

## THE EVOLUTION OF THE LAYERED DOMAIN STRUCTURE OF TGS AND RS SINGLE CRYSTALS\*

BY K. DĄBROWSKA, W. DASZCZYŃSKA AND A. JAŚKIEWICZ

Institute of Experimental Physics Wrocław University\*\*

(Received August 3, 1976)

In this paper we present the results of an investigation of evolution towards equilibrium of a layered domain structure formed during phase transition in isolated RS and TGS single crystals. The equilibrium domain structure of an ideal crystal was defined by Fousek (1969) as the structure with a periodic pattern and with zero net polarization. So far, real structures in equilibrium were analysed using the condition of zero net polarization. In this paper, we have used not only the above condition, but also the periodicity of domain structure. It was shown that the evolution of a layered domain structure towards equilibrium may be divided into two processes. At the beginning of the evolution, the domains tend to increase in thickness while the number of domains taken per unit length perpendicular to the wall diminishes. After that, the processes improving the periodicity of the domain structure take place. It was observed that the decrease in the number of domains per unit length increases the depolarization energy of the domain arrangement. This depolarization energy diminishes, however, when the domain structure is no longer disordered by changes in number of domain walls.

### 1. Introduction

The process of domain formation during phase transition in a ferroelectric crystal is controlled by the requirement that the electrostatic energy diminishes. This requirement, the main cause of the occurrence of the domain structure in ferroelectrics, follows the analogical condition put forth by Landau (1937), for the ferromagnetic domain structure. The electrostatic energy diminishes when a single domained crystal divides into a poly-domained one (Mitsui and Furuichi, 1953). During this division, antiparallel domains and transition layers between these domains are formed. The layers cause energy expenditures and thus are acting as agents inhibiting the division of domains into smaller ones.

---

\* This work has been subsidized by the Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław.

\*\* Address: Instytut Fizyki Doświadczalnej, Uniwersytet Wrocławski, Cybulskiego 36, 50-205 Wrocław, Poland.

At the end, the domain structure exhibiting crystallographical characteristics of twinning and of minimum free energy should be realized (Zheludev and Shuvalov, 1957).

The process of domain structure formation is a rather complex one, it consists of the nucleation of domains, their growth by the forward and sidewise motion of domain walls until coalescence of domains is achieved. In the end, the evolution process of the freshly formed domain structure towards equilibrium takes place. The nucleation, random in space and in time, is the main cause of deviation of a freshly formed domain structure from equilibrium.

In investigating the evolution of the domain structure towards equilibrium, we must have some criteria for recognizing a domain structure close to equilibrium. According to Fousek (1969), the domain pattern of the sample should be periodic with zero macroscopic polarization. In the first investigations of evolution, the problem of equilibrium was not considered. The first observations of evolution of domain structure carried out by Taurel and Gilletta (1965) reported that TGS crystals left for a longer time at room temperature contained larger domains than at the beginning of the experiment. Moravec and Konstantinova (1968), investigating the layered domain structure of TGS crystals, have found that the number of domains, taken per unit length perpendicular to the wall, is diminishing with time after the structure has been freshly formed. Konstantinova and Stankowska (1970), Stankowska (1973) have investigated the changes with time in the number of domains for samples with various cooling rates. The decrease with time in the number of domains was observed for all cooling rates, but the number of domains changed least for an abrupt cooling of the sample from 100°C to room temperature. All the changes in number of domains were registered at room temperature.

In the investigation of DS, both criteria for equilibrium of DS given by Fousek (1969) should be taken into account. In this paper, we shall present a method of analysis of the domain structure near equilibrium. This method, will give information about the difference between the free energy of the domain structure and the free energy of the equilibrium DS. We will observe changes in the domain number and at the same time the periodicity of the domain structure.

## 2. The energy of unperiodical arrangement of domains

The free energy of a ferroelectric crystal divided into domains is given by the sum of the depolarization energies of the domains and by the wall energies. For the free energy  $F$  of a layered domain structure, per unit surface area of the crystal, we can write

$$F = NS\sigma + \sum_{n=1}^{N+1} F_d(n), \quad (1)$$

where  $N$  is the density of domain walls in the direction perpendicular to the wall,  $S$  — the area of a domain wall,  $\sigma$  — the wall energy density,  $F_d(n)$  is the depolarization energy of the  $n$ -th domain. An unperiodical domain structure will be treated as composed of domains in the shape of parallelepipeds, where  $d$  is the width,  $D$  is the thickness and  $l$  is the length

of a domain. The depolarization energy of a parallelepiped spontaneously polarized along the thickness for which  $D \gg d$ , is given by the formula

$$F_d(n) = \frac{\pi P_S^2}{\sqrt{\epsilon_D \epsilon_d}} d_n^2 l, \quad (2)$$

where  $\epsilon_D, \epsilon_d$  are electric permittivities along the thickness and the width of the parallelepiped. The above formula can be easily obtained from a formula given by Landau (1957) for the depolarization energy of an elliptical cylinder. For the depolarization energy of the sample for which the domain width distribution is known we get the depolarization energy equal to

$$\sum_{n=1}^N F_d(n) = \frac{\pi P_S^2 l}{\sqrt{\epsilon_D \epsilon_d}} \sum_{n=1}^N d_n^2. \quad (3)$$

Thus introducing (3) into (1) and taking into account the relation  $S = l \cdot D$ , we have

$$F = N l D \sigma + \frac{\pi P_S^2 l}{\sqrt{\epsilon_D \epsilon_d}} \sum_{n=1}^N d_n^2. \quad (4)$$

The above formula allows us to describe the energy of a crystal divided into domains which are far from being periodic in arrangement. Inserting  $d_n = d$  and  $N = d^{-1}$  into (4), we have

$$F = \frac{l D}{d} \sigma + \frac{\pi P_S^2 l}{\sqrt{\epsilon_D \epsilon_d}} d. \quad (5)$$

It is easy to see that our formula contains the well known formula for the free energy of a crystal divided into domains forming a periodic structure (e. g. Kittel, 1949; Mitsui and Furuichi, 1953). The difference is in the value of the coefficient in the depolarization energy term. It is due to various approximation methods used to estimate the depolarization energy.

### 3. Experimental

The TGS samples were cut from the (001) growth region of the crystal in the form of plates 1 mm thick, oriented perpendicular to the  $b$  axis. After a prolonged heating in dry air at a temperature of 355 K for 22 hours and for 1 hour, the samples were cooled down at the rate 0.05 K/min, until 324 K was achieved. After approaching this temperature, the cooling rate was further reduced to 0.008 K/min in the phase transition region. After tempering for some time at a temperature somewhat below  $T_c$  the samples were cooled at a rate of 0.5 K/min to room temperature. Then at this temperature the domain structure was revealed by etching. The samples were kept at room temperature in order to observe the evolution of the domain structure. At certain temperatures the sample was etched and

the distribution of the domain width determined. Fig. 1 shows a photograph of the domain structure of the sample. It is to mention that the domain structure during investigations remained a layered one without traces of deterioration for instance without division into elliptical domains.

Investigations of the evolution of the domain structure were carried out taking into account not only the changes with time in the number of domains per unit length but

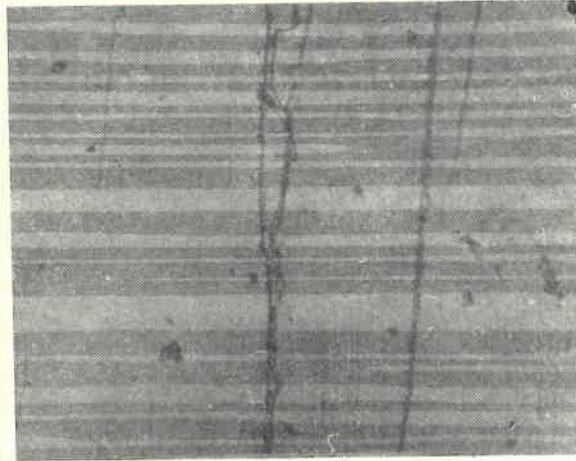


Fig. 1. A photograph of the domain structure of TGS crystal (the growth pyramid (001)) revealed at room temperature

also the distribution of domain widths. The last characteristic of the sample provides a deeper insight into the process of evolution of DS (Jaśkiewicz et al., 1976). An example of the domain width distribution is shown in Fig. 2. Using the above distribution, the relative parts  $S_+$  and  $S_-$  of the crystal surface corresponding to the domain polarized up and down, respectively, were calculated (Fousek and Safrankova, 1965). The relative value

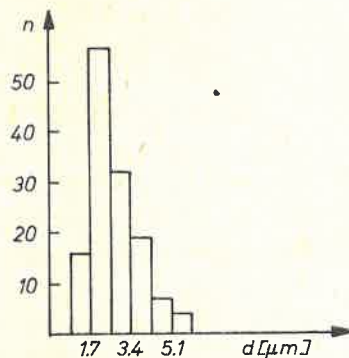


Fig. 2. An example of the domain width distribution of a layered DS revealed in TGS sample at room temperature



of polarization changes with time oscillating about zero with an amplitude in the range  $\pm 0.03$  of the maximum value of the polarization.

Fig. 3 and Fig. 4 give the changes with time of the linear density of the number of domains for the same sample. Using the photographs of domain structure on the above

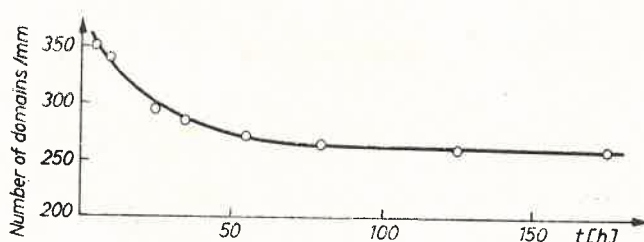


Fig. 3. The changes with time of the linear density in the number of domain in the direction perpendicular to the wall for TGS sample tempered for 1 hour at a temperature  $T = T_c - 0.5$  K

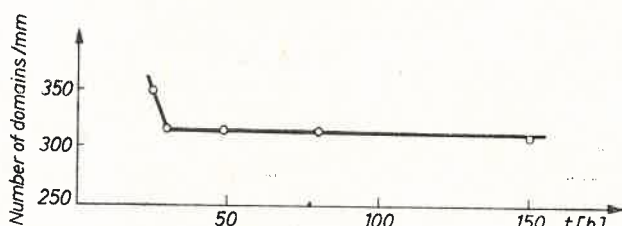


Fig. 4. The changes with time of the linear density in the number of domains in the direction perpendicular to the wall for TGS sample tempered for 22 hours at a temperature  $T = T_c - 0.5$  K

sample, the domain width distribution was determined (an example of this is shown in Fig. 2). For each of the domain width distributions, the depolarization energy of the domain structure was calculated using formula (3). The dependence on time of the depolarization energy  $F_d$  and the wall energy  $F_w$  of the domain structure for the same sample are given in Fig. 5 and Fig. 6. The wall energy density  $\sigma$  was estimated using the Zhirnov (1958) formula and the data for TGS given by Safrankova (1970).

Monocrystals of RS were grown in the paraelectric phase. The samples were cut in the plane (100) perpendicular to the ferroelectric axis. Domain structure was observed in polarized light. Domain widths were measured by a micrometric ocular. Before observation, the samples were kept at 303 K for 20 hours. The observation temperature was 294 K. The phase transition occurred in two ways for the two twinned samples.

1. After heating the sample was cooled at the rate of about 0.05 K/min. The rate of cooling was reduced to 0.005 K/min in the range 298 K — 295 K.

2. The cooling process was made such as in the above case but the sample was kept for 2 hours in the vicinity of 0.05 K below Curie point. Phase transition temperature was determined from capacity measurements of a sample cut from a region neighbouring the examined sample. Temperature was measured by a thermocouple. The set of two thermostates gave temperature stabilization to within 0.002 K. Energetic changes in time such formed domain structures were investigated.

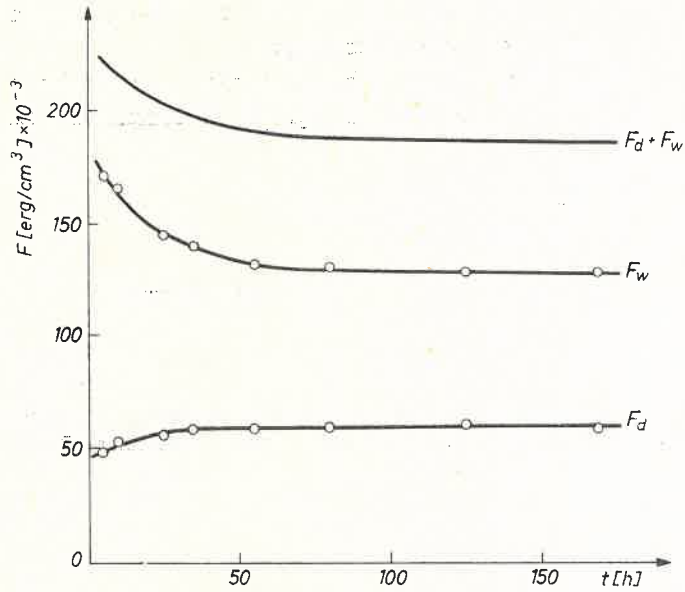


Fig. 5. The depolarization and wall energy change during evolution of TGS crystal tempered for 1 hour at a temperature  $T = T_c - 0.5 \text{ K}$ ; the wall energy density  $\sigma = 49 \text{ erg}/\text{cm}^2$

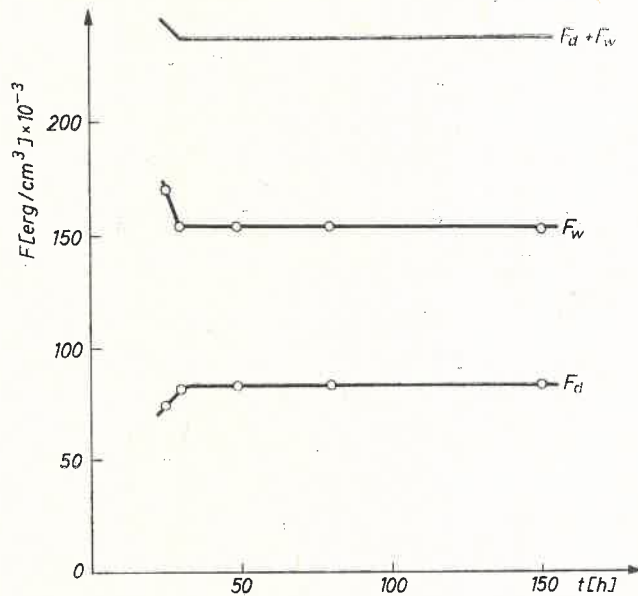


Fig. 6. The depolarization and wall energy change during evolution of TGS crystal tempered for 22 hours at a temperature  $T = T_c - 0.5 \text{ K}$ ; the wall energy density  $\sigma = 49 \text{ erg}/\text{cm}^2$

The observed domain structure is shown in Fig. 7. For the sample with thickness 1.8 mm, the average domain width varied from 12 to 14  $\mu\text{m}$ ; for the sample with thickness 1.2 mm, a narrow domain structure with average domain width 6.5  $\mu\text{m}$  was obtained.

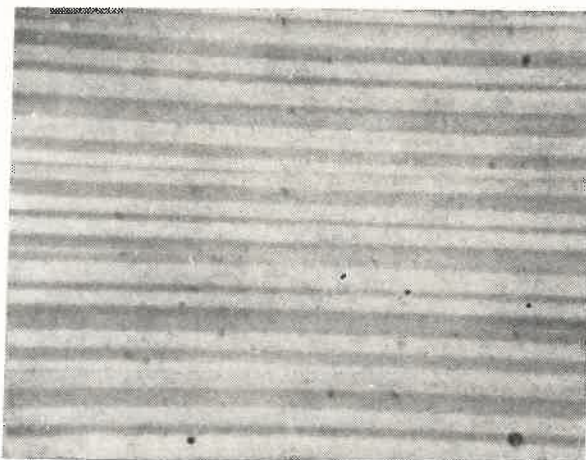


Fig. 7. A photograph of the domain structure of Rochelle Salt crystal. The observation temperature was 294K

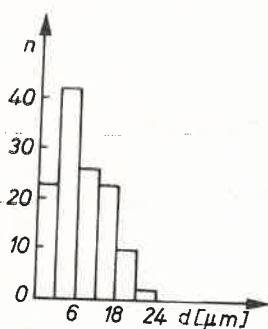


Fig. 8. The distribution of domain width in RS sample at a temperature of 294 K

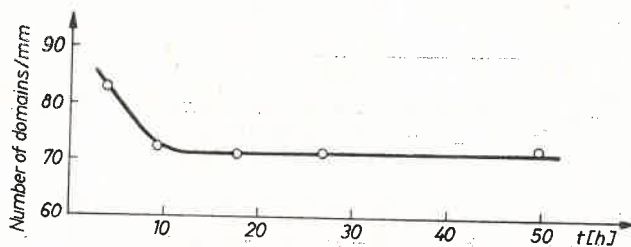


Fig. 9. The changes with time of the linear density in the number of domains in the direction perpendicular to the wall for RS samples; the cooling rate 0.005 K/min; the thickness of the sample 1.8 mm

Fig. 9 and Fig. 10 give the changes with time in the linear density of the number of domains. Using the photographs of domain structure, the domain width distribution was determined (example is shown in Fig. 8). For each of the domain width distribution,

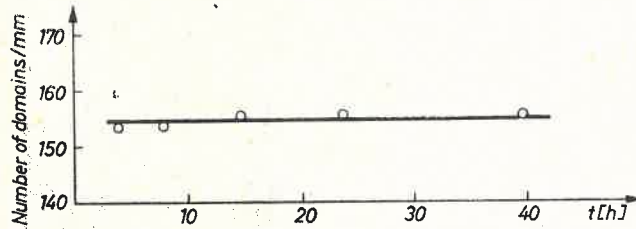


Fig. 10. The changes with time of the linear density in the number of domains in the direction perpendicular to the wall for RS crystal tempered for 2 hours at a temperature  $T = T_c - 0.05$  K; the thickness of the sample 1.2 mm

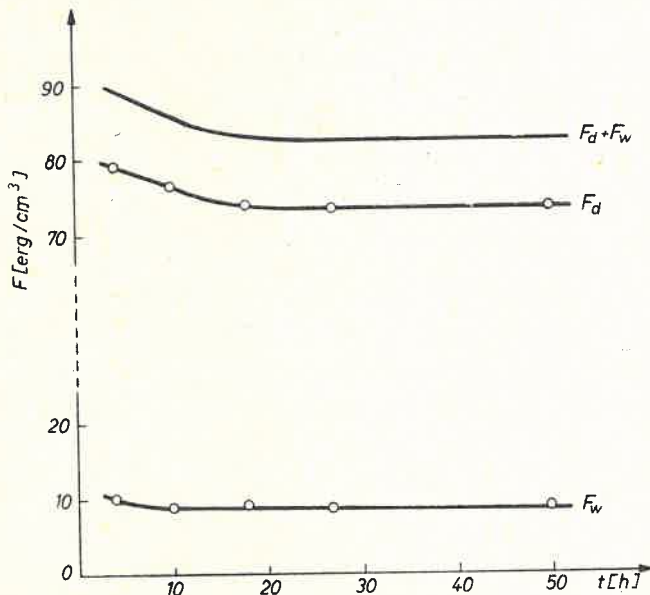


Fig. 11. The depolarization and wall energy change during evolution of RS crystal; the thickness of the sample 1.8 mm, the wall energy density  $\sigma = 0.012$  erg/cm<sup>2</sup>

there was calculated, using formula (3), the depolarization energy of the domain structure. The dependence on time of the depolarization energy  $F_d$  and the wall energy  $F_w$  of the domain structure are given in Fig. 11 and Fig. 12. The wall energy density  $\sigma$  was estimated using the formula of Zhirnov (1958) and his results.



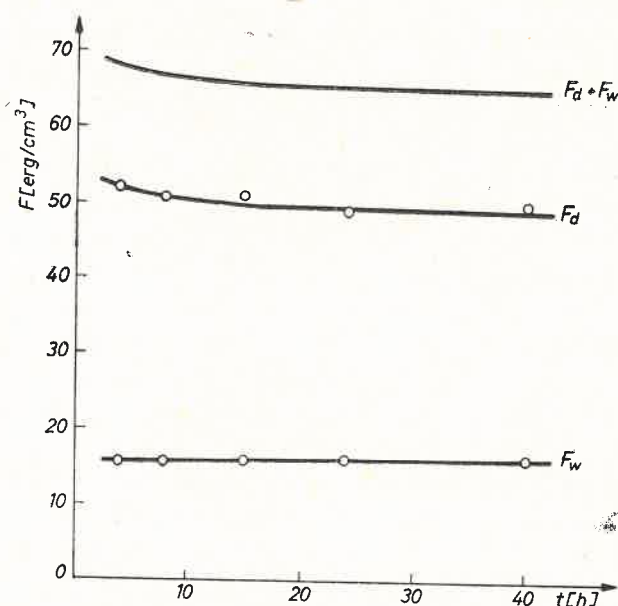


Fig. 12. The depolarization and wall energy change during evolution of RS crystal tempered at a temperature  $T = T_c - 0.05$  K; the thickness of the sample 1.2 mm, the wall energy density  $\sigma = 0.012$  erg/cm<sup>2</sup>

#### 4. Discussion and conclusion

It was shown that the layered domain structure in equilibrium must meet the demand of its periodicity as well as the demand of equal area of domains polarized in the opposite direction.

We see that the investigation of the periodicity of the domain structure gives us a possibility for a better understanding of the evolution process of the domain structure of the ferroelectric crystals. The evolution process may be divided into two subsequent processes. At first, the change in the number of domains takes place. This changes cause larger disturbances in the domain structure. Very often, during changes in the number of domains, a deviation from periodicity of the domain structure is increased. After the number of domains remains constant, the domain structure becomes more ordered and the periodicity of the domain structure increases. It was observed that the rate of the evolution process decreases at temperatures far below transition temperature and as well for the aged samples.

Figs 5 and 6 give the dependence of the depolarization energy and the wall energy of the same sample of TGS crystal. One can see that the energy changes caused by the disordered arrangement of domains are relatively small compared to the depolarization energy or to the wall energy. Therefore, the process of approaching periodicity may be observed only if changes in energy caused by diminishing the number of domain walls are small.

The domain structures were obtained each time after a prolonged heating at 353 K and at a prescribed cooling rate through the phase transition region. One can see that the domain structures hold for a long time (22 hours) near the phase transition temperature

attains equilibrium at much shorter time than the DS of the sample hold at a temperature much below  $T_c$ .

Fig. 11 and 12 give the dependence on time of the depolarization energy and the wall energy of DS of Rochelle Salt. The DS was formed very near the transition temperature. The number of domains change very little for both DS. The main changes of DS were in this case due to an improved periodicity. In order to be able to compare the domain structure contribution to the energy of the crystal, for each sample, the energy density of the sum of all energies pertaining to the domain structure was calculated. One can see that the wall energy and the depolarization energy of the investigated domain structures are of the same order of magnitude.

The present investigations have also shown that a decrease in the number of domains very often induces an increase in the unperiodical arrangement of domains. This disordering process is a dominant one for samples experiencing abrupt cooling in the phase transition region. The conditions for an arrangement of domains stabilized in time and meeting the equilibrium demands are the aim of the investigation to follow.

#### REFERENCES

- Fousek, J., Proc. of the European Meeting of Ferroelectricity Saarbrücken 147, 1969.  
 Fousek, J., Safrankova, M., *Jap. J. Appl. Phys.* **4**, 403 (1965).  
 Jaśkiewicz, A., Daszczyńska, W., Dąbrowska, K., Wrocław University, Inst. of Exp. Physics, Preprint 1976.  
 Kittel, Ch., *Rev. Mod. Phys.*, **21**, 541 (1949).  
 Konstantinova, W. P., Stankowska J., *Kristallografiya*, **15**, 382 (1970).  
 Landauer, R., *J. Appl. Phys.* **28**, 227 (1957).  
 Mitsui, T., Furuichi, J., *Phys. Rev.* **159**, 193 (1953).  
 Moravec, F., Konstantinova, W. P., *Kristallografiya* **13**, 284 (1968).  
 Safrankova, M., *Czech. J. Phys.* **B7**, 797 (1970).  
 Stankowska, J., Czosnowska, E., *Acta Phys. Pol.* **A43**, 641 (1973).  
 Taurel, L., Gilletta, F., Proc. Int. Meeting on Ferroelectricity Prague 1966, p. 43.  
 Zheludev, J. S., Shuvalov, L. A., *Kristallografiya* **1**, 681 (1956).  
 Zhirnov, V. A., *Zh. Exp. Teor. Fiz.* **35**, 1175 (1958).