

on each turn around the dislocation. Each resulting twin can act as a growth center so that the edges of the platelet can grow uniformly.

This mechanism should be applicable to many other structures besides that of silicon carbide. It seems clear that, in all cases in which the screw dislocation process is presumed to account for growth through addition of layers, the problem of lateral propagation of the substrate or initial layers will arise. In many structures, although not all, it will be found that, just as in the discussion of Fig. 11, the presence of a twin plane will make propagation in some specific direction, or set of directions, easier than for any possible direction in the untwinned structure. The growth system would then combine lateral extension of an initial layer array containing one or more twins, with the addition of further layers by the screw mechanism.

It has been pointed out to us by Hamilton that Frank⁷ and Amelinckx⁸ have explained interlacing spiral patterns observed on SiC as being due to directional dependence of growth velocity. The detailed bonding mechanism proposed by Billig² for adding layers in the diamond structure may be operative in α -SiC; the directions of best growth would rotate 60° with each twin, resulting in the observed interlacing. It is thus apparent that all mechanisms proposed for dendritic growth may be operative in the vapor growth of α -SiC as well.

Some effects of twinning on enhanced crystal growth have been reported by Frank⁹, and by Dawson.¹⁰

⁷ F. C. Frank, *Phil. Mag.* **41**, 200 (1951).

⁸ S. Amelinckx, *Nature* **168**, 431 (1951).

⁹ F. C. Frank, *Discussions Faraday Soc.* **5**, 186 (1949).

¹⁰ I. M. Dawson, *Proc. Roy. Soc. (London)* **A214**, 72 (1952).

Switching Mechanism in Triglycine Sulfate and Other Ferroelectrics

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The reversal of the spontaneous polarization in a ferroelectric crystal is governed by two mechanisms: the nucleation of new domains and the growth of these domains by domain wall motion. We have investigated the switching properties of triglycine sulfate (TGS) as a function of applied electric field, temperature, and thickness of the samples.

It is proposed that at low fields nucleation is the slower mechanism and hence dominates the switching process while at high fields domain wall motion determines the rate of switching. The former process leads to an exponential dependence of switching time on applied electric field and the latter to a linear dependence.

A model for the nucleation and domain wall motion is treated mathematically and is compared with experimental observations. The shape of the switching current pulse was found to yield much information. The shape depends strongly on the applied electric field and is correlated with the nucleation time as well as the domain wall motion time. The asymmetry of the pulse increases with decreasing field and can be associated with the interaction between domains and domain nuclei. This interaction in various ferroelectrics is discussed and its relation to the switching is considered.

1. INTRODUCTION

A NUMBER of investigators have dealt with the problem of determining the mechanism by which the spontaneous polarization in a ferroelectric material is reversed. Merz,^{1,2} Little,³ Wieder,⁴ Landauer-Young-Drougard,^{5,6} Chynoweth,⁷ Miller,⁸ and Burfoot⁹ have examined this process in BaTiO₃ while similar studies have been conducted on Rochelle salt (RS) by Wieder¹⁰

on guanidine aluminum sulfate hexahydrate (GASH) by Prutton¹¹ and Wieder¹² and on triglycine sulfate (TGS) by Pulvari and Kuebler.¹³ From these studies it is generally concluded that two steps are involved in the switching process: nucleation of ferroelectric domains at the surface of the sample followed by growth of these domains through the crystal by domain wall motion.

It is assumed, on the basis of phenomenological arguments, that nucleation of domains is a statistical process while the domain wall motion is assumed to be controlled by a kind of viscous drag.

In this paper we shall discuss the switching properties of triglycine sulfate (TGS), a ferroelectric discovered

¹ W. J. Merz, *Phys. Rev.* **95**, 690 (1954).

² W. J. Merz, *J. Appl. Phys.* **27**, 938 (1956).

³ E. A. Little, *Phys. Rev.* **98**, 978 (1955).

⁴ H. H. Wieder, *Phys. Rev.* **99**, 1161 (1955).

⁵ Landauer, Young, and Drougard, *J. Appl. Phys.* **27**, 752 (1956).

⁶ R. Landauer, *J. Appl. Phys.* **28**, 227 (1957).

⁷ A. G. Chynoweth, *Phys. Rev.* **110**, 1316 (1958).

⁸ R. C. Miller, *Phys. Rev.* **111**, 736 (1958).

⁹ J. C. Burfoot, *Proc. Phys. Soc. (London)* **73**, 641 (1959).

¹⁰ H. H. Wieder, *Phys. Rev.* **110**, 29 (1958).

¹¹ M. Prutton, *Proc. Phys. Soc. (London)* **B70**, 1064 (1957).

¹² H. H. Wieder, *Proc. Inst. Radio Engrs.* **45**, 1094 (1957).

¹³ C. F. Pulvari and W. Kuebler, *J. Appl. Phys.* **29**, 1742 (1958).

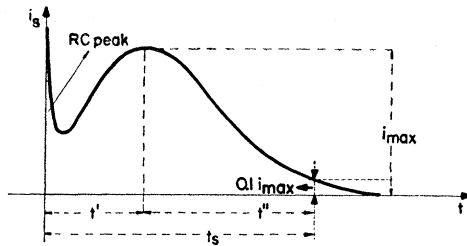


FIG. 1. Observed switching current i_s versus time t in a ferroelectric crystal. Symmetry m is arbitrarily defined as t'/t'' .

by Matthias, Miller, and Remeika¹⁴ and whose dielectric properties were investigated by Hoshino, Mitsui, Jona, Pepinsky,¹⁵ and by Pulvari and Kuebler.¹³ TGS possesses a low coercive field and a relatively large spontaneous polarization which makes it highly suitable for these investigations.

2. EXPERIMENTS

The switching in TGS was studied by the conventional technique in which one measures the current i_s which flows through a series resistor to the crystal electrodes as a function of time t . First, an electrical square pulse is used to align all the dipoles in one direction, then a second pulse of opposite polarity is used to measure the switching current as function of time. The behavior of current with time is shown in Fig. 1.

The quantities of interest are: i_{\max} , the maximum switching current; t_s , the switching time; t' , the rise time; t'' , the decay time; and $m = t'/t''$, the symmetry of the pulse, as indicated in the figure. Three of these parameters, i_{\max} , t_s , and m , are sufficient to define all five quantities. All five variables are functions of the applied field, the temperature, the geometry and the history of the sample. For a given temperature the switching time t_s decreases and the maximum switching current i_{\max} increases with increasing applied electric

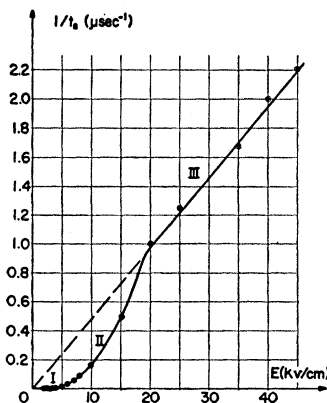


FIG. 2. Reciprocal switching time $1/t_s$ versus applied field E in TGS.

field, while the switched charge remains constant. This charge is equal to:

$$Q_s = 2P_s\sigma = t_s i_{\max} f, \quad (1)$$

where P_s is the spontaneous polarization, σ is the electrode area and f is a factor of the order of 0.5 to 1.0, which allows for the shape of the i_s-t curve. If f remains constant, i_{\max} and $1/t_s$ show exactly the same dependence on the magnitude of the field.

2.1. Field Dependence of the Switching Time in Triglycine Sulfate (TGS)

In Fig. 2, $1/t_s$ is plotted as a function of applied field E . The curve can be subdivided into 3 parts: a first part (I), which is curved, a second part (II), which is less curved and a third part (III) which is linear and whose extrapolation passes through the origin or very close to it. Between parts II and III there occurs an inflection point (see Prutton¹⁶ on the polarization

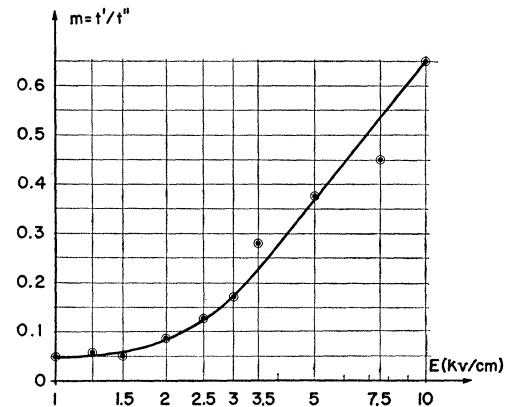


FIG. 3. Symmetry m of the switching pulse versus electric field E in TGS.

reversal process in ferroelectrics). In region III there is apparently a linear dependence of $1/t_s$ on E :

$$1/t_s = kE. \quad (2)$$

Unfortunately the available voltage range in part III is too small to permit establishing this relation unambiguously.

Part I, on the other hand, can be fitted over 4 decades by an exponential law (see Merz¹ in BaTiO₃) of the form:

$$(1/t_s) = (1/t_0) \exp(-\alpha/E), \quad (3)$$

where t_0 and α are constants.

2.2. Shape of the Switching Pulse in TGS

An investigation of the shape of the switching current as a function of applied field shows that the symmetry $m = t'/t''$ depends strongly on the applied field as shown in Fig. 3. At a field strength of 10⁴

¹⁴ Matthias, Miller, and Remeika, Phys. Rev. **104**, 849 (1956).

¹⁵ Hoshino, Mitsui, Jona, and Pepinsky, Phys. Rev. **107**, 1255 (1957).

¹⁶ H. Prutton, J. Brit. Inst. Radio Engrs. **19**, 93 (1959); Fig. 3.

v/cm, m is of the order of 0.5. With decreasing field the symmetry is reduced and for very low fields m reaches a value m_0 which is low but not zero. The dependence of the "rise time" t' on the field E in the low-field region is shown in Fig. 4. It depends quadratically on E except at extremely low fields where an exponential behavior can be observed. An exponential behavior is expected for very low fields since m_0 is then constant and t_s depends exponentially on the field.

2.3. Thickness Dependence of the Switching Time

For field strengths larger than 10^4 v/cm a quadratic dependence of the switching time on thickness of the sample is observed, (Fig. 5). In this experiment a voltage pulse of 500 v was applied to samples of thicknesses between 0.005 cm and 0.05 cm corresponding to fields of 10^4 to 10^5 v/cm. For field strengths smaller than 10^4 v/cm no simple relation between switching time and thickness could be found.

2.4. Switching in Steps at Low Fields

If a pulse of duration greater than the switching time is applied to a ferroelectric crystal, it is switched

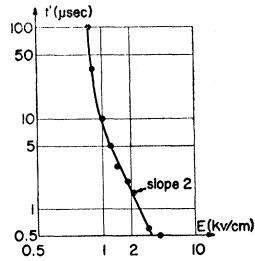


FIG. 4. Rise time t' of the switching pulse versus applied field E in TGS.

completely and a normal current pulse is observed [Fig. 6(a)]. On the other hand, if voltage pulses much shorter than t_s are applied there is no net reversal of polarization even upon successive unidirectional switching. The switching transient appears as shown in Fig. 6(b). There is a critical pulse length t^* at which the crystal begins to switch and if a series of pulses each longer than t^* is applied, the polarization can completely be reversed [Fig. 6(c)]. It is interesting to note that in this case the shape of the individual small current pulses fit together and add up to the normal pulse except for the initial peaks A, B, C, D, E, F . The critical time t^* depends on the amplitude of the applied pulse: it is a very small fraction of t_s at very low fields and almost equal to t_s for fields of about 20 kv/cm (see also Zen'iti *et al.*¹⁷).

2.5. Heating Experiments

In order to distinguish between processes which take place at the crystal surface and those occurring in the

¹⁷ Zen'iti, Husimi, and Kataoka, J. Phys. Soc. Japan 13, 661 (1958); Fig. 3.

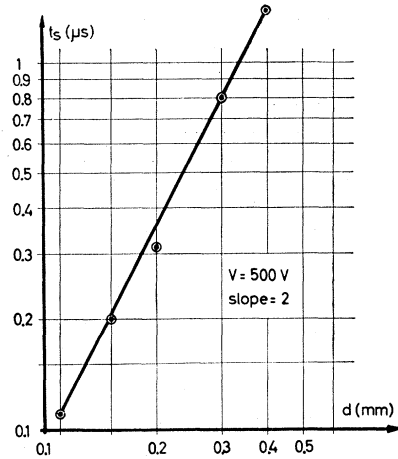


FIG. 5. Switching time t_s versus thickness d of the sample. Applied voltage = 500 v.

bulk, the influence of inhomogeneous heating of the sample was investigated. A small heater was placed in front of the electrode of a TGS sample for a time short enough to influence the temperature of the surface only. It is anticipated that the surface temperature primarily determines the nucleation rate, whereas the temperature of the bulk affects primarily the domain wall motion.

At low switching fields ($< \sim 10^4$ v/cm) surface heating has a large influence on the length of the switching pulse, but less on its rise time. With high switching fields the surface heating has a strong effect on the rise time of the switching transient but not on the decay time (and hence the change in pulse length is not so pronounced as in the former case).

At low fields with heating times of the order of a few seconds during which only the surface is warmed, the pulse becomes narrower and higher. Upon cooling

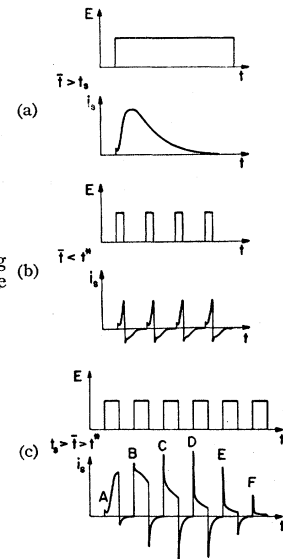


FIG. 6. Full and partial switching current i_s versus time t in TGS. The length of the individual pulse is t .

the pulse returns to its original shape passing through the same intermediate stages as appeared during warming. If, on the other hand, the crystal is warmed for a period of the order of 30 minutes a pronounced difference is observed between the heating pulse shape and that occurring during cooling. During heating the pulse initially becomes narrower and higher as previously and upon continued heating, the pulse becomes so narrow as to be nearly unobservable. Upon cooling the decay time rapidly returns to its initial value while the rise time remains unobservable. After about 15 minutes of cooling the pulse is once more back to its original shape. This asymmetry between heating and cooling is interpreted to be a consequence of nonuniform heating in which the bulk remains cool while the surface warms quickly, and nonuniform cooling during which the bulk remains warm while the surface cools quickly. Further discussion of these phenomena will be found below.

3. DISCUSSION OF FIELD AND THICKNESS DEPENDENCE OF THE SWITCHING TIME

In the introduction a two-step process was proposed for the switching in ferroelectrics: nucleation of domains and domain wall motion. The experimental results just discussed will be interpreted on the basis of this model. Let us define the "nucleation time t_n " as the time necessary to form all nuclei, from the first to the last, and the "domain wall motion time, t_d " the time necessary for one domain to grow through the sample. The total switching time can then be approximated by

$$t_s \cong t_n + t_d. \quad (4)$$

We assume that the domain wall motion can be described by

$$v = d/t_d = \mu E = \mu V/d, \quad (5)$$

where d is the distance the wall travels and μ is the mobility of the domain wall. In Eq. (5) the coercive field strength for domain wall motion is neglected. This assumption agrees with the experimental results.

From Eq. (5) it follows that

$$1/t_d = \mu E/d = KE = \mu V/d^2, \quad (6)$$

with $K = \mu/d$.

On the other hand, we assume in our model that the nucleation of new domains is governed by a statistical law, in which at low fields, the probability of forming new domains depends exponentially on the applied field in the following¹ way:

$$p_n = p_0 \exp(-\alpha/E),$$

and hence

$$(1/t_n) = (1/t_0) \exp(-\alpha/E). \quad (7)$$

This particular dependence of nucleation time on electric field fits our experimental results on TGS as will be shown, and further this form is the same as that found for BaTiO₃.¹ By proper choice of the parameters

K , t_0 , and α of Eqs. (6) and (7), one can fit the low-field range of the experimental curve with Eq. (7) and the high-field range with Eq. (6), as is shown in Fig. 7. Since $1/t_s = 1/(t_n + t_d)$, one can conclude that the switching time t_s is determined principally by the slower of the two mechanisms (nucleation or domain wall motion). At low fields (region I of Figs. 2 and 7) the rate of nucleation is low so that the switching is primarily governed by the nucleation ($t_n \gg t_d$) which then leads to an exponential law for the switching time [Eqs. (4) and (7)]. On the other hand, we have to assume that at high fields (region III of Figs. 2 and 7) the rate of nucleation is extremely large so that the switching time is primarily determined by the velocity of the domain walls ($t_d \gg t_n$). This then leads to the linear dependence of $1/t_s$ on E , Eqs. (4) and (6), as observed experimentally. Since it appears that at high fields $t_d \gg t_n$, then t_n must deviate from the behavior described in Eq. (7) at fields higher than 15 kv/cm and must decrease much faster than described by this equation. With this assumption, the fit with the experimental results is very good (Fig. 7).

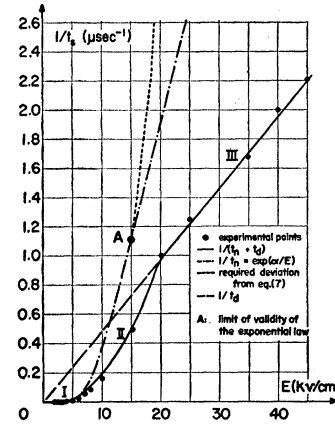


FIG. 7. Reciprocal switching time $1/t_s$, domain wall motion time $1/t_d$, and nucleation time $1/t_n$ versus applied field E for TGS.

Also the quadratic thickness dependence of the switching time at high fields ($E > 10^4$ v/cm) as shown in Fig. 5 fits our model [see Eq. (6)].

At this point, however, it is important to distinguish between domain wall motion in the forward and sidewise directions. The fact that we do observe a quadratic dependence on crystal thickness indicates that in TGS the forward motion is very much faster than any sidewise motion, under the assumption that the mobility μ is not field dependent.

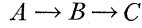
Before we can discuss other experimental results we have to develop our model further, which will be done now.

4. FURTHER DEVELOPMENT OF THE PROPOSED MODEL

Some of the properties of the nucleation time t_n , domain wall motion time t_d , rise time t' and decay time t'' are summarized in Tables I and II. It can be concluded from the relationships described in Tables I and

II that it is not unreasonable to attempt to correlate the shape of the switching pulse with the two switching mechanisms by identifying t'' with t_n and t' with t_d . It is difficult, however, to understand why the rise time, which precedes the decay time, should be due to domain wall motion, which must follow nucleation.

For the reversal of polarization we consider three states for each nucleus:



(A) latent nucleus, not formed yet; number= n_1 ; (B) nucleus formed; number= n_2 ; (C) nucleus grown through the sample; number= n_3 .

4.1. Transition (B)–(C)

For the transition (B)–(C) we assume that (a) all the nuclei start growing as soon as they are formed; (b) they grow primarily in the forward direction; (c) they all take the same time, t_d , to grow through the crystal and (d) the contribution of each growing domain to the observed current is not constant during its growing process. The contribution to the observed current can vary with the position of the growing domain because first, the velocity can be a function of position and

TABLE I. Relationship between t_d and t_n .

Low fields	Intermediate fields	High fields
$t_d \ll t_n$ $t_s \cong t_n = t_0 \exp(\alpha/E)$	$t_d \cong t_n$	$t_d \gg t_n$ $t_s \cong t_d = (KE)^{-1}$

second the rate of change of the neutralizing charge on the electrode area (which is the measured current) can also depend on position. The latter point is a consequence for example of a conical shaped domain growing with uniform velocity through the crystal. Although alternative models can be employed to describe these experiments, the one suggested above is the simplest one which fits the experimental evidence.

If we denote the total number of nuclei, latent, formed and growing, and already grown, by

$$N = n_1 + n_2 + n_3, \quad (8)$$

and the fraction already formed by

$$\nu = \frac{n_2 + n_3}{N} = \frac{N - n_1}{N}, \quad (9)$$

we can write for the number dn of domains created between the time τ and $\tau + d\tau$

$$dn = N (dv/dt)_{t=\tau} d\tau. \quad (10)$$

Their contribution to the current at the time t is

$$di_s = N (dv/dt)_{t=\tau} \eta d\tau, \quad (11)$$

where the time t is the time at which an observation

TABLE II. Properties of t' and t'' .

Low fields	Intermediate fields	High fields
$t' \ll t''$ $t_s \cong t'' = t_0 \exp(\alpha/E)$	$t' \cong t''$	could not be measured

is made (the pulse is applied at $t=0$) and represents the time at which a particular domain is formed. The quantity η is a function of the interval $(t-\tau)$ and represents the contributions to the total current due to the growth of a single domain. The total current is then

$$i_s(t) = N \int_0^t \left(\frac{dv}{dt} \right)_{t=\tau} \eta d\tau. \quad (12)$$

We assume, like Landauer, Young, and Drougard⁵ that η first increases and then decreases. One can explain the decreasing part of η , because when the apex of the conical domain reaches the opposite electrode its contribution to the current will fall rapidly as the angle between the domain wall and the plane of the electrode approaches 90° (Fig. 8). If it is assumed that the decreasing tail of the switching pulse of a single domain carries most of the charge (which would correspond to the observed shape of the Barkhausen pulse⁷), then it suffices to consider only that part of η corresponding to this tail. Since a rapidly decreasing function of any arbitrary form lead to essentially the same conclusion we have taken, for simplicity, the following relationship:

$$\eta = \eta_0 \exp[-(t-\tau)/\tau_2], \quad (13)$$

where η_0 and τ_2 are constants and $(t-\tau)$ is equal to zero at the time when the nucleus is formed.

By integration of Eq. (13) it is seen that the charge collected on the electrode due to the growth of a single domain increases during growth according to an exponential law. Hence it is necessary to make an arbitrary definition of t_d which for our purposes is chosen as

$$t_d = 2.3\tau_2. \quad (14)$$

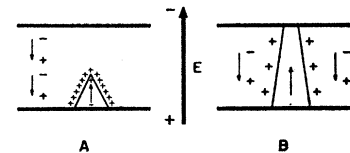
Combining Eqs. (12) and (13), we have

$$i_s(t) = N\eta_0 \int_0^t \left(\frac{dv}{dt} \right)_{t=\tau} \exp\left(-\frac{t-\tau}{\tau_2}\right) d\tau. \quad (15)$$

From this we can calculate the shape of the switching current once we know the rate of the creation of new nuclei. By differentiation of Eq. (9) we obtain

$$Ndv/dt = -dn_1/dt, \quad (16)$$

FIG. 8. Figure demonstrating the growth of domains through the sample.



which with Eq. (15) leads to

$$i_s(t) = -\eta_0 \int_{t=\tau}^t \left(\frac{dn_1}{dt} \right)_{t=\tau} \exp\left(-\frac{t-\tau}{\tau_2}\right) d\tau. \quad (17)$$

4.2. Transition (A) — (B)

To evaluate Eq. (17) it is necessary to calculate dn_1/dt from the transition (A) — (B). We have assumed that this transition is governed by a statistical law. The statistical law implies that infinite time is necessary to form all the nuclei. We therefore redefine the nucleation time t_n as the time necessary to form 90% of the nuclei. In the case that $p_1 = \text{const} = 1/\tau_1$ (see below)

$$t_n = 2.3\tau_1. \quad (18)$$

The probability p_1 of the transition (A) to (B) is in general a function of n_1, n_2, n_3 , and t , where only two of the n 's are independent (Eq. 8). It is furthermore assumed that p_1 is independent of time.

The fact that p_1 is a function of n_2 and n_3 can be interpreted as an interaction between domains and nuclei; the number of growing and already grown domains influences the probability of the formation of new nuclei. As a first approximation it can be assumed that this interaction is nearly the same whether the existing domain is small or has already grown through the sample. That is, we express p_1 in the form

$$p_1 = f(n_2 + n_3), \quad (19)$$

and since $n_2 + n_3 = N - n_1$, we can write p_1 as a function of n_1 alone, i.e.,

$$dn_1/n_1 = -p_1(n_1)dt, \quad (20)$$

with the boundary condition

$$n_1(0) = N.$$

As demonstrated below, the simplifying assumption that p_1 is constant results fortunately in an expression which accounts for a major fraction of the experimental results. This assumption implies that there is no nucleus-domain interaction.

Assume $p_1 = 1/\tau_1$ to be constant, then Eq. (20) can easily be integrated yielding

$$n_1 = N \exp(-t/\tau_1), \quad (21)$$

which leads to

$$-(dn_1/dt)_{t=\tau} = (N/\tau_1) \exp(-\tau/\tau_1). \quad (22)$$

Substituting Eq. (22) into Eq. (17) gives

$$i_s(t) = i_0 [\exp(-t/\tau_2) - \exp(-t/\tau_1)], \quad (23)$$

with

$$i_0 = \frac{\eta_0 N}{\tau_1(1/\tau_1 - 1/\tau_2)}.$$

This expression is shown in Fig. 9 and will be discussed in the next section. The maximum of the current occurs at a time equal to the "rise time" t' that can be

obtained by differentiating Eq. (23) and equating it to zero. With Eqs. (14) and (18) we obtain

$$t' = \frac{1}{2.3} \frac{\ln(t_d/t_n)}{1/t_n - 1/t_d}. \quad (24)$$

5. DISCUSSION

5.1. Shape of the Switching Pulse

Equation (23) which describes the switching time under the condition of p_1 being constant is shown in Fig. 9. The switching pulse is approximated by the difference of two exponentials with the time constants τ_1 and τ_2 . The shorter of the two time constants appears as the rise time and the larger as the total switching time regardless of which happens first. (The rise time is here defined as the time required to obtain 90% of the maximum current.) Thus we can write [see Eqs. (4), (14), and (18)]: (a) at low fields ($t_d \ll t_n$), the rise time $t' \cong t_d$, the decay time $t'' \cong t_s$; (b) at higher fields ($t_d \cong t_n$), the rise time $t' \cong t_d \cong t_n$, the decay time $t'' \cong t_d \cong t_n$; which explains the results listed in Tables I and II. Introducing Eqs. (6) and (7) into Eq. (24), we obtain for the rise time at low fields (E small, $t_n \gg t_d$)

$$t' \cong \frac{\alpha d}{2.3\mu E^2}, \quad (25)$$

which shows the inverse square dependence of t' on field E as observed experimentally (Fig. 4).

On approaching very small electric fields the point is reached where the switching is determined by the rate of nucleation alone. If no interaction between domains and nuclei occurs, the current then becomes

$$i_s = \text{const}(d\nu/dt) = \text{const} \exp(-t/\tau_1), \quad (26)$$

which means that $t' = 0$ and hence the pulse symmetry $m = t'/t''$ should also be zero. Experimentally, however, one observes that m approaches a finite value m_0 which is different from zero.

It is then apparent that one cannot neglect entirely the interaction between domains and nuclei. Nucleus formation could be either hindered or enhanced by the depolarizing effects of the adjacent domains. Further, the presence of a favorably oriented domain could enhance the probability of forming a nucleus (if the shape allows it), since fewer domain walls would be required. From the present model and experiments it appears that enhancement is predominant. This

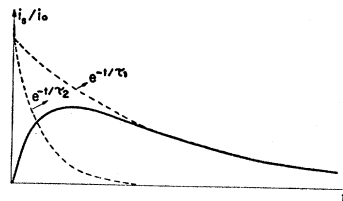


FIG. 9. Calculated switching current i_s versus time t in TGS.

enhancement of nucleation adjacent to an already formed domain gives the appearance of a sidewise domain wall motion. This is to be distinguished from a true sidewise motion in which the walls move in steps of a single row of dipoles at a time. The present experiments do not decide between these two phenomena and only the former is under consideration.

If the nucleations are aided by existing domains, then ϕ_1 increases with ν and from Eq. (9) ϕ_1 decreases with increasing n_1 . Taking Eq. (9) into account, one can write Eq. (20) as

$$N(d\nu/dt) = n_1 \phi_1(n_1), \quad (27)$$

where $\phi_1(n_1)$ is an increasing function with decreasing n_1 . Thus, the rate of nucleation shows a maximum because, at $t=0$, $d\nu/dt$ starts increasing since $\phi_1(n_1)$ is increasing. However, at a time t_0' when the number of latent domains n_1 becomes small $d\nu/dt$ must decrease. We define t_0'' as the time it takes for $d\nu/dt$ to decrease from its maximum value to 10% of it. The ratio t_0'/t_0'' can therefore be taken as a measure of interaction between nuclei and domains because if the interaction is large then t_0' becomes large and t_0'' small. At low electric fields where the current is proportional to the rate of nucleation [Eq. (26)] the ratio t_0'/t_0'' is identical with m_0 so that m_0 is not only a measure of the symmetry of the switching pulse but also a measure of the interaction between the nuclei and existing domains. The smaller m_0 , the smaller the interaction. For TGS the presence of nucleus-domain interaction was revealed by the finite experimental value for $m_0 \cong 0.05$.

5.2. Partial Switching Phenomena

In Sec. 2.4 a series of experiments were described in which pulses shorter than the switching time were applied to the crystals and the corresponding switching transients observed. In the case where $t < t^*$ [Fig. 6(b)] the net charge switched with each input pulse is zero, though the charge transferred in each direction is much greater than that associated with the stray capacitance in the system. Further, the switching transient does not have a simple exponential shape. This is interpreted to indicate that during the "on" time of the pulse domains nucleate and start to grow across the crystal. When the field is removed, however, these domains return to their initial state of polarization and no permanent switching results. It can be concluded, therefore, that the critical time t^* (2.4) is identified with domain wall motion time and under the condition of this experiment no permanent switching can take place even if very many successive pulses are applied.

In cases where $t^* < t < t_s$ the switching transients appear as shown in Fig. 6(c). In each successive pulse, some of the domains grow across the crystal and remain so polarized while others collapse back as shown by the negative portion of the pulse, until, after several pulses have been applied, the entire sample is switched. Since

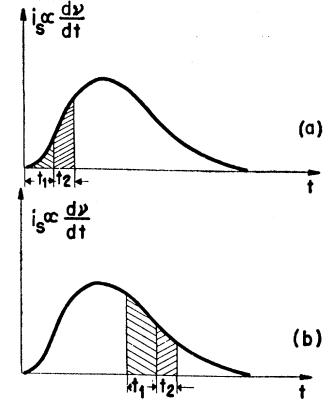


FIG. 10. Figure demonstrating the shape of the current pulses at incomplete switching. The rate of nucleation $d\nu/dt$ is plotted versus time.

the charge switched with each successive pulse increases initially and then decreases just as in the total switching pulse [Fig. 6(a)], the domains which have remained polarized increase the probability of forming new nuclei as is assumed in the present model. Further, the initial peak on each transient becomes progressively larger (these peaks, *A*, *B*, *C*, *D*, *E*, *F*, are very much larger than those caused by stray capacitance). This is interpreted in the following manner. The domains progress through the crystal in the form of cones until the apices reach the opposite electrode. At this point the walls become perpendicular to the electrode surfaces and the domains assume a more cylindrical shape. If the field is switched off before all the domains have attained this cylindrical configuration, those in which the angle between the wall and the surface is appreciably less than 90° , even if the apices of the cones have reached the opposite electrode, will collapse. At the low fields used in these experiments the switching current is determined by the rate of nucleation only and if we denote with t_1 the time it takes for the domains to reach the other surface and with t_2 the time it takes them to open up, it follows from Fig. 10 that the second shaded area represents nearly the current which flows when the corresponding pulse is applied whereas the first shaded area represents the peak which is due to the collapsed domains of the previous pulse. At the later stages [Fig. 10(a)] the first shaded area is much larger than in the earlier stages [Fig. 10(b)], which explains why the peaks *E* and *F* are larger than peaks *B* and *C*.

5.3. Heating Experiments

We have assumed in 2.5 that the heating of the surface accelerates the nucleation of new domains whereas the heating of the bulk accelerates the domain wall motion. Furthermore, we concluded that the rise time of the switching pulse at low fields is determined by the domain wall motion time and at high fields by the nucleation time. The contrary is true for the decay time. Thus heating the surface should affect the decay time of the pulse when low fields are applied and the rise time of it when high fields are applied.

TABLE III. Values of m_0 and P_s for different materials.

Material	m_0	P_s (μ coul/cm ²)
GASH	< 1/50	0.35
TGS	1/20	2.2
RS	1/10	0.24
Thiourea	$\frac{1}{2}$ estimated by Goldsmith ^a	3.2
LiH ₃ (SeO ₃) ₂	1	15.0
BaTiO ₃	1 from Merz ^b	26.0

^a G. J. Goldsmith (private communication).

^b See reference 1.

If the whole crystal is heated and then the heater is removed, one expects that the surface cools considerably while the bulk retains the heat, so that the domain wall motion is faster than at room temperature, while the nucleation rate is the same. Hence during cooling the rise time of the pulse remains much shorter than at room temperature. These observations are consistent with the proposed model.

6. COMPARISON WITH OTHER FERROELECTRIC MATERIALS

In BaTiO₃ one finds an exponential law [Eq. (3)] up to 50 kv/cm.¹ At low fields this material switches in steps like TGS when many pulses are applied. Using our model we thus conclude that in BaTiO₃ the switching is very strongly dominated by nucleation, even more so than in TGS. Furthermore, one finds in BaTiO₃ a very symmetrical switching pulse which is practically independent of applied field, that is $m = m_0 = 1$. This behavior is explained by our model by assuming a very strong nucleus-domain interaction.

Some recent experiments by Miller^{8,18} using the etching technique¹⁹ show that the domains in BaTiO₃ do grow sidewise. He found that the sidewise wall velocity varies exponentially with field, according to Eq. (3). It is rather difficult to interpret this result in terms of a normal sidewise motion, whose velocity should be expected to be linear with field. It can, however, be interpreted according to our model by assuming a continuous formation of new nuclei along the edges of a switched region. This, however, indicates the presence of a strong nucleus-domain interaction in

agreement with our observations of a large m_0 . The quantity m_0 for a number of ferroelectric materials is shown in Table III. If one compares the values of m_0 with the values of the spontaneous polarization P_s one finds that m_0 and thus the interaction between domains and nuclei increases with P_s although, of course domain-nucleus interaction cannot depend on P_s alone. The only exception in this table seems to be Rochelle salt.

Experiments of Husimi and Kataoka²⁰ on BaTiO₃ can be interpreted on the basis of our "switching in parts" results with TGS. Applying pulses of 2 kv/cm they observed a switching time of the order of 10 μ sec. With pulses of 1 μ sec duration the polarization could be reversed; however, with pulses of 0.5 μ sec duration it was not possible to do so with a reasonable number of pulses. These results can be explained by assuming that the domain wall motion times at fields of 2 kv/cm is of the order of 0.5 μ sec. If pulses shorter than 0.5 μ sec are applied the growing domains collapse upon removal of the field. With the value for the thickness given by the authors one can deduce a forward mobility of 14 cm²/v sec. This value is much higher than the one formerly estimated¹ by calculating the mobility from the slope of the linear part of the $1/t_s$ versus E curves. Because up to fields of 20 kv/cm the switching in BaTiO₃ is controlled by the nucleation, the linear part in the $1/t_s$ versus E curve is not due to domain wall motion as was assumed before. The linear part due to domain wall motion would appear at much higher fields.

Recent experiments by Stadler²¹ demonstrate that at very high fields BaTiO₃ shows the following field strength dependence of the switching time:

$$1/t_s = kE^3.$$

This behavior cannot be explained by our model without making additional assumptions.

7. ACKNOWLEDGMENTS

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¹⁹ J. A. Hooton and W. J. Merz, Phys. Rev. **98**, 409 (1955).

²⁰ K. Husimi and K. Kataoka, J. Appl. Phys. **29**, 1247 (1958).

²¹ H. L. Stadler, J. Appl. Phys. **29**, 1485 (1958).