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Unstable point domains in ferroelectrics

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It is shown by employing statistical-mechanical considerations that unstable point domains can nucleate in ferroelectrics under the influence of low electric fields under certain conditions. A fixed number of domains are in equilibrium in the given field, but evaporate as soon as the field is removed. The theory predicts a peculiar variation of the dielectric constant under the given conditions. $KNbO_3$, $PbNb_2O_6$, and $(NH_2CH_2COOH)_3{\cdot}H_2SO_4$ (TGS) are used as test cases. It is possible to calculate the critical volume, the critical energy of nucleation, and the wall energy. The wall-energy calculations show that these nucleations are different in character from the thermally stable point domains that nucleate at the sites of the dislocations. Further, it is found that these unstable domains nucleate at the sites of the excess vacancies in ferroelectric crystals. Since such low fields as are required for nucleation exist in crystals even in the absence of the externally applied field on account of the space charges, it follows that some point domains of this type should normally exist in crystals, as has already been found experimentally. Thus, the theory can distinguish between stable point domains and unstable ones, clearing the existing confusion in this respect, and providing the rationale for the existence of both types of point domains.

I. INTRODUCTION

The existence of point domains of some sort was anticipated as early as 1963—64 to explain the switching in ferroelectric crystals.[1-3] Fuchs and Liesk[4] then observed under the electron microscope point domains with widths down to 200 Å. Later, Bradt and Ansell[5] reported the observation of the nucleation of a 90° domain in $BaTiO_3$ at the dislocation site, the domain dimensions being about 100 Å. The wall-energy observations of Fuchs and Liesk are, however, not in agreement with the accepted values of the domain-wall energies of the thermally stable domains. Thus, the point domains observed by Fuchs and Liesk were probably of different character than those observed by Bradt and Ansell. It is interesting that Fuchs and Liesk had used electric fields while making their observations. As a continuation of this, and the ideas suggested by our earlier work on $KNbO_3$,[6-8] a theoretical treatment based on statistical mechanics is now developed, and it satisfactorily distinguishes the point domains of lower wall energies from the point domains of the type observed by Bradt and Ansell.

II. THEORY OF POINT DOMAINS

Since the early work of Merz,[9] it is now well established that an electric field can cause nucleation of domains. Further, such nucleations are much more likely to occur if there are strain sites in the crystal. In fact, the experiments of Bradt and Ansell[5] were based on this principle. We had also found in $KNbO_3$[8] that dislocation loops can nucleate domains. Hence, in the present theory, the nucleation of domains is taken as a reasonable assumption, to be confirmed later by experimental verification.

Let the nucleation sites available for nucleation be N_ϕ per unit volume. Also, let the number of domains nucleated per unit volume be N for the applied electric field E.

Since the order in which these N sites are filled is immaterial, the total number of ways this can be done is given by

$$W=\frac{N_\phi!}{(N_\phi-N)!N!} . \tag{2.1}$$

This nucleation process will increase the configurational entropy of the system according to the Boltzmann relation

$$\Delta S=k\ln W . \tag{2.2}$$

We have, therefore,

$$\Delta S=k\ln\frac{N_\phi!}{(N_\phi-N)!N!} . \tag{2.3}$$

The change in the Helmholtz free energy is

$$\Delta F=\Delta U-T\Delta S , \tag{2.4}$$

where ΔU is the change in the internal energy due to various factors considered below. T is the absolute temperature. If ΔF is negative, the given number of nucleations will remain in equilibrium under the influence of the applied electric field at the given temperature.

If we neglect the mutual interactions of these nucleated domains, ΔU can be written as

$$\Delta U=N\Delta U' , \tag{2.5}$$

where nucleation of a single domain changes the internal energy by $\Delta U'$.

Now $\Delta U'$ is comprised of (i) the negative electrostatic energy, (ii) the positive surface energy of the newly created domain walls, (iii) the positive depolarizing energy, (iv) the positive strain energy, and (v) a negative factor due to a decrease in the internal energy of the crystal by the nucleation of a domain at the site of nucleation, which reduces the local strain. Factors (ii)—(v) depend strongly on the size and shape of the domain. Let their sum be E'. So we have

$$\Delta U' = -2P_sEV + E' , \tag{2.6}$$

where P_s is the spontaneous polarization of the crystal and V the volume of the domain nucleated. Hence, we have

$$\Delta F = N(E' - 2P_sEV) - Tk \ln \frac{N_\phi !}{(N_\phi - N)! N!} . \tag{2.7}$$

For thermal equilibrium, this must be minimum with respect to N, and its first derivative with respect to N must vanish. By using Stirling's approximation, we obtain

$$\ln \frac{N}{N_\phi - N} = \frac{2P_sEV - E'}{kT} . \tag{2.8}$$

Thus, Eq. (2.8) gives the required relation between the number of nucleations N and the electric field E. On differentiation with respect to E, Eq. (2.8) gives

$$\left(\frac{dN}{dE}\right)_E = \frac{2P_sV}{kT}(N_\phi - N)\frac{N}{N_\phi} \tag{2.9}$$

if dE'/dE and dV/dE are negligible.

For N domains nucleated, the change in the electrostatic energy is $-2P_sEVN$. This is E times a factor $-2P_sVN$. We assume a linear relation between the electric field and the electrostatic energy change, which gives

$$NV = g , \tag{2.10}$$

where g is a constant, since P_s is already a constant.

Now, when all the possible nucleation sites are filled, the nucleation process is complete, and no further nucleations can occur even though the electric field E is increased. The value of N corresponding to this situation differs from N_ϕ as seen later in Sec. III. If V_ϕ is the volume of the domain nucleating at that stage, we have, using the Eq. (2.10),

$$NV = (N_\phi - N_{\text{eq}})V_\phi , \tag{2.11}$$

where N_{eq} represents the number of sites remaining finally unfilled.

If we put

$$\left(1 - \frac{N_{\text{eq}}}{N_\phi}\right) = f , \tag{2.12}$$

where f is a constant for the crystal, the equation (2.9) can be written as

$$\left(\frac{dN}{dE}\right)_E = \frac{2P_sV_\phi f}{kT}(N_\phi - N) = \mu(N_\phi - N) , \tag{2.13}$$

where μ is a constant given by

$$\mu = \frac{2P_sV_\phi f}{kT} . \tag{2.14}$$

Equation (2.13) gives on integration

$$e^{\mu E} = \frac{N_\phi}{N_\phi - N} , \tag{2.15}$$

applying the condition that $N=0$ at $E=0$. The fraction N/N_ϕ nucleated in the field E is given by

$$\frac{N}{N_\phi} = (1 - e^{-\mu E}) . \tag{2.16}$$

Let the change in polarization on nucleation of a single domain be β, where

$$\beta = 2P_sV . \tag{2.17}$$

β may change somewhat with the values of the electric field.

Now, if ΔN domains are nucleated on application of the electric field ΔE at E, the change in polarization shall be ΔP, where

$$\Delta P = \Delta N \beta . \tag{2.18}$$

In ferroelectrics, the general equation for the dielectric constant

$$\frac{\epsilon}{\epsilon_0} = \frac{1}{\epsilon_0}\frac{dP}{dE} - 1 \tag{2.19}$$

can be approximated by

$$\frac{\epsilon}{\epsilon_0} = \frac{1}{\epsilon_0}\frac{dP}{dE} \tag{2.20}$$

because of the high polarizability of the materials.

In the present case, the increase in polarization ΔP due to nucleation of the domains will contribute to the increase in the dielectric constant over the dielectric constant measured without any bias field. Let this increase be denoted by $(\epsilon/\epsilon_0)'$. Hence, now

$$\left(\frac{\epsilon}{\epsilon_0}\right)' = \frac{1}{\epsilon_0}\frac{dP}{dE} ,$$

where ΔP is given by Eq. (2.18). We get from Eq. (2.8)

$$\frac{dP}{dE} = \left[\beta\left(\frac{dN}{dE}\right)_E + \Delta N\left(\frac{d\beta}{dE}\right)_E\right]$$

and

$$\left(\frac{\epsilon}{\epsilon_0}\right)' = \frac{1}{\epsilon_0}\left[\beta\left(\frac{dN}{dE}\right)_E + \Delta N\left(\frac{d\beta}{dE}\right)_E\right] . \tag{2.21}$$

Neglecting the second term in comparison with the first in the right-hand side of Eq. (2.21), we get

$$\left(\frac{\epsilon}{\epsilon_0}\right)' = \frac{1}{\epsilon_0}\beta\left(\frac{dN}{dE}\right)_E . \tag{2.22}$$

Substituting for $(dN/dE)_E$ from Eq. (2.13), we have

$$\left[\frac{\epsilon}{\epsilon_0}\right]' = \frac{1}{\epsilon_0}\beta\mu(N_\phi - N) \tag{2.23}$$

$$= \frac{1}{\epsilon_0}\beta\mu N_\phi e^{-\mu E} \tag{2.24}$$

using Eq. (2.15). Writing Eq. (2.24) in ln form, we get

$$\ln\left[\left[\frac{\epsilon}{\epsilon_0}\right]'\right] = \ln\left[\frac{\beta\mu N_\phi}{\epsilon_0}\right] - \mu E \ . \tag{2.25}$$

Setting

$$\frac{\beta\mu}{\epsilon_0} = C \ , \tag{2.26}$$

where C is a constant, we get

$$\ln\left[\left[\frac{\epsilon}{\epsilon_0}\right]'\right] = \ln(CN_\phi) - \mu E \ . \tag{2.27}$$

Equation (2.27) gives the variation of $(\epsilon/\epsilon_0)'$ with the bias field E, which can be easily verified experimentally.

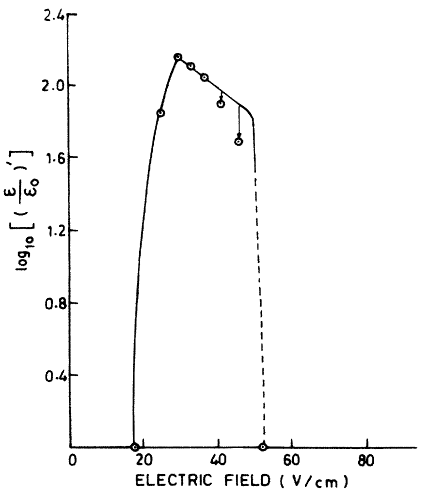

FIG. 2. Variation of $\log_{10}[(\epsilon/\epsilon_0)']$ with the bias field E in $PbNb_2O_6$ single crystals at 1 KHz. Note the rapid deviation from the straight-line nature due to the high value of N_ϕ in the crystal as compared to the equilibrium number of vacancies, N_{eq}.

III. EXPERIMENTAL VERIFICATION

To the extent that the constant C in Eq. (2.27) remains constant, the equation predicts a straight-line behavior for the variation of $(\epsilon/\epsilon_0)'$ with the electric field. Also, it should be interesting to compare the experimental results for different ferroelectric materials. Presently, $KNbO_3$, $PbNb_2O_6$, and $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) have been used as the test cases. The results on them are shown in Figs. 1, 2, and 3, respectively, at the measurement frequency 1 kHz.

The graphs in all the figures clearly distinguish the regions where the equation is followed from the regions where it is not. The straight lines give a fairly good fit confirming the general validity of the theory and the assumptions and approximations used in it. It can be noted that the straight-line behavior is better followed for the lower values of N again in conformity with the theory. The range over which the fit is good is wide for TGS, less than that for $KNbO_3$, and very limited for $PbNb_2O_6$. Also, the sudden fall in $(\epsilon/\epsilon_0)'$ is very pronounced for $PbNb_2O_6$, less so for $KNbO_3$, and hardly perceptible for TGS. These peculiarities can also be understood in terms of the theory as seen later in the section. Furthermore, the calculation of N_ϕ will lead us to a sensible guess about the identification of the nucleation sites with the strain sites in the crystal, which should be quite interesting.

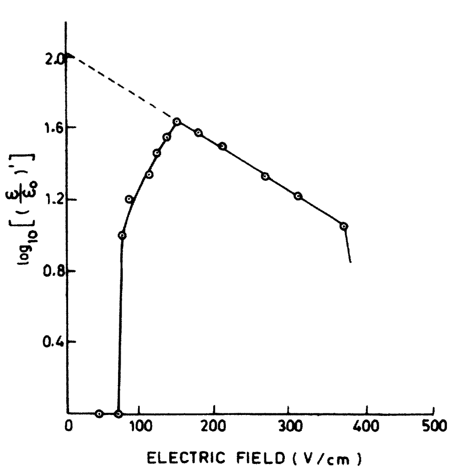

FIG. 1. Variation of $\log_{10}[(\epsilon/\epsilon_0)']$ with the bias field E in $KNbO_3$ single crystals at 1 KHz.

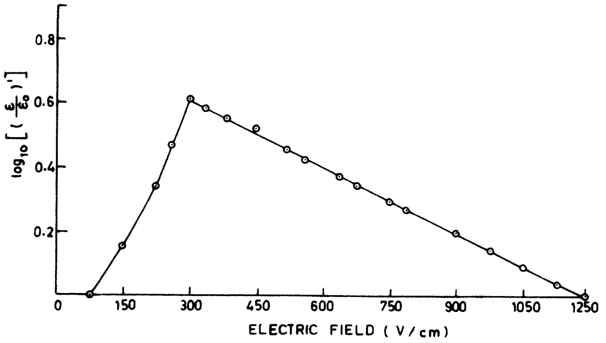

FIG. 3. Variation of $\log_{10}[(\epsilon/\epsilon_0)']$ with the bias field E in TGS single crystals at 1 KHz. The straight-line nature is observed over the entire range due to N_ϕ being nominally higher than N_{eq}.

Figure 1 for $KNbO_3$ gives, by calculation of the slope of the straight line,

$$\mu=(0.1008\pm0.005)\times10^{-6}\ \mathrm{m/V} \tag{3.1}$$

and

$$CN_\phi=104.70\pm1.10\ . \tag{3.2}$$

Equation (2.14) can now be used to calculate V_ϕ. Taking $T=300$ K and $P_s=26\ \mu$C, we get

$$V_\phi=(2.14\pm0.40)\times10^{-25}\ \mathrm{m}^{-3}\ , \tag{3.3}$$

taking $f=0.375$. The reason for using this value of f is explained later in the section. The small value of the volume of the domains clearly indicates that the domains are fit to be called point domains.

Now, we have

$$\beta=2P_sV=2P_sV_\phi\frac{V}{V_\phi}=\mu kT\frac{V}{V_\phi}$$

and

$$C=\frac{\beta\mu}{\epsilon_0}=\frac{1}{\epsilon_0}\mu^2kT\frac{V}{V_\phi}\ . \tag{3.4}$$

Since $V/V_\phi=(N_\phi/N)f$ by Eq. (2.11), we have

$$C=\frac{1}{\epsilon_0}f\mu^2kT\frac{N_\phi}{N}\ . \tag{3.5}$$

It is possible to plot N/N_ϕ as a function of E from Eq. (2.16), and this type of variation for $KNbO_3$ is shown in Fig. 4. Since the best fit for the straight-line behavior (Fig. 1) is on the lower side of N, we use $N/N_\phi=0.15$ for the calculation of C in Eq. (3.5). From Figs. 1 and 4 one can see that the straight-line behavior begins at about this value of N/N_ϕ. The value of N_ϕ can then be obtained from the value of CN_ϕ given in Eq. (3.2). We find

$$N_\phi=(3.92\pm0.18)\times10^{22}\ \mathrm{m}^{-3}\ . \tag{3.6}$$

This value of N_ϕ suggests that the strain sites in question are point defects. If results on different ferroelectric materials are taken into consideration, one can come to the conclusion that the point defects are excess vacancy sites. For example, the excess vacancies are high in melt-grown crystals like $KNbO_3$ and $PbNb_2O_6$ as compared to those existing in solution-grown crystals like TGS. Hence, if excess vacancies are the nucleation sites, $N-N_{\mathrm{eq}}$, where N_{eq} can now be taken as the equilibrium number of vacancies, shall be quite high for $KNbO_3$ and $PbNb_2O_6$, but quite low for TGS, and this should be reflected in the Figs. 1, 2, and 3 in a particular way. We find for $KNbO_3$ from Fig. 4 that N/N_ϕ is 0.375 when the nucleation process is nearly complete. Since at this stage $N=N_\phi-N_{\mathrm{eq}}$, we have

$$\frac{N_\phi-N_{\mathrm{eq}}}{N_\phi}=f=0.375\ . \tag{3.7}$$

It is this value of f that has been used earlier for the calculation of V_ϕ.

When N_ϕ is not much greater than N_{eq}, as in TGS, f will be quite small, and the entire nucleation process will involve the nucleation of only a small fraction of the existing sites. Since for small values of N/N_ϕ, the straight-line fit, as required by Eq. (2.27), is better, we should get a better straight-line fit for TGS as compared to $KNbO_3$ and $PbNb_2O_6$, as is indeed found from the Figs. 1, 2, and 3. Also, if N_ϕ is smaller, $(\epsilon/\epsilon_0)'$ should be correspondingly smaller according to Eq. (2.27). This explains the relatively lower values of $(\epsilon/\epsilon_0)'$ observed in TGS. In TGS, $\log_{10}[(\epsilon/\epsilon_0)']$ decreases much more slowly with the electric field than in $KNbO_3$ and $PbNb_2O_6$. This can be understood in terms of Eqs. (2.13) and (2.14), which give a lower rate for $(dN/dE)_E$ for the lower value of f. Finally, the sudden fall in $(\epsilon/\epsilon_0)'$ as is observed in $KNbO_3$, and very markedly in $PbNb_2O_6$, is not observed in TGS. This important observation can also be explained on the basis of associating the nucleation sites with the excess vacancies. There are two possible explanations for the sudden fall of $(\epsilon/\epsilon_0)'$ at particular values of E (for example, 375 V/cm in the case of $KNbO_3$). Either $d\beta/dE$ changes catastrophically at this value of E, or the very law for choosing the nucleation sites changes. While there is no apparent reason for the former, there are grounds to suspect the latter. From Fig. 4 it is seen that N/N_ϕ at 375 V/cm is 0.33, and the number of sites that remains still available at this stage is equal to $(N_\phi-N_{\mathrm{eq}}-N)$. Since $N_{\mathrm{eq}}/N_\phi=0.625$ from Eq. (3.7), we get the number of sites available at 375 V/cm as only $0.072N_{\mathrm{eq}}$. This means that the deviation from the equilibrium value of the vacancies is only about 7%. The nondegenerate condition existing at the lower values of E does not exist now, and the order in which the domains are nucleated does not remain immaterial. Hence, the experimental observation of a sudden fall in the dielectric constant is completely in agreement with basic statistical principles. This also fully justifies the application of the statistical mechanics to the problem.

One can now understand why there is no drastic fall of $(\epsilon/\epsilon_0)'$ in the case of TGS. Since f is small, the number of sites available for nucleation continues to be large till the nucleation process is complete, allowing for the validi-

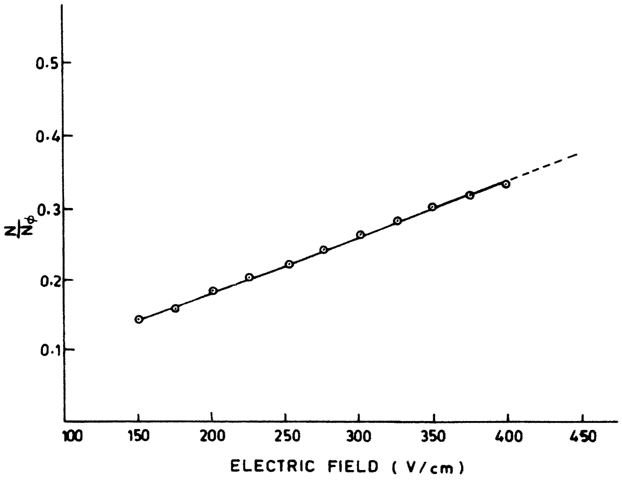

FIG. 4. Graph showing the variation of the fraction of the domains nucleated, N/N_ϕ, with the applied electric field E.

ty of Eq. (2.27) over the entire range.

Finally, it is understandable that the nucleation process should stop at $N = N_\phi - N_{eq}$. If the nucleation process were to continue after that, the energy of the system would increase rather than decrease, since N_{eq} vacancies are required for the minimum energy of the crystal. Thus the experimental evidence as well as theoretical expectations confirm that the excess vacancies in crystals are indeed the nucleation sites. One can also obtain a rough estimate of N_{eq} for $KNbO_3$ from Eqs. (3.6) and (3.7) and see if its value is reasonable. We find that $N_{eq} = (2.45 \pm 0.12) \times 10^{22}$ m^{-3}, which is again in proper order.

Since the excess vacancies in $PbNb_2O_6$ are much higher than those in $KNbO_3$, giving a much higher value of f, we should expect a more severe response in $PbNb_2O_6$ as compared to that in $KNbO_3$, as is found experimentally. We do find in Fig. 2 for $PbNb_2O_6$ that the straight line is obtained over a very limited range and that there is a highly catastrophic fall in $(\epsilon/\epsilon_0)'$. Indeed, the test cases $KNbO_3$, $PbNb_2O_6$, and TGS cover the widely varying conditions that can exist in various ferroelectric materials, and the successful understanding of all their peculiarities observed experimentally in terms of the theory provides an excellent experimental verification of the theory of the point domains developed here.

IV. WALL ENERGY, CRITICAL ENERGY OF NUCLEATION AND THE PHYSICAL STATE OF THE POINT DOMAINS

By using Fig. 4 and the relation $NV = V_\phi f N_\phi$, the volume of the domain nucleated for any field E can be calculated. If the small point domains are assumed to be spherical in shape, the critical radius of nucleation can be readily obtained. This variation of r_{cr}, the critical radius of nucleation, with E for $KNbO_3$ is shown in Fig. 5. These values of r_{cr} are useful in the calculation of the wall energy and the critical energy of nucleation at various fields.

To a first degree of approximation, one can write that the change in the energy of the crystal energy on nucleation of a domain, ΔW, is the sum of the increase in the surface energy, the reduction in the electrostatic energy, and the increase in the strain energy. Hence,

$$\Delta W = 4\pi r^2 \alpha - (\tfrac{4}{3}\pi r^3)(2P_s E) + \tfrac{4}{3}\pi r^3 Q \ , \tag{4.1}$$

where α is the surface energy in units of J/m^2 and Q the increase in the strain energy density in units of J/m^3. The first derivative of ΔW with respect to r must vanish for criticality, which gives

$$r_{cr} = \frac{2\alpha}{2P_s E - Q} \ . \tag{4.2}$$

Substitution of this value of r_{cr} in Eq. (4.1) gives

$$\Delta W = \frac{16}{3} \frac{\pi \alpha^3}{(2P_s E - Q)^2} \tag{4.3}$$

$$= \tfrac{4}{3}\pi r_{cr}^2 \alpha \ . \tag{4.4}$$

Finally, Eq. (4.2) gives that the critical limit of nucleation is given by E_{cr} when

$$2P_s E_{cr} = Q \ . \tag{4.5}$$

Equations (4.2) and (4.3) can now be rewritten in the form of E_{cr}, which gives

$$r_{cr} = \frac{\alpha}{P_s(E - E_{cr})} \tag{4.6}$$

and

$$\Delta W_{cr} = \frac{8}{3} \frac{\pi \alpha^3}{P_s(E - E_{cr})} \ . \tag{4.7}$$

Since the small electric signal used for the measurement of the dielectric constant is sufficient to cause nucleation

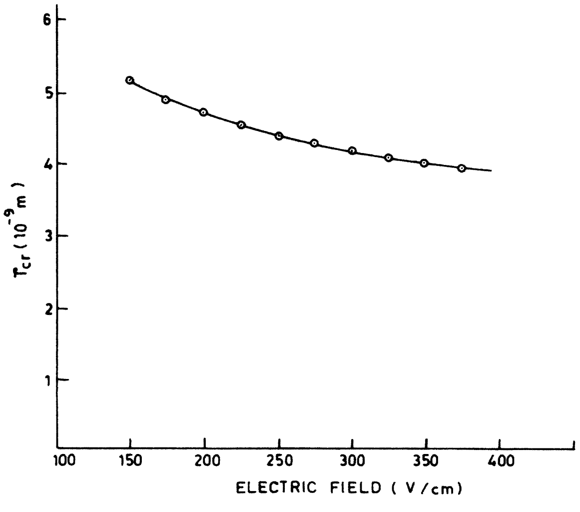

FIG. 5. Graph showing the variation of the critical radius of nucleation, r_{cr}, with the bias field E.

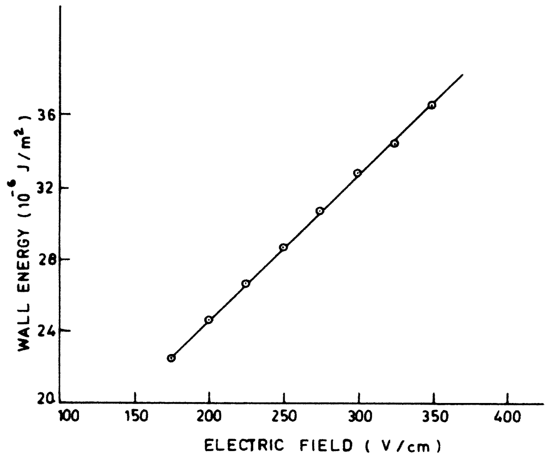

FIG. 6. Graph showing the variation of the wall energy with the bias field E.

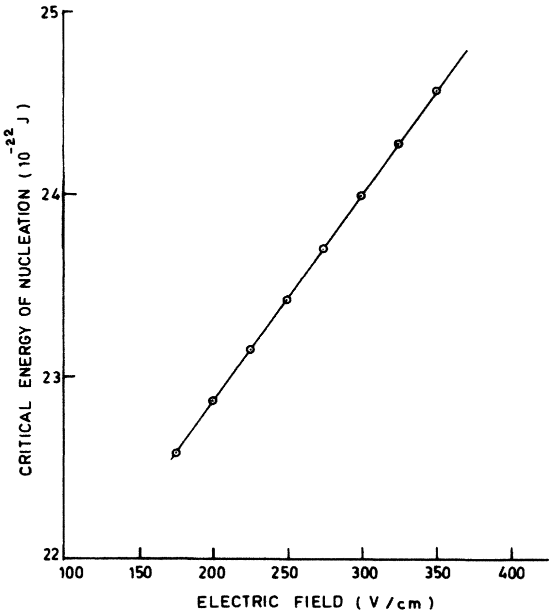

FIG. 7. Graph showing the variation of the critical energy of nucleation, ΔW_{cr}, with the bias field E.

of the point domains, it is obvious that E_{cr} is quite small as compared to the values of the biasing fields used in the measurement. Hence, for calculation of α and ΔW_{cr} from Eqs. (4.6) and (4.7), respectively, the factor E_{cr} can be neglected. Figures 6 and 7 show these variations for α and ΔW_{cr}, respectively. The calculations are valid only where the straight-line behavior is observed, and only points up to that stage have been shown in the graphs.

It is seen that the wall energy for these domains is about a hundred times lower than the generally accepted values of the wall energies for thermally stable domains. Also, the critical energies of nucleation are very low (about 10^{-8} J for a thermally stable domain[8]). It is clear that the physical state of these domains is distinct from that of the thermally stable domains. This is also obvious from the fact that these domains disappear as soon as the nucleating field is removed. Apparently, the physical state of these domains is an unstable state. From the original energy state E_1 the crystal jumps to the lower state E_2 with nucleation of domains on application of the electric field E. After removal of the field, the energy jumps up to the state E_3 that is higher than E_1. State E_3, being unstable with unstable domains, the crystal jumps to state E_1 with redissolution of the unstable domains when the applied field E is removed.

Furthermore, it follows that such unstable domains should be present in ferroelectric crystals without application of any external electric field. The space charges and polarization waves with associated electric fields should give rise to these domains, since the field requirements are small. As the local fields fluctuate, the dimensions of these domains fluctuate; also, the domains may disappear and appear again. This fluctuating state existing in crystals is quite interesting from the scattering point of view. Indeed, Mendelson[10] used the idea of transient microdomains in analyzing the problem of central peaks.

V. CONCLUSION

It is thus seen that both stable and unstable point domains can exist in ferroelectric crystals, as observed by Bradt and Ansell[5] and Fuchs and Liesk,[4] respectively. While the stable point domains are nucleated at the dislocations, the unstable ones are nucleated at the sites of the vacancies because of the excess vacancies present in crystals. The unstable character leads to fluctuations, which can be quite important in the critical phenomena, scattering problems, etc. Furthermore, they can play a role in switching, as anticipated much earlier,[1-3] and it would be interesting to reconsider the switching mechanisms in light of the information now obtained.

ACKNOWLEDGMENT

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