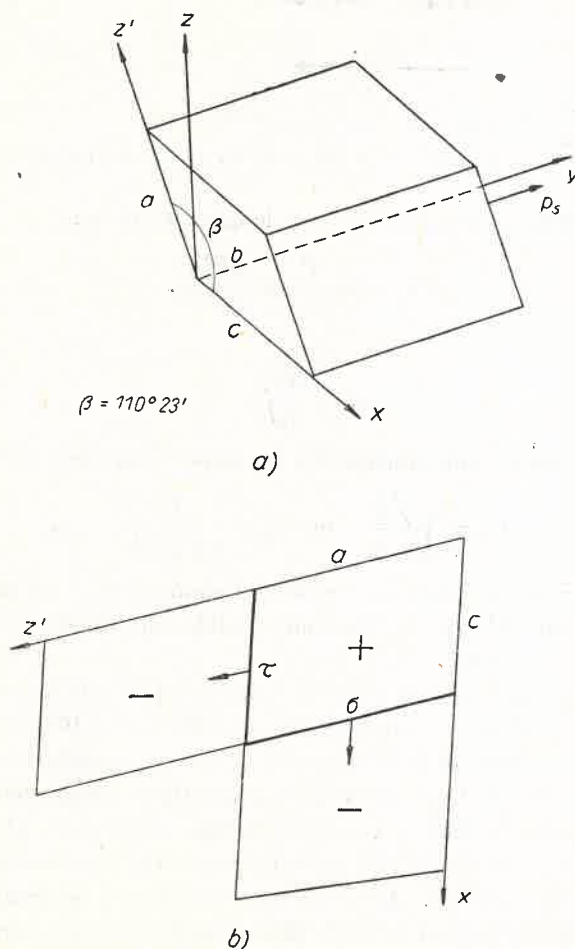

$\beta = 110°23'$

a)

b)

Fig. 7. Unit cell of TGS (a), and possible domain wall shifts during switching of polarization (b)

The elementary cell of TGS (Fig. 7a) was determined with accuracy by Hoshino *et al.* (1957) using the X-ray method. We have: $a = 9.41$ Å, $b = 12.64$ Å (ferroelectric axis), $c = 5.13$ Å. Spontaneous polarization P_s points in the y-direction, and the axes z' and x make an angle of about $110°$. Domain walls σ and τ between cells of opposite polarization are shown in Fig. 7b. Suppose the domain wall σ to move by c in the x-direction, or the wall τ to move by a in the z'-direction when polarization in the two adjacent cells is reversed. If the ion (or ions) responsible for polarization reversal moves by a distance of δ the domain wall is shifted by a distance of c or a. We have:

$$\left. \begin{aligned} v_j &= \frac{\delta}{a}\, v_s, \\[2mm] E_k &= \frac{1}{2}\, M_j\, \frac{1}{cb} \left(\frac{\delta}{a}\right)^2 v_s^2 \end{aligned} \right\} \quad \tau \text{ moves } by\ a \text{ in the } z'\text{-direction}$$

or

$$\left. \begin{aligned} v_j &= \left(\frac{\delta}{c}\right)^2 v_s, \\[2mm] E_k &= \frac{1}{2}\, M_j\, \frac{1}{ab} \left(\frac{\delta}{c}\right)^2 v_s^2 \end{aligned} \right\} \quad \sigma \text{ moves by } c \text{ in the } x\text{-direction}$$

where M_j denotes the effective mass of the ion (ions), v_j and v_s velocities of the ion wall, respectively, $1/cb$ and $1/ab$ — the number of elementary cells per unit surface observed in the a or c-direction, respectively, E_k — the kinetic energy per 1 cm² of the wall in motion, taken in the appropriate direction.

Thus, the effective masses per cm² of the walls are:

$$\varrho_a = \frac{M_j \delta^2}{a^2 cb}, \tag{5a}$$

$$\varrho_c = \frac{M_j \delta^2}{c^2 ab}. \tag{5b}$$

It should be pointed out that the elementary cell of TGS contains two molecules (Fig. 8). We shall now calculate the main ion displacements within the unit cell when its polarization is reversed. First of all it is seen from equations (5a) and 5b) that

$$\frac{\varrho_a}{\varrho_c} = \frac{c}{a} \cong 0.61. \tag{6}$$

The effective mass of the domain wall strongly depends on the direction of its motion. We will consider, in general, a more realistic situation in which the domain wall extends over many unit cells of the crystal. Some authors (*e.g.*, Petroff 1969) measured the domain wall width and found a value varying from tens to about 500 Å. The domain wall can consist of many different layers in which the spontaneous polarization varies slowly from parallel to antiparallel direction with respect to the polarization in the adjacent domain. As the

wall moves by a distance of a or c, the ions in the unit cells within the wall undergo smaller displacements, which can be calculated if the domain wall width is known. We have:

$$D = N^a \cdot a = N^c \cdot c,$$

where N is the number of unit cells within the wall. Furthermore:

$$\left.\begin{aligned} v_j &= \left(\frac{\delta}{N^a a}\right) v_s, \\[2mm] E_k &= \frac{1}{2} M_j \frac{1}{cb} \frac{\delta^2}{N^a a^2} v_s^2 \end{aligned}\right\} \quad \tau \text{ moves by } a \text{ in the } z'\text{-direction}$$

and

$$\left.\begin{aligned} v_j &= \left(\frac{\delta}{N^c c}\right) v_s, \\[2mm] E_k &= \frac{1}{2} M_j \frac{1}{ab} \frac{\delta^2}{N^c c^2} v_s^2 \end{aligned}\right\} \quad \sigma \text{ moves by } c \text{ in the } x\text{-direction}$$

The effective masses per cm^2 are:

$$\varrho_a^{(N^a)} = \frac{M_j \delta^2}{N^a a^2 cb}, \tag{7a}$$

$$\varrho_c^{(N^c)} = \frac{M_i \delta^2}{N^c c^2 ab}. \tag{7b}$$

Taking $D = 500$ Å we obtain:

$$N^a \cong 53 \quad \text{and} \quad N^c \cong 87. \tag{8}$$

In order to calculate the value of $M_j \delta^2$ we have to take into account the displacements of the atoms in the cell. As shown by Hoshino *et. al* (1957), the distance between and $O'_{III} - O'_{II}$ in $O'_{III} - - - H \ldots O'_{II}$ is 2.34 Å, and the hydrogen atom is situated closer to the O'_{III} atom than to the O'_{II} atom when the polar axis points in the negative direction of the ferroelectric b-axis (Fig. 8). Furthermore, the glycine ion III is coplanar whereas the glycine ion II forms a noncoplanar zwitterion. In the noncoplanar glycine II the nitrogen atom sticks out of the molecular plane by a value of 0.26 Å. When the polarization is reversed, the hydrogen atom shifts to a position closer ot O'_{II} and, as a result, glycine III becomes a noncoplanar zwitterion and glycine II coplanar. In brief, the roles of both glycines are interchanged. The short hydrogen bond plays an essential role in the polarization process of TGS (hydrogen works as a trigger). The main reversible dipole, according to Hoshino *et al.*, is the coplanar glycine I whose molecular plane makes an angle of 12.5° with the $Y = 1/4$ plane. This angle is changed to $-12.5°$ (with respect to the $Y = 1/4$ plane) when the polarization of the unit cell is reversed. The exact positions of all glycine I atoms in the unit cell are presented in Table II. In the last two columns, also positions Δ with respect to the $Y = 1/4$ plane, and masses m are given, respectively. The displacements of atoms when the glycine I rotates by an angle
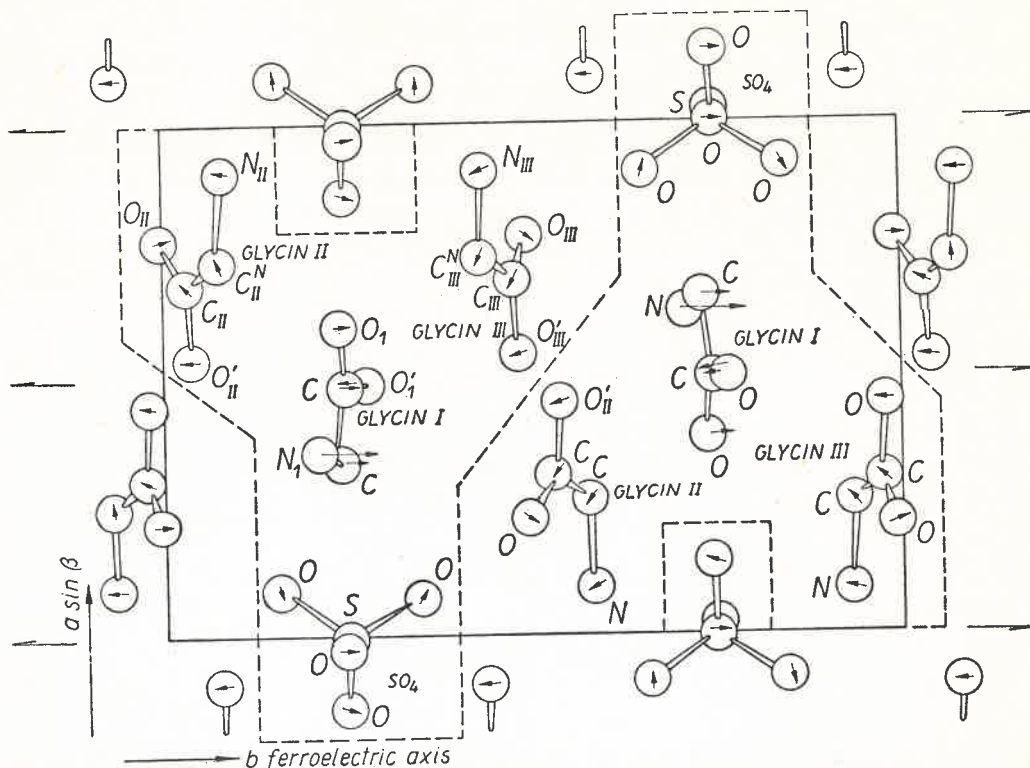
Fig. 8. Projection along the c-axis of the TGS unit cell of negative polarity (after Hoshino *et al.*, 1957)

TABLE II

Atoms in glycine I ion

Atom	x	y	z	Å	m (g)
O	0.6064	0.2393	1.0746	−0.145	$1.336 \cdot 10^{-23}$
O′	0.4935	0.2718	0.6668	+0.275	$1.336 \cdot 10^{-23}$
C	0.4905	0.2472	0.8727	−0.069	$1 \cdot 10^{-23}$
C_N	0.3348	0.2361	0.9049	−0.240	$1 \cdot 10^{-23}$
N	0.3595	0.2110	1.1639	−0.488	$1.17 \cdot 10^{-23}$

of 25° degrees during polarization reversal is shown in Fig. 9. The effective mass of all the atoms in motion when the polarization is reversed can be calculated if we write the expression for the kinetic energy of these atoms. For simplicity, all rotations will be approximated by translations. In glycine II and III the displacements of the 4 nitrogen atoms by $u = 0.26$ Å will also be taken into account. We have:

$$E_k = \frac{1}{2} m \left(\frac{\xi}{\Delta t} \right)^2 = 4 \left[\frac{1}{2} m_N \left(\frac{u}{\Delta t} \right)^2 + 2 \left[\frac{1}{2} m_0 \left(\frac{2\Delta_0}{\Delta t} \right)^2 + \frac{1}{2} m_{0'} \left(\frac{2\Delta_{0'}}{\Delta t} \right)^2 \right] + $$

$$+2\left[\frac{1}{2}\,m_{C_N}\left(\frac{2\Delta_{C_N}}{\Delta t}\right)^2+\frac{1}{2}\,m_N\left(\frac{2\Delta_N}{\Delta t}\right)^2\right],$$

$$m\xi^2 = 4m_N u^2+8m_0(\Delta_0^2+\Delta_{0'}^2)+8m_{C_N}(\Delta_{C_N}^2+\Delta_N^2),$$

where m and ξ denote the reduced mass and displacement, respectively, and Δt the switching time. Taking the numerical values of Table II, one finds:

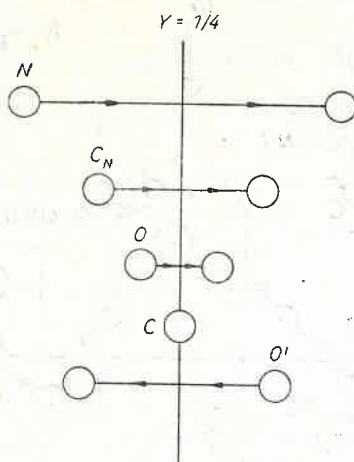$$m\xi^2 = 3.709 \cdot 10^{-39} \text{ g cm}^2.$$

Fig. 9. Displacements of atoms with respect to the $Y = 1/4$ plane in glycine I during polarization reversal

Other small displacements of atoms in the SO_4 groups are neglected. The effective mass per cm^2 of the wall as well as the resonance frequencies can now be calculated. Substituting the following numerical values in equations (4), (5a), (5b), (7a) and (7b) we obtain:

$$a = 9.41 \text{ Å}, \quad b = 12.64 \text{ Å}, \quad c = 5.73 \text{ Å}, \quad P_s = 7.5 \cdot 10^3 \text{ e.s.u.},$$

$$m\xi^2 = 3.71 \cdot 10^{-39} \text{ gcm}^2, \quad \chi_0 = 3.43, \quad D = 10^{-3} \text{ cm},$$

$$N^a = 53, \quad N^c = 87:$$

$$\varrho_a = 0.578 \cdot 10^{-10} \text{ g/cm}^2,$$

$$\varrho_c = 0.948 \cdot 10^{-10} \text{ g/cm}^2,$$

$$\varrho_a^{(N^a)} = 1.09 \cdot 10^{-12} \text{ g/cm}^2,$$

$$\varrho_c^{(N^c)} = 1.09 \cdot 10^{-12} \text{ g/cm}^2,$$

The effective mass $\varrho_c^{(N^c)}$ has to be equal to $\varrho_a^{(N^a)}$ because the domain wall width was chosen independently of the direction of wall motion. The appropriate resonance frequencies are:

$$\nu_r \text{ (for } \varrho_a) = 5.96 \cdot 10^9 \text{ Hz},$$

$$\nu_r \text{ (for } \varrho_c) = 4.40 \cdot 10^9 \text{ Hz},$$

$$\nu_r \text{ (for } \varrho^N) = 4.16 \cdot 10^{10} \text{ Hz}.$$

The direction of wall displacement plays an important role only when the wall thickness measured in lattice units is very small (e.g., $N = 1$).

It is necessary to point out that the observed wall thickness in TGS varies in a wide range, from tens to several hundred Å. Thus, the resonance frequency is displayed in a band from 10^9 to 10^{11} Hz. This is in good agreement with the observed dispersion band presented in Fig. 4. The slow decrease in ε with increasing frequency of the measuring field is, however, not clear as yet.

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