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Autor: Fatuzzo, Ennio

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The Reversal of the Spontaneous Polarization in Guanidine Aluminium Sulfate Hexahydrate

by Ennio Fatuzzo

Laboratories RCA Limited, Zurich, Switzerland

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Abstract. The switching in Guanidine Aluminium Sulfate Hexahydrate (GASH) was studied in particular at high electric fields. The samples were subjected to electrical and thermal treatment and their switching was studied under different conditions. As a result of these studies, it appears that at high fields the domain wall motion time is longer than the nucleation time and hence controls the switching process.

1. Introduction

Guanidine Aluminium Sulfate Hexahydrate (GASH) was reported to be ferroelectric by HOLDEN, MATTHIAS, MERZ, REMEIKA¹). Some of its properties were first investigated by these authors²) and later by WIEDER³) and by PRUTTON⁴). They found that the reciprocal switching time $1/t_s$ depends at low fields exponentially on the applied field, like BaTiO_3 ⁵) and at higher fields linearly on E .

In this paper we shall describe some new experimental results on the switching in GASH. In particular, the linear high field part is discussed in detail because in this range GASH appears to behave differently from other ferroelectrics. FATUZZO and MERZ⁶) have worked out a model for Triglycine Sulfate (TGS) which can explain the switching properties in this material satisfactorily. One purpose of this paper is to show how this can be applied to GASH. Throughout the paper, the same symbols and definitions are used as in Ref. ⁶).

2. Preparation of the Samples

GASH has a pronounced cleavage plane perpendicular to the ferroelectric axis which facilitates the preparation of thin plates. The samples were first cleaved into rather thin plates and then ground with abrasive powder and alcohol. The thickness of the samples was between 0.2 mm to 0.3 mm. Evaporated silver electrodes were used.

3. Experimental Results

Two kinds of samples, showing a somewhat different behavior can be found. In one of them, type I, the switching time t_s is comparatively long and the pulse is very asymmetrical up to very high fields. In the other one, type II, t_s is considerably shorter and the switching pulse is almost symmetrical for fields higher than 1 KV/cm; the «symmetry»⁶⁾ which is defined as rise time t' over decay time t'' being equal to one.

Most samples were found to be of type II and only a few were of type I. By ageing, samples of type I usually became of type II. Furthermore, type I behavior can only be observed when the waiting time T between a positive and a negative applied pulse is very long (5 msec or longer). When T is reduced to zero, every sample shows type II behavior.

3.1. *Type I Samples.* We have studied the dependence of the switching time t_s on the applied field E . In Figure 1 the $1/t_s$ versus E curve is plotted for a "Type I" sample when the "waiting time T " between opposite pulses is long and when T is zero. In the first case (T long) t_s is one order of magnitude larger than in both the second case ($T = 0$) and for crystals of type II. If the waiting time T is equal to zero, t_s has the same magnitude as in type II crystals and the switching pulse is symmetrical.

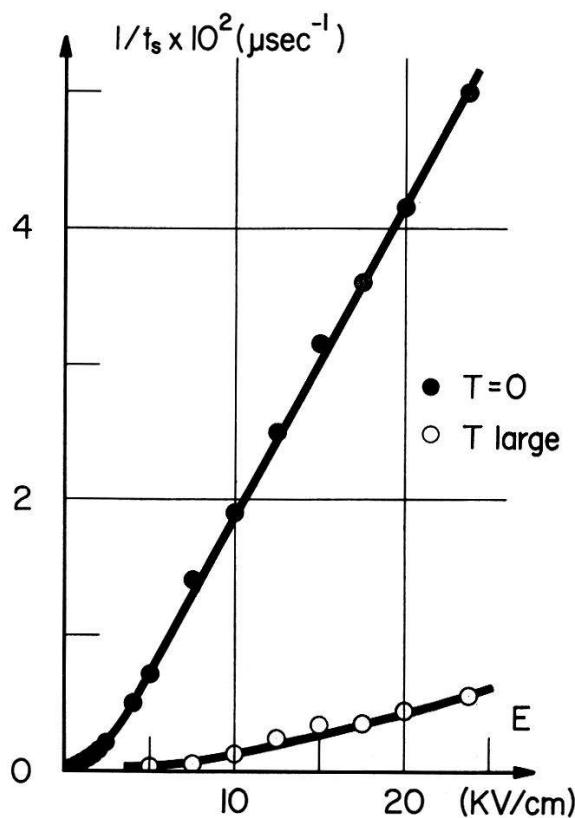


Fig. 1

$1/t_s$ is plotted versus the field E for a «type I» crystal, when the waiting time T between opposite pulses is large and when $T = 0$

In Figure 2 the switching current i_s is plotted versus time t for the case that T is long. It can be seen that i_s decreases exponentially with t .

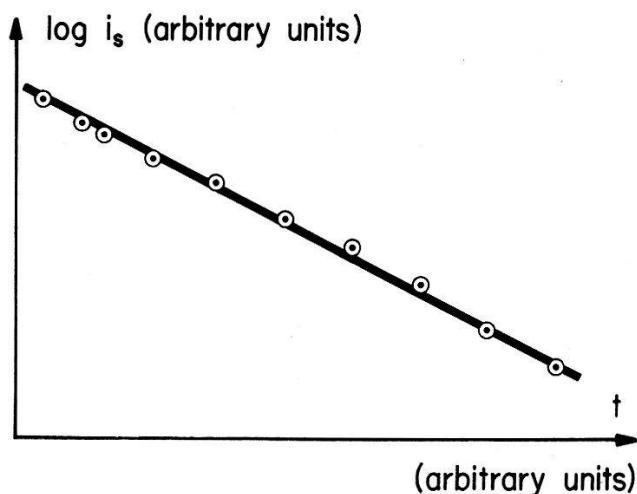


Fig. 2

The decreasing part of the asymmetrical switching pulse (obtained when T is large on type I crystals) is here plotted in semilog. scale. It follows from this graph that i_s can be fitted by an equation of the type: $i_s = i_0 \exp(-t/b)$

In Figure 3 the "rise time"⁶⁾ t' of the current pulse is plotted versus field E for the case that T is long: $1/t'$ varies almost quadratically with E .

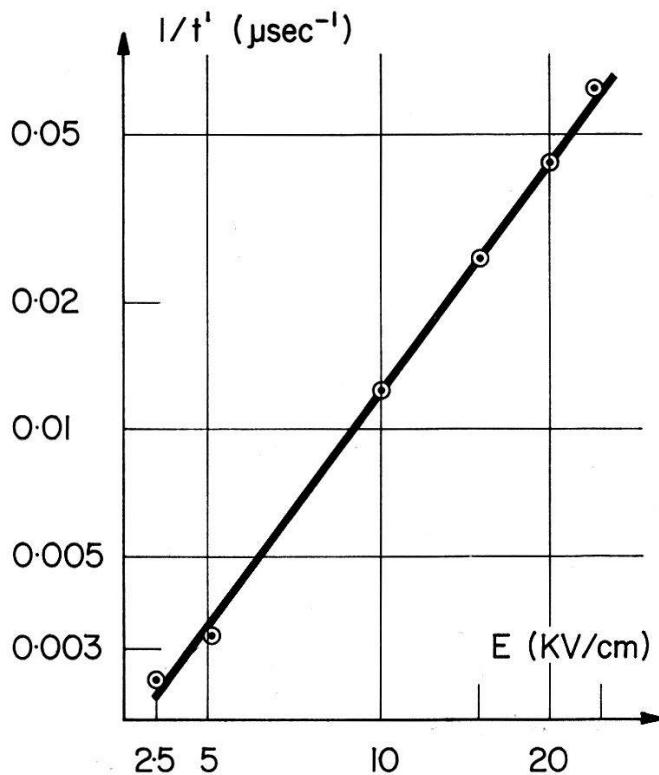


Fig. 3

The «rise time» t' of the pulse obtained when T is large on type I crystals is here plotted versus field E . It follows that: $t' \propto 1/E^2$

3.2. *Type II Samples.* In Figure 4 the $1/t_s$ versus E curve is plotted for a "type II" sample; one can notice a good linear part up to fields of 40 KV/cm. The shape of the switching pulse is symmetrical and independent of the waiting time T . The switching time t_s is found to be proportional to the square of the thickness d , when the applied voltage V is kept constant (Fig. 5).

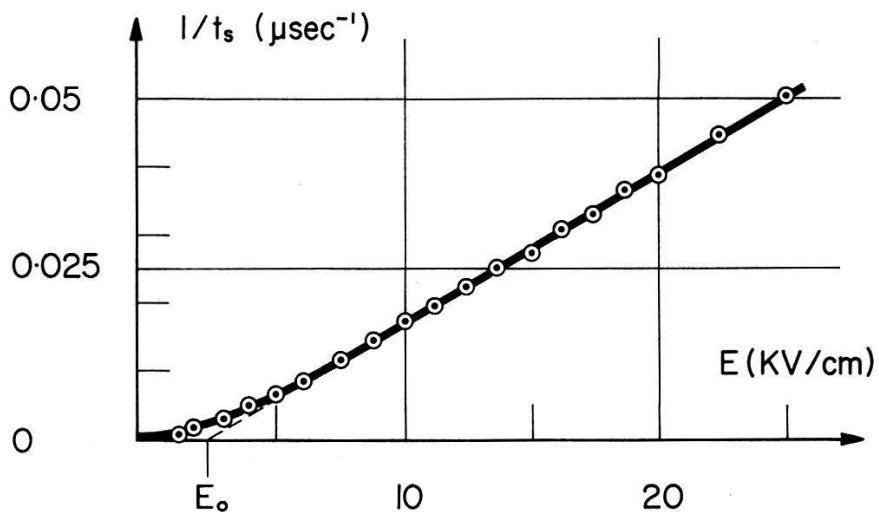


Fig. 4

$1/t_s$ versus the field E for type II crystals. It is apparent that $1/t_s$ is linear with E .

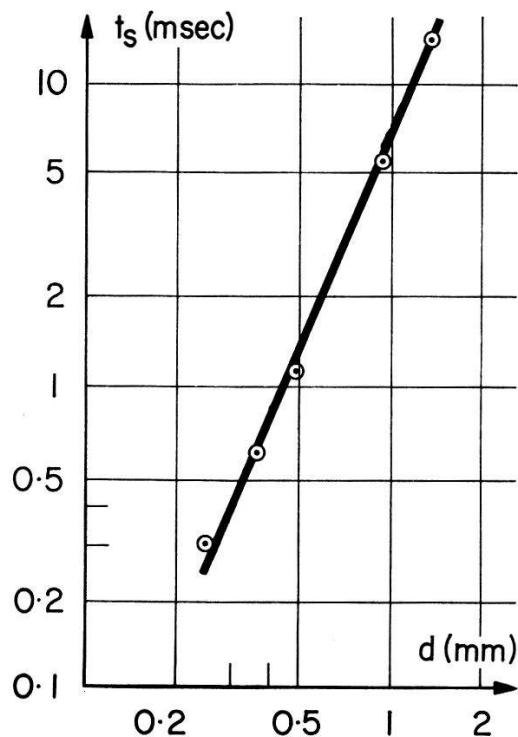


Fig. 5

By applying a constant voltage V on a crystal and varying its thickness d , one can plot t_s versus d . It appears here that: $t_s \propto d^2$

Heating experiments have been performed, according to the technique described for TGS in Ref. ⁶). In these experiments the crystal is heated from one side and the resulting changes in switching current are being investigated. In some ferroelectrics, e. g. $\text{LiH}_3(\text{SeO}_3)_2$, the switching time decreases very much within a few seconds upon heating. When the heater is removed, the switching time goes back to the initial value within a few seconds. On the other hand, in GASH, it takes several minutes to change the switching time t_s by just 10% or 20% under the same conditions of heating or cooling.

Experiments on switching in parts have been performed, similar to those made on TGS by FATUZZO and MERZ ⁶). In these experiments pulses are applied which are too short to reverse the polarization completely. As in TGS ⁶) it was found that there is a critical pulse length time $t^* < t_s$ which still allows complete switching of the polarization if many of them are applied. If the pulse length time is smaller than t^* then it is impossible to reverse the polarization even if very many pulses are applied. In GASH it was found that this time t^* is very long, about half the switching time t_s .

The shape of the switching current pulses depends very much on the polarization state of the crystal. If the first applied pulse (positive pulse) is so short that not all the dipoles are switched, the second (negative) switching pulse is strongly modified. If we denote the "rise time" ⁶) of

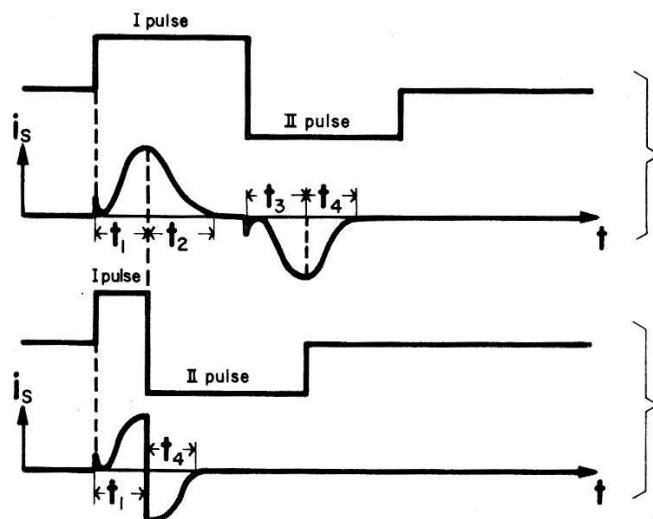


Fig. 6a

Two opposite pulses are applied to the crystal; the waiting time T is zero. The current i_s is plotted versus t . It should be noticed that the switching pulses are almost symmetrical.

Fig. 6b

The first applied pulse is made shorter, so that the last part of the charge does not have time to switch. Then the II switching pulse is deformed; the "rise time" becomes equal to zero. This indicates that the charge that switched last during the first pulse, switches first during the second pulse and viceversa.

the positive and negative pulses with t_1 and t_3 respectively and the "decay time" with t_2 and t_4 , the following is obtained from Figure 6. If the first applied pulse is so short that t_2 is zero (Fig. 6 b) it results that in the second switching pulse the rise time t_3 is zero. The same is true for the first pulse if one reduces the length of the second applied pulse.

If the waiting time T between opposite pulses is made different from zero (Fig. 7), then part of the charge switches back due to the fact that some domains collapse upon removal of the field. The rise time of the second pulse becomes then zero.

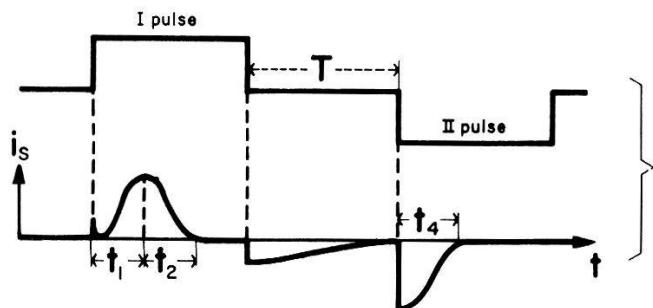


Fig. 7

A "waiting time" T is introduced between the opposite pulses. Part of the charge switched with the I pulse collapses back and the "rise time" of the II pulse becomes again zero. This indicates that the charge that collapses back during the waiting time is the charge that would have switched first in the II pulse and hence the charge that switched last in the I pulse

4. Discussion

4.1. *Type I Samples.* In discussing the experimental results obtained for GASH, we have to refer to the model developed for TGS by FATUZZO and MERZ⁶). Let us first consider the type I samples. From a comparison with the model⁶) it appears that "type I" crystals are crystals in which over the whole range of electric fields used the domain wall motion time t_d , which is the time to move a wall through the crystal, is much shorter than the nucleation time t_n which is the time to nucleate all domains, from the first to the last one. The following facts substantiate this situation: (I) the very asymmetrical switching pulse combined with the fact that $1/t' \propto E^2$ (see Eq. (25) of Ref. 6) and (II) the fact that the "decay time" of the switching pulse follows an exponential law of the form

$$i_s = i_0 \exp(-t/b)$$

as shown in Figure 2 (see Eq. (23) of Ref. 6 when $\tau_1 \ll \tau_2$).

It is not obvious why in the "type I" crystals the nucleation time is so abnormally long. However, assuming this, it is easy to explain why the pulse becomes so much shorter when the waiting time T is made

zero: in this case, the nucleation time is reduced so much that t_n becomes much smaller than t_d , which is in agreement with the observations in TGS⁷). In other words, when $T = 0$, also t_n/t_d becomes zero; all the nuclei are formed at the same time and grow together. The shape of the switching pulse is then due to the growth by domain wall motion. The field at which t' starts deviating from the square law should allow the calculation of the nucleus-domain interaction⁶). However, no such deviation is encountered in GASH (Fig. 3). Hence only a maximum limit for the domain-nucleus interaction in GASH can be given. The lowest value observed in GASH for the interaction is only $m_0 = 0.02$ ⁶), which is very small compared to other ferroelectrics.

4.2. Type II Samples. To fit the behavior of the type II samples with the model⁶) we have to assume that $t_n \ll t_d$. This is supported by the following experimental facts described in section 3.2: (I) the linearity of $1/t_s$ versus applied fields E up to very high fields, (II) the heating experiment, (III), the "switching in parts" experiment and (IV) the proportionality between t_s and the square of the sample thickness (Eq. 6 of Ref. 6).

Let us now try to explain the experimental results represented in Figures 6a, 6b, 7. From Figure 7 it is apparent that some domains are collapsing back upon removal of the field, which indicates the presence of an electric bias. Since the hysteresis loop of this sample, however, does not appear to be biased we are brought to the assumption that some regions are biased in one direction and others in the opposite direction, so that normally they cancel each other. As soon as the pulse of one polarity is applied, the regions having the "right" polarization switch first. It is therefore expected that the regions which switch first upon application of a pulse of one polarity, switch last when a pulse of opposite polarity is applied. This could be verified as shown in Figure 6b.

If there is a waiting time T between the two pulses, it is expected that the biased regions which have switched *last* with the first pulse should collapse back when the field is removed. This is apparent from Figure 7; the charge that collapses back is the charge that switched last during the first pulse.

5. Conclusions

The switching in GASH can be described by the model developed in Reference⁶) for TGS, with some additional assumptions.

It appears that the nucleus-domain interaction is very low, and that crystals which appear "unbiased" really consist of regions biased in opposite directions. These regions play a very important part in the switching.

At high fields we observed that the reciprocal switching time varies proportionally with $(E - E_0)$. We, furthermore, know that in this region

the switching is controlled by domain wall motion, as discussed above, from which follows that the wall velocity must vary proportionally to $(E - E_0)$.

In this respect GASH differs from TGS because in TGS the extrapolation of the high field part of the $1/t_s$ curve passes through the origin⁶⁾ whereas in GASH the extrapolation of the high field part cuts the E axis at E_0 . It thus appears that GASH behaves similar to a ferromagnetic material where one also finds a critical field H_0 (coercive field) below which there is no domain growth. However, WIEDER³⁾ found that even below E_0 switching still occurs in GASH and that in the low field region the switching time depends exponentially on the field like in all other ferroelectrics⁴⁾⁶⁾⁸⁾. No simple explanation can be given for this behavior and for the lack of an inflection point in the $1/t_s$ versus E curve in GASH.

6. Acknowledgments

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References

- ¹⁾ HOLDEN, MATTHIAS, MERZ and REMEика, Phys. Rev. 98, 546 (1955).
- ²⁾ HOLDEN, MERZ, REMEика, and MATTHIAS, Phys. Rev. 101, 962 (1956).
- ³⁾ WIEDER, Proc. Inst. Radio Engrs. 45, 1094 (1957).
- ⁴⁾ PRUTTON, Proc. Phys. Soc. (London) B 70, 1064 (1957).
- ⁵⁾ MERZ, Phys. Rev. 95, 690 (1954).
- ⁶⁾ FATUZZO and MERZ, Phys. Rev. 116, 61 (1959).
- ⁷⁾ FATUZZO, Helv. Phys. Acta 31, 309 (1958).
- ⁸⁾ MERZ, J. Appl. Phys. 27, 938 (1956).