

X-RAY TOPOGRAPHIC STUDY OF DOMAIN WALL MOVEMENT IN T. G. S.

Abstract. — During the X-Ray study of domains in ferroelectric T. G. S., we noticed random fluctuations of the X-Ray intensity diffracted by the sample. These fluctuations are shown to be related with domain boundaries oscillations due to a thermal gradient between the faces and the core of the sample, as the external temperature of the sample fluctuates. The understanding of this effect led us to attribute a special specific heat to the domain boundaries. The specific heat of a multidomain sample is therefore bigger than that of a monodomain sample. The increase of the number of domains and therefore of the walls in the vicinity of the Curie point allows us to give, with a semi-quantitative agreement, an interpretation for the difference between the specific heat increase observed experimentally (Taraskin [9] and Strukov [10]) and the increase predicted by the thermodynamical theory.

1. Introduction. — Ferroelectric domain boundaries in T. G. S. have been observed for the first time inside the crystal with X-Ray transmission topography (Lang method [1]) by J. F. Petroff [2], who explained their visibility. The polarization varies inside the domain wall. Due to piezoelectrically induced strains, this region diffracts X-Rays with a high reflecting power, and domain walls are visible with certain reflections, particularly with 140 reflections. For these reflections, a diffracted intensity I_w proportional to the domain wall volume (not negligible because domain wall width is $\delta \simeq 0.5 \mu\text{m}$ according to Petroff (2)) must be added to the intensity I_c diffracted by the perfect crystal and by the defects (dislocations, etc...) included in the crystal. The bigger the number of domains and the smaller the number of defects, the more important I_w becomes relatively.

The influence of temperature on T. G. S. can be felt in two ways : through a static effect and a dynamical effect.

2. Static temperature effect. — The number of domains as revealed on X-Ray topographs (Fig. 1) and the X-Ray intensity increase with temperature from room temperature to the Curie point (Fig. 2). At the Curie point, 49 °C, domains and domain walls disappear, the X-Ray intensity falls down (Fig. 2) and stays at this low value at temperatures higher than the Curie temperature. This dependence of the X-Ray intensity on temperature in ferroelectric crystals has been observed for the first time by Miyake [3] on Rochelle salt.

3. Dynamical temperature effect. — The effect of a thermal gradient ($\Delta T/\Delta x$) on a T. G. S. sample is very important in the ferroelectric phase, where domain walls are present, and negligible in the paraelectric



FIG. 1. — Section topographs of the same area of a T. G. S. sample at different temperature. 140 reflection (21 x).

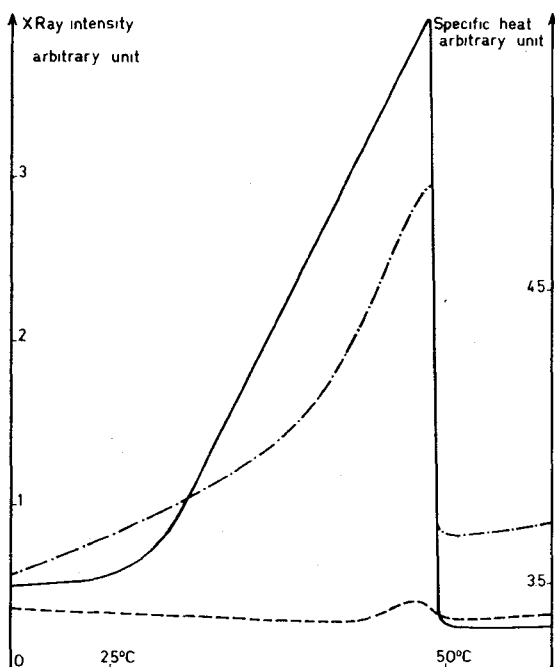


FIG. 2. — The dependence with temperature of : 1) The X-Ray intensity : 140 reflection (domains are visible) (solid curve) ; 200 reflection (domains are not visible) (broken curve). 2) The specific heat : Strukov measurements (10) (interrupted curve).

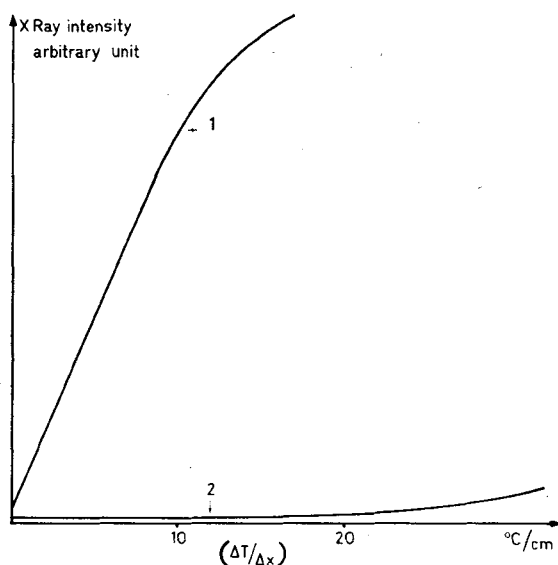


FIG. 3. — The X-Ray intensity dependence with thermal gradient ($\Delta T/\Delta x$) : 1) The crystal is in the ferroelectric phase ; 2) The crystal is in the paraelectric phase.

phase (Fig. 3). Indeed, a thermal gradient acts as a force on moving ions in a dielectric sample (i. e. Marvan [4]). If we suppose, in addition, that these ions are the ions responsible for the polarization inside the domain walls, and are not free, but bonded, it is equivalent to attribute to the domain walls a special specific heat C_w . If the temperature of the wall varies by ΔT , the energy per unit area of the wall will vary by

$\Delta W = C_w \Delta T$. In a thermal gradient ($\Delta T/\Delta x$), the unit area of the wall will be submitted to a force

$$F = \frac{\Delta W}{\Delta x} = C_w \frac{\Delta T}{\Delta x}.$$

A thermal gradient $\Delta T/\Delta x$ is therefore equivalent to an electric field E applied to the sample :

$$C_w \frac{\Delta T}{\Delta x} = 2 P_s E$$

where P_s is the spontaneous polarization.

4. Fluctuations of the X-Ray intensity. — The intensity of the X-Ray diffracted beam, for reflections showing the domain walls, presents random fluctuations which have been proved to be connected with random fluctuations of the external temperature of the sample and with the presence of domain walls in the samples : fluctuations disappear when the crystal is made a single domain and above Curie temperature. Numerical values of the relative amplitude of the fluctuations ($\Delta I_w/I_w = 1.6$) compared with the variation of the temperature ($\Delta T = 0.12^\circ\text{C}$) showed that it could not be explained by the static effect of temperature.

On the contrary, it is explained by the dynamical effect if we suppose that an oscillating thermal gradient of 0.25°C/cm amplitude is established between the faces and the core of the crystal (5 mm thick), when the external temperature of the sample fluctuates, since T. G. S. is a bad thermal conductor.

We obtain similar X-Ray intensity fluctuations with an oscillating electric field of 30 V/cm (10^{-1} C. G. S.) or a thermal gradient of 0.25°C/cm with a period of 180 s.

This enables us to determine the specific heat $C_w = 6 \times 10^3\text{ erg/cm}^2\text{ }^\circ\text{C} = 10^8\text{ erg/cm}^3\text{ }^\circ\text{C}$ (with $\delta = 0.5\text{ }\mu\text{m}$). An oscillating electric field as well as a thermal gradient induce oscillations of the domain walls : the amplitude x_0 of the oscillation displacement of the wall can be calculated from the theoretical results by Kittel [5] and Sannikov [6], using experimental data given by Fousek [7], and making the same assumption on the origin of the polarization as Bersuker [8]. Taking into account the particular domain structure we had in our experiments on fluctuations, as revealed on X-Ray topographs, we obtain $x_0 = 0.16\text{ }\mu\text{m}$. As we have seen before, the X-Ray intensity I_w due to domain walls is proportional to the domain wall width δ . Here domain walls are moving, the volume of the additional deformed crystal and the additional X-Ray intensity (ΔI_w) are now proportional to $2x_0$:

$$\frac{\Delta I_w}{I_w} = \frac{2x_0}{\delta} = 0.6.$$

The order of magnitude is in agreement with our experimental result ($\Delta I_w/I_w = 1.6$). A better agreement would be illusive, because of the unaccuracy in determin

ing the contribution I_w of the walls to the X-Ray intensity in this experiment.

5. Interpretation of specific heat measurements by Taraskin [9]. — An additive specific heat due to domain walls compared with an additive X-Ray intensity could give an interpretation for the qualitative analogy between specific heat and X-Ray intensity dependence with temperature (Fig. 2 [10]).

Numerically we can account for the jump of the specific heat in the vicinity of the Curie point observed by Taraskin [9] and not completely explained by the thermodynamical theory.

Near the Curie point in the ferroelectric state, domains are small and numerous; the volume of the walls is therefore important. We estimate it from our section topographs and from our X-Ray intensity measurements.

At 25 °C :

$$C_1 = C_c + v_1 C_w \quad I_1 = I_c + v_1 I_w = 12$$

(arbitrary units).

Where $C_c(I_c)$ is the specific heat (X-ray intensity) of a monodomain sample and v_1 the wall volume in one cm^3 of crystal. We estimate from our section topograph

$$v_1 = 2.5 \times 10^{-3} \text{ cm}^3 \quad \text{with} \quad \delta = 0.5 \mu\text{m}.$$

At $T \simeq T_c$ in the ferroelectric phase

$$C_2 = C'_c + v_2 C'_w \quad I_2 = I_c + v_2 I'_w = 109.$$

Where C'_c is the specific heat of a monodomain sample

at $T \simeq T_c$, $C'_w(I'_w)$ the specific heat (X-ray intensity) per unit volume of the wall at $T \simeq T_c$.

At $T \simeq T_c$ in the paraelectric phase

$$C = C'_c \quad I = I_c = 6.$$

The thermodynamical theory gives

$$C''_c - C'_c = 0.24 \times 10^7 \text{ C. G. S.}$$

We suppose that the specific heat of the domain walls has the same dependence with temperature as the X-ray intensity I_w , that means $I_w/C_w = I'_w/C'_w$. Then, from our X-ray measurements and from $C_w = 10^8 \text{ C. G. S.}$, we can deduce $v_2 C'_w = 0.4 \times 10^7 \text{ C. G. S.}$ therefore,

$$C_2 - C = 0.64 \times 10^7 \text{ C. G. S.}$$

The experimental measurement of Taraskin [9] gives

$$C_2 - C = 0.5 \times 10^7 \text{ C. G. S.}$$

This is in good agreement considering that our calculations are made with the assumption that I_w and C_w vary in the same way from the room temperature to the Curie point.

In conclusion, if we assume that supplementary specific heat can be associated to the domain walls, we can explain X-ray intensity fluctuations with temperature.

Further, it appears that the domain structure contributes to the specific heat jump observed experimentally.

It would be interesting to find a microscopic origin for the specific heat of the domain walls.

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