

Mechanism for the Sidewise Motion of 180° Domain Walls in Barium Titanate

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An important unanswered question concerning the sidewise motion of 180° domain walls in single crystal BaTiO₃ is the mechanism by which the boundaries move. This paper considers two possible models. One model assumes that the wall motion results from the repeated nucleation of steps along existing parent 180° domain walls and that the nucleation rate is the controlling factor in the propagation of the wall. The second model investigated involves paired screw dislocations of opposite sense which propagate the wall in a manner analogous to certain types of crystal growth.

Many features of the experimental data are consistent with the nucleation model. The nucleated steps are assumed to be triangular slabs along the wall and about one lattice constant thick. For a field of 300 v cm⁻¹, the critical nucleus is calculated to be 7×10⁻⁶ cm wide (along the electroded crystal surface) and 16×10⁻⁶ cm high (along the ferroelectric axis). For limited ranges of field, the model gives a wall velocity dependence on field of $v \propto \exp(-\delta/E)$,

which agrees with experiment. The magnitude of the calculated activation field δ agrees with experiment if the energy of the additional wall consequent on a nucleation is set equal to 0.4 ergs cm⁻². The calculated temperature dependence of δ is through $P_s^3 T^{-1} \epsilon_a^{-1}$ and is in fair quantitative agreement with experiment. The approximately square domains observed in the low field region are consistent with the model, and the change in shape of the domains observed at higher fields can likewise be explained if slightly different wall energies are assumed for the edges of the nucleated steps on the two different types of 180° domain walls.

The screw dislocation model does not predict a wall velocity $v \propto \exp(-\delta/E)$ in a straightforward way. It is only with certain unrealistic restrictions on the dislocation density or the wall mobility that this model will give the correct form of v . However, it is suggested that this mechanism may contribute to the wall motion with fields of a few thousand volts per centimeter or higher.

INTRODUCTION

THERE are considerable experimental data in the literature on the sidewise motion of 180° domain walls in single crystal BaTiO₃; however, the measured characteristics of the wall motion have not been described in terms of a specific mechanism. The present paper discusses two possible mechanisms for the wall motion, one of which is shown to be compatible with many of the important features of the experimental data.

Before discussing the two models, some of the important aspects of the data will be summarized. The wall velocity v as a function of the applied electric field E has been measured¹ over a velocity range of about eight decades, 10⁻⁷ cm sec⁻¹ to 10 cm sec⁻¹. The field dependence of the velocity over a range of several decades in velocity is described by

$$v = v_\infty \exp(-\delta/E), \quad (1)$$

with v_∞ and δ field independent. However, v_∞ and δ are not constant over the entire range. In fact, $-d \ln v / d(1/E)$ increases slightly with field.¹ There is no evidence of a well defined coercive field, i.e., a field E_c below which the wall will not move. Equation (1) has been found to apply for velocities as low as a few angstroms per second.² There is likewise no evidence that the wall velocity depends on the size of the domains. The data include domains whose widths vary from about 5×10⁻⁴ cm to 10⁻² cm.^{1,3} Data of a preliminary nature show that the wall velocity for a given field depends to some extent on the impurity content of the crystal.³ Limited data¹ indicate that the tempera-

ture variation of the activation field δ is 1% °C⁻¹ in the neighborhood of room temperature.

It has been found that there are at least two types of 180° domain boundaries which move under the influence of an applied field.¹ The intersections of these boundaries with the crystal surface are either parallel or at 45° to the crystalline a axes. The relative ease with which the two types of boundaries move is field dependent. The published quantitative data^{1,3} on the field dependence of the wall velocity pertain to the walls which are at 45° to the a axes. Lastly, under certain conditions, the 180° domain walls do not appear to be parallel to the ferroelectric axis of the crystal.⁴⁻⁷ A complete theory should, of course, be capable of explaining in a convincing way the body of experimental facts mentioned above. Unfortunately, a theory encompassing all the data has not been found; however, one of the two models proposed in this paper is consistent with much of the data.

It is generally agreed that the 180° domain wall does not move sidewise in a continuous manner as a unit parallel to itself on an atomic scale. This type of motion is excluded on the basis of energy considerations which arise out of the high value of the estimated wall energy, 1-10 ergs cm⁻², and the estimated one to a few lattice constants thickness of the wall.^{4,8,9} Nakamura¹⁰ has suggested that screw dislocations may permit sidewise 180° wall motion to take place with applied

⁴ W. J. Merz, Phys. Rev. **95**, 690 (1954).

⁵ E. A. Little, Phys. Rev. **98**, 978 (1955).

⁶ D. P. Cameron, IBM J. Research Develop. **1**, 2 (1957).

⁷ R. C. Miller, Phys. Rev. **111**, 736 (1958).

⁸ W. Kanase and H. Takahasi, J. Phys. Soc. Japan **12**, 464 (1957).

⁹ V. A. Zhirnov, J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 1175 (1958) [translation: Soviet Phys. JETP **35**, 822 (1959)].

¹⁰ T. Nakamura, J. Phys. Soc. Japan **9**, 425 (1954).

¹ R. C. Miller and A. Savage, Phys. Rev. **115**, 1176 (1959).

² R. C. Miller and A. Savage (unpublished).

³ R. C. Miller and A. Savage, Phys. Rev. **112**, 755 (1958).

fields of the magnitude of those employed in recent experiments.¹ It will be shown that over the measured field range screw dislocations probably do not play an important role, if any at all, in the sidewise motion of the domain walls.

It has been pointed out that the wall may move through a nucleation type mechanism^{11,12} and that nucleation may be more favorable adjacent to an existing 180° domain wall over points in the crystal remote to the wall.¹³ The emphasis of the present paper is on a nucleation model for the wall motion, a model which will be shown to be consistent with a number of the salient features of the experimental data given earlier. The initial considerations which led to this model were put forth by Anderson in 1953.¹¹

In a recent paper¹⁴ Abe has considered the growth of 180° domains in BaTiO₃. The analysis includes some features which are somewhat similar to those described in the present text. Abe assumes that the depolarization energy can be neglected in the solution of the problem; however Abe does not justify this assumption with rigorous considerations. In the present treatment, the depolarization energy is not neglected and it is found that the depolarization energy does indeed affect the form of the solution of the problem.

NUCLEATION MODEL

Several investigators^{4,15} have shown that the electric field dependence of the probability for the nucleation of reversed domains can be of the form $\exp(-\text{const}/E)$. This field dependence is of the same form as that found for the sidewise wall motion where $v \propto \exp(-\text{const}/E)$ and therefore suggests that a nucleation mechanism may control the wall motion, i.e., nucleations occur along a 180° domain boundary and serve to propagate the boundary in a sidewise direction. In the following analysis, it is assumed that the wall moves through a nucleation mechanism and that the rate controlling process is the nucleation of steps along a wall, and not the subsequent growth of the nucleated steps.

The energy change consequent on the formation of a nucleus of volume V and domain wall area A can be written as

$$\Delta U = -2P_s EV + \sigma_w A + U_d, \quad (2)$$

in which σ_w is the wall energy per unit area, P_s the spontaneous polarization and U_d the depolarizing energy. The theory of the nucleation of reversed domains in BaTiO₃ at points remote to existing domain walls gives very large energies for the critical nucleus.¹² The energies estimated are of the order of $10^8 kT$. Therefore one seeks nuclear shapes and situations which appear to be capable of giving much smaller energies

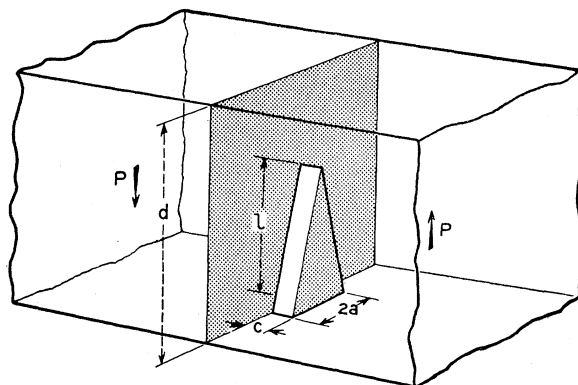


FIG. 1. Schematic drawing of a triangular step on a 180° domain wall. The applied electric field is parallel to the spontaneous polarization on the left side of the figure.

for the critical nucleus. Consider the nucleation of steps on a 180° domain wall. The additional domain wall consequent on the nucleation of steps of certain shapes may be made quite small. It will be shown that nucleations of this sort can lead to energies which are many orders of magnitude less than $10^8 kT$ and which are consistent with a thermal activation process for the formation of the critical nucleus.

It is assumed that the plane of the 180° domain wall is parallel to the ferroelectric axis of the crystal and that the steps are triangular in shape as shown in Fig. 1. Other shapes investigated by the authors, e.g., semicircular and square, were less successful than the one shown in Fig. 1. The dimensions of the step will be determined by a balance between the energy terms given in Eq. (2). The only additional domain walls which must be created during the nucleation event are the two edges, each of area $c(l^2 + a^2)^{1/2}$. For ease of calculation, the crystal thickness d is taken to be much larger than the height l of the nucleus. It will be shown that this condition is easily satisfied. The assumption is also made that the 180° domain wall is very thin, an assumption which is in agreement with all the theoretical estimates^{4,8,9} of the wall thickness.

The shape of the nucleus shown in Fig. 1 is not one of the family of general ellipsoids so that the calculation of the depolarizing energy term in Eq. (2) cannot be carried out in the usual manner in which a depolarizing factor is used. Furthermore, the dimension c will eventually be taken to be about one lattice constant so that an approximation of the nucleus by one of the general ellipsoids is not justified. The depolarizing energy has been calculated using a method suggested by Anderson,¹¹

$$U_d = \frac{1}{2} \iint \frac{\rho_1 \rho_2}{\epsilon r_{12}} d\tau_1 d\tau_2. \quad (3)$$

In this expression ρ_1 and ρ_2 are charge densities in volumes $d\tau_1$ and $d\tau_2$ separated by a distance r_{12} . The dielectric constant of the medium is ϵ . In the present

¹¹ P. W. Anderson (private communication).

¹² R. Landauer, J. Appl. Phys. **28**, 227 (1957).

¹³ G. H. Wannier (private communication).

¹⁴ R. Abe, J. Phys. Soc. Japan **14**, 633 (1959).

¹⁵ A. G. Chynoweth, Phys. Rev. **110**, 1316 (1958).

case, the only uncompensated charge will be that arising from the finite divergence of the spontaneous polarization on the two edges of the nucleus. Since these walls are assumed to be very thin and narrow, ρ_1 and ρ_2 will be replaced by a linear charge density $2P_s c \sin \theta$ where 2θ is the apex angle of the nucleus. The dielectric constant in ferroelectric BaTiO₃ is anisotropic so that in order to carry out the calculation indicated in Eq. (3), it is necessary to make a transformation¹² which changes the ratio of the z to the x and y dimensions by a factor of $(\epsilon_a/\epsilon_c)^{1/2}$. The quantities z and ϵ_c refer to the dimensions and dielectric constant, respectively, along the ferroelectric axis, while x , y , and ϵ_a refer to the a axes which are normal to the ferroelectric axis. After the transformation has been made, the medium can be treated as isotropic. U_d is found to be

$$U_d = 8P_s^2 \frac{c^2}{\epsilon_a} \frac{a^2}{l} \ln \frac{2a}{eb}. \quad (4)$$

The lattice constant b comes into the expression as the lower limit of r_{12} . The portion of Eq. (4) which involves $\ln 2$ arises from the interaction between charges on the two opposite sides, while the remaining part, $\ln(a/eb)$, is twice the interaction of the charges along one side.

The total energy change consequent on a nucleation along the wall, given by Eq. (2), can now be written as

$$\Delta U = -2P_s E a l c + 2\sigma_w c (a^2 + l^2)^{1/2} + 8P_s^2 (c^2 a^2 / \epsilon_a l) \ln(2a/eb). \quad (5)$$

The dimensions a^* and l^* of the critical nucleus as well as the activation energy ΔU^* are determined by the conditions

$$\partial \Delta U / \partial a = 0 \quad \text{and} \quad \partial \Delta U / \partial l = 0. \quad (6)$$

The width of the step c is taken to be as small as possible, one lattice constant, so that the minimum activation energy can be determined. The small variation of ΔU with a through $\ln a$ will be ignored. For ease of presentation, it is convenient to rewrite U_d in the form

$$U_d = 2\sigma_p b a^2 / l, \quad (7)$$

where

$$\sigma_p = (4P_s^2 b / \epsilon_a) \ln(2a/eb). \quad (8)$$

The conditions given in Eq. (6) applied to Eq. (5) yield

$$a^* = \frac{\sigma_w}{P_s E} \frac{(\sigma_w + 2\sigma_p)}{(\sigma_w + 3\sigma_p)}, \quad (9)$$

and

$$l^* = \frac{\sigma_w^{1/2}}{P_s E} \frac{(\sigma_w + 2\sigma_p)}{(\sigma_w + 3\sigma_p)^{1/2}}. \quad (10)$$

In the calculation, a^2/l^2 and higher order terms have been neglected compared to unity. It will be shown that this is a good approximation. Then ΔU^* can be

written

$$\Delta U^* = \frac{4b}{P_s E} \sigma_p (\sigma_w + 2\sigma_p) \left(\frac{\sigma_w}{\sigma_w + 3\sigma_p} \right)^{3/2}. \quad (11)$$

Anticipating a little, it will turn out that $\sigma_p > \sigma_w$ so that Eqs. (9), (10), and (11) can be approximated by

$$a^* = \frac{2}{3} (\sigma_w / P_s E), \quad (12)$$

$$l^* = 2\sigma_w^{1/2} \sigma_p^{1/2} / \sqrt{3} P_s E, \quad (13)$$

and

$$\Delta U^* = (8b/3\sqrt{3}) \sigma_p^{1/2} \sigma_w^{3/2} / P_s E. \quad (14)$$

The rate of nucleation is proportional to $\exp(-\Delta U^*/kT)$ so that if the sidewise wall motion is controlled by nucleations of this sort and if the number of nucleations per unit length of wall is not field dependent, the wall velocity can be expressed by

$$v \propto \exp(-\Delta U^*/kT), \quad (15)$$

or

$$v \propto \exp\left(-\frac{8b}{3\sqrt{3}} \frac{\sigma_p^{1/2} \sigma_w^{3/2}}{P_s E k T}\right). \quad (16)$$

Equation (16) is appealing since it is consistent with some of the experimental data. For limited ranges of E , i.e., several decades in velocity, Eq. (16) predicts a wall velocity which should vary with E as $\exp(-\text{const}/E)$. The small variation of σ_p with E through $\ln a^*$ will result in a theoretical activation field,

$$\delta_i \equiv -\frac{d \ln v}{d(1/E)} = \frac{1}{kT} \frac{d \Delta U^*}{d(1/E)}, \quad (17)$$

which decreases slightly with increasing field. However, nucleation steps of nb , $n > 1$, become more probable as the field increases so that one might expect that this effect tends to increase δ_i with field. It will be shown that in the measured field range steps with $n > 1$ are unlikely and therefore probably do not contribute to the wall motion. The data¹ show that $-d \ln v / d(1/E)$ increases by about 30% as the field increases from several hundred volts per centimeter to about 1500 v cm⁻¹. In any case, for limited ranges of electric field, the field dependence of the velocity given by Eq. (16) is in agreement with the data.

One would not expect a well-defined coercive field with a nucleation mechanism for the wall motion. This is in agreement with experiment.

Equation (16) also explains the shapes of the single domains observed in the low field region. It has been found that the 180° domain walls can move in a direction parallel to the a axes more easily than in any other direction.⁷ In the low field region where δ_i/E is large, motion of the wall in the direction in which δ_i is a minimum should be highly favored. This direction is parallel to the a axes where the minimum step is b , one lattice constant. The activation energy for a minimum step, for example, in a direction 45° to the

a axes is $2\frac{1}{2}$ as large as the activation energy for a minimum step parallel to the a axes.

The experimental data on the temperature dependence of the wall velocity which cover a range of 12°C give a change of 1% in δ per degree centigrade.¹ Several theoretical investigations^{4,8} have concluded that the 180° domain wall energy varies as P_s^2 . Therefore, if it is assumed that the temperature dependence of the wall energy is through a dependence of σ_w on P_s^2 , then δ will vary with temperature as $P_s^3 T^{-1} \epsilon_a^{-\frac{1}{2}}$. With the data for P_s and ϵ_a as a function of temperature given by Merz,^{16,17} $(d/dT)(P_s^3 T^{-1} \epsilon_a^{-\frac{1}{2}})$ results in a change of δ , equal to 0.6% °C⁻¹. Thus, there is fair agreement between the temperature dependence of the experimental and theoretical values of δ .

So far no mention has been made of the magnitude of δ , σ_p , σ_w , etc. If the model is correct, the magnitude of δ should, of course, be equal to the experimental value. One difficulty in estimating δ is the value to use for the wall energy σ_w . Theoretical values of the 180° domain wall energy range from about 1 to 10 ergs cm⁻² and pertain to large area walls which are in the plane of the ferroelectric axis.^{4,8,9} In the present case, the wall is very small in area (only one lattice constant wide) and the wall is not in the plane of the ferroelectric axis. Therefore, there is no assurance that the theoretical estimates of the wall energy are relevant to the walls under consideration here; however, one would guess that the order of magnitude was correct. The approach which has been taken is to equate the experimental and theoretical values of δ and solve for the wall energy. The experimental values of δ apply to the walls which are at 45° to the a axes so that the minimum nucleation step is not one lattice constant b , but $b\sqrt{2}$. Therefore, the b which appears in Eqs. (8) and (16) should be replaced with $b\sqrt{2}$. The experimental value of δ will be taken as 4000 v cm⁻¹ (13.3 esu) which is the figure obtained from measurements in the low field region on thick crystals where surface layer effects should be minimized.² The equation

$$\delta = 13.3 \equiv \delta_t = \frac{16}{3} \frac{2^{\frac{1}{2}}}{\sqrt{3}} \frac{b^{\frac{1}{2}}}{kT} \frac{\sigma_w^{\frac{1}{2}}}{\epsilon_a^{\frac{1}{2}}} \left(\ln \frac{a^* \sqrt{2}}{eb} \right)^{\frac{1}{2}} \times \left(1 + \frac{1}{2 \ln(a^* \sqrt{2}/eb)} \right) \quad (18)$$

with a^* given by Eq. (12) is then solved for σ_w . The appropriate dielectric constant ϵ_a is the clamped crystal value, 2000.¹² The lattice constant b is 4Å. For an applied field of 300 v cm⁻¹, one finds $\sigma_w = 0.42$ ergs cm⁻² which is as expected within an order of magnitude of the theoretical estimates. Other relevant quantities are $a^* = 3.6 \times 10^{-6}$ cm, $l^* = 16 \times 10^{-6}$ cm and $\sigma_p = 2.7$ ergs cm⁻². The ratio of the wall energy term in

Eq. (2) to the depolarizing energy term is 3. The total energy ΔU^* is 5×10^{-13} ergs, or about 12 kT . The assumption made earlier that $l^*/d \ll 1$ is a good approximation as d is of the order of 10^{-2} cm. Also, $\frac{1}{2}(a^*/l^*)^2$ is small compared to unity as assumed earlier in determining ΔU^* .

The possibility of steps nb with $n > 1$ was suggested as an explanation for the increase of $-d \ln v/d(1/E)$ with field. From Eqs. (8) and (14) it follows that for small n

$$\Delta U_n^* = n^{\frac{1}{2}} \Delta U_1^*, \quad (19)$$

where ΔU_1^* is the activation energy for the minimum step and ΔU_n^* the value of ΔU^* for a step n times the minimum. With steps of nb , the wall velocity becomes

$$v = \text{const} [\exp(-\Delta U_1^*/kT) + 2\exp(-2^{\frac{1}{2}} \Delta U_1^*/kT) + 3\exp(-3^{\frac{1}{2}} \Delta U_1^*/kT) + \dots] \quad (20)$$

Even with the largest field for which data are available, about 5 esu, the second term is only 7% of the first one. Thus, in the measured field range steps greater than the minimum probably do not occur with sufficient frequency to have much effect on the wall motion. Therefore, the theoretical value of δ is described by Eq. (18) which predicts a decrease of δ with field of about 20% as E goes 1 to 5 esu. The small increase of the experimental value of δ with field remains unexplained by the model.

With applied fields of about 1000 v cm⁻¹, octagonal shaped domains have been observed.¹ Thus, in this field region, the walls which are parallel to the a axes and those which are at 45° to the a axes move with the same velocity. This means

$$\sqrt{2} \exp(-\Delta U_{45}^*/kT) = \exp(-\Delta U_0^*/kT), \quad (21)$$

with

$$E \approx 1000 \text{ v cm}^{-1}.$$

Equation (21) requires that the wall energy be slightly different for nucleations on the two types of 180° domain walls. The wall energy for nucleations on the wall which is parallel to the a axes must be about 30% larger ($\sigma_w = 0.56$ ergs cm⁻²) than the σ_w calculated earlier.

What can be said regarding the subsequent growth of the activated nucleus? The ratio of l/a , which is about 4 for the critical nucleus, in most cases cannot possibly remain constant as the step attains its final size. The final value of a cannot be greater than the width of the parent domain which can, of course, be several orders of magnitude less than the crystal thickness. Since the data show that the wall velocity does not depend on the size of the parent domain, it seems likely that the final value of a is the same for all domains, therefore less than the smallest ones measured, several microns in diameter. On the other hand, l most likely approaches d as the step grows. In addition, there are theoretical considerations which also indicate that

¹⁶ W. J. Merz, Phys. Rev. **91**, 512 (1953).

¹⁷ W. J. Merz, Phys. Rev. **76**, 1221 (1949).

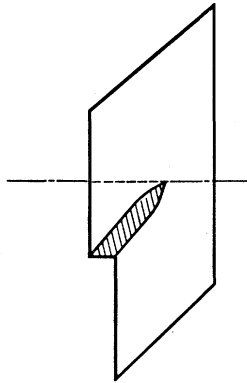


FIG. 2. Step in a 180° domain wall which occurs when the wall is pierced by a screw dislocation normal to the wall.

the width a should not remain constant as $l \rightarrow d$. The depolarizing energy can decrease, and therefore tend to increase the value of a beyond a^* , as the nucleus approaches the opposite side of the crystal for at least two reasons. First, the interaction of the polarization charge on the sides of the nucleus with the opposite electrode will reduce the depolarizing energy; and secondly, as the nucleus grows, the polarization charge in the side walls may be partially compensated by free charge within the crystal. Another important point is that sidewise motion of a wall moving in a continuous manner parallel to itself is considered to be very unlikely. Therefore, the activated nucleus would prefer to grow in such a way that the amount of sidewise motion of the edges was kept small. This would favor a final value of a not much larger than a^* . The edges of the full grown nucleus are probably parallel, or nearly parallel, to the ferroelectric axis since there is less energy associated with a wall which has no polarization charge on it, i.e., parallel to the ferroelectric axis, than a wall which is slanted with respect to the ferroelectric axis. For the reasons given above, it therefore seems likely that the final shape of the grown nucleus is that of a thin narrow slab, one lattice constant thick, d in length and something larger than a^* in width.

The nucleation model described above explains many aspects of data; however, the model is not entirely satisfactory. Some of the data have not been explained and in addition, several assumptions of uncertain validity have been made, e.g., the large area domain wall is a plane parallel to the ferroelectric axis and the fields given in the data (the applied voltage divided by the crystal thickness) are the local fields in the region where nucleations are thought to occur. The dislocation model described below has also been investigated in some detail since it provides another mechanism for sidewise wall motion with small applied fields.

DISLOCATION MODEL

In the following analysis the crystal will be treated as an isotropic medium, and the depolarizing energy will be ignored. These two approximations permit a

brief presentation and do not significantly affect the qualitative conclusions presented.

It was suggested by Nakamura¹⁰ that the presence of a screw dislocation could materially affect the motion of the domain wall. The reason is basically that if the wall is pierced by a dislocation whose Burgers vector has a component perpendicular to the wall, it becomes impossible for the wall to be flat. As shown in Fig. 2, there must exist a step in the wall which extends outward from the dislocation. Sidewise motion can then be accomplished by merely "screwing" the step around the dislocation in the appropriate sense, and one might expect an activation energy for this process considerably below that required for the bodily motion of the wall.

Now it is not, of course, realistic to consider the presence of but one dislocation; but it is necessary to consider only those dislocations whose direction and Burgers vector both have a component perpendicular to the wall (thus pure edge dislocations perpendicular to the wall are ruled out). Let there be 2β such dislocations per unit area of the wall, of which half are right-handed screws and half left-handed. Each one of these is then a terminal point of a wall step of the type shown in Fig. 2; but these steps, instead of running out indefinitely, now end on another dislocation of opposite sense.

In the discussion which follows, it will be important to know the distribution in length of the steps. Note that the energy of a step of length l is σbl , and that two different types of distributions are possible. If the temperature or the dislocation density is low, each step will proceed to the nearest opposite dislocation available, with $\langle l \rangle_{Av} \approx \beta^{-1/2}$; whereas at high temperatures or densities the average l will be thermally determined, with $\langle l \rangle_{Av} \approx kT/\sigma b$.

Consider now Fig. 3, which shows what will happen to a wall step connecting two dislocations when an electric field is applied. In this case the straight line is no longer the equilibrium curve for the step. For the isotropic case it is easily to show that if the depolarizing energy is ignored, the step will be a circular arc whose radius of curvature is given by

$$R = \sigma / 2EP_s, \quad (22)$$

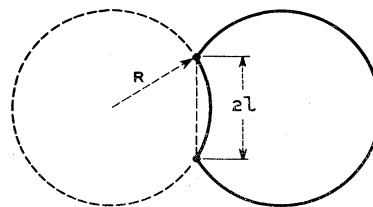


FIG. 3. Effect of an electric field on the shape of the step produced in a 180° domain wall by paired screw dislocations of opposite sense. The 180° domain-boundary is in the plane of the figure. For $R > l$, there are in general two circular arcs which connect the ends of the step. The smaller one gives a stable configuration, while the larger one is unstable and expands out.

with the direction of bowing determined so as to increase the volume of energetically favored polarization. As Fig. 3 indicates, there are in general two possible arcs of given curvature connecting two points; it turns out that of these the shorter one is stable, whereas the longer one is unstable. In other words, once the larger arc is reached, it becomes energetically favorable for it to expand without limit.

Now it is an important feature of this configuration that if $R < l$ the construction of Fig. 3 is impossible; that is, a step of length $2l$ possesses no stable form if

$$E > \sigma/2Pl. \quad (23)$$

Instead, the wall will expand in the sequence of Fig. 4, continually sending out "ripples" which give rise to a continuous advance of domain wall into or out of the plane of the drawing. This mechanism bears an obvious similarity to some processes of crystal growth and of mechanical yield.¹⁸

Consider the consequences of such a mechanism. Assume first that

$$\beta^{-1}\sigma b \gg kT, \quad (24)$$

so that each wall step goes from its initial dislocation to the nearest available dislocation of opposite sense. If these are randomly distributed, the probability $p(l)dl$ of a step having a half-length between l and $l+dl$ is given by

$$p(l)dl = -d[\exp(-4\pi\beta l^2)]. \quad (25)$$

Therefore the fraction $f(E)$ of "active" sources, that is, of steps whose length is greater than the critical value given by Eq. (23) is

$$f(E) = - \int_{l=\sigma/2EP_s}^{\infty} d[\exp(-4\pi\beta l^2)] \\ = \exp(-\pi\beta\sigma^2/E^2P_s^2). \quad (26)$$

Now this $f(E)$ may be taken as the approximate form of the dependence of wall velocity on applied field for the present mechanism. Since the experiments reveal a dependence whose exponent contains E^{-1}

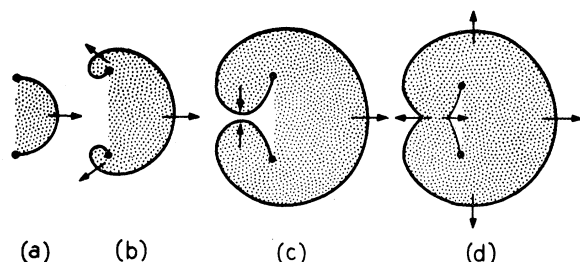


FIG. 4. Motion of the step in a 180° domain wall when the applied field is sufficiently large so that the step possesses no stable form. This mechanism serves to propagate the wall into or out of the plane of the figure.

¹⁸ See, for example, W. T. Read, Jr., *Dislocations in Crystals* (McGraw-Hill Book Company, Inc., New York, 1953).

rather than E^{-2} , one must choose among the following three conclusions.

(I) The distribution of dislocations is not random, but such that the integration in Eq. (26) yields an $\exp(-\delta/E)$ law.

(II) The concentration of dislocations is so low that, even at the lowest experimental fields, *all* the sources are active; so that the rate-limiting process in the wall motion is actually in the spreading of the "ripples."

(III) The concentration of dislocations is so high that, even at the highest experimental fields, virtually *none* of the sources are active, and wall motion occurs by some other process.

Regarding conclusion I, an E^{-1} exponent can be obtained if one assumes a preference of dislocations of opposite sense to be close together. In particular, it is required that given a dislocation piercing the wall, the probability per unit wall area of finding a dislocation of opposite sense be inversely proportional to the distance between the two. Such a distribution, if it existed, would have to arise during the original process of crystal growth. Although it is true that dislocations of opposite sense attract each other, there appears to be no plausible reason for assuming that a very exact inverse distance distribution results.

Regarding conclusion II, the experimental measurements² go down to about 100 v cm^{-1} so that according to Eq. (23) the average distance between dislocations would have to be well above $4 \times 10^{-5} \text{ cm}$. This would be somewhat surprising in a crystal grown under such drastic nonequilibrium conditions. In any case, one would expect the "ripples" to move out according to a mobility-type law rather than an exponential of inverse field.

Accordingly, conclusion III is left as the most plausible one. With fields of a few thousand volts per centimeter, Eq. (25) requires an average distance between dislocations less than about 10^{-6} cm . It should be noted that this is approximately the length of step that would be thermally excited near room temperature, so that regardless of the density of dislocations, some active sources should appear at a few thousand volts cm^{-1} . This may possibly explain the slight wall velocity increase over the ordinary exponential law which has been observed at higher fields.

It remains to consider the possibility that, even though few or no "active" sources exist, the "passive" ones might occasionally be thermally excited to the unstable position of Fig. 3 and thus act as nucleation centers. Now it is easy to see that at the lower experimental fields such a process is not likely to contribute appreciably to the wall motion. The reason is that if the wall energy in the step is very small compared to the activation energy required to reach the unstable state, the step has no particular advantage as a nucleation center over other points of the crystal. At very high fields, on the other hand, such an activated process may begin to contribute, thus providing a continuous

transition with increasing field to the mechanism of the previous paragraph.

SUMMARY

Two mechanisms have been investigated to explain the experimental data on the sidewise motion of 180° domain walls in single crystal BaTiO_3 . A nucleation model which assumes that the wall motion is controlled by the nucleation of triangular steps along existing 180° walls satisfactorily explains much of the data. Over limited field ranges, the model predicts a wall velocity $v \propto \exp(-\delta/E)$, as observed. The theoretical and experimental values of δ agree if the wall energy σ_w is set equal to 0.4 ergs cm^{-2} , a value in order of magnitude agreement with theoretical estimates of the wall energy. The shapes of the domains observed in the low field region are in agreement with the model. Furthermore, provided that slightly different wall energies are assumed for nucleations on parent walls parallel and at 45° to the crystalline a axes, the model

accounts for the change in domain shapes observed with field in the neighborhood of 1000 v cm^{-1} . The measured temperature dependence of the wall velocity is in fair agreement with the nucleation model which gives a variation of the activation field δ with temperature through $P_s^3 T^{-1} \epsilon_a^{-1/2}$.

A screw dislocation mechanism has also been discussed. If it is assumed that the screw dislocations of both senses are randomly distributed in the crystal, and that they are not too close together, then the expected form of the wall velocity is $v \propto \exp(-\text{const}/E^2)$ which is not in agreement with experiment. The possibility that screw dislocation sources may become active at higher fields is suggested. Such a process may account for the observed small increase in $-d \ln v/d(1/E)$ with field.

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Extension of the Madelung Method for the Evaluation of Lattice Sums

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The Madelung formulas for the electrostatic potential of a linear or planar Bravais lattice of ions, neutralized by a uniform distribution of charge, are extended to the lattice sums over a linear or planar Bravais lattice involving two-body interactions of the type R^{-n} (R , interatomic distance; $n > 0$), evaluated at points outside the lattice. The application of these generalized Madelung formulas in the evaluation of the specific face energy for neutral planes of an ionic solid of composition MX is briefly discussed.

1. INTRODUCTION

A WELL-KNOWN method for the evaluation of electrostatic lattice potentials is the so-called *Madelung method*.¹ In essence, the method involves the expansion of the electrostatic potential of a Bravais lattice of point charges, neutralized by a uniform distribution of charge, into a Fourier series of complex exponentials with the required periodicity. The series that one obtains do not converge rapidly inside the lattice itself, and thus the relevant results of the method are the formulas for the electrostatic potential generated by a neutralized linear or planar Bravais lattice in its surroundings. We will show that these formulas can be easily extended to the case of lattice sums over a linear or planar Bravais lattice involving interactions between pairs of atoms which decrease with some power of the distance, such as the van der Waals interactions, evaluated at points outside the lattice. In effect the

formulas given by Hove and Krumhansl² for interaction energies of this type between a semi-infinite cubic or square lattice of atoms and an atom outside it, as well as the expressions given by Benson and his co-workers³ for various lattice sums of interest in the theory of the surface energy of ionic crystals, can be regarded as particular applications of the generalized Madelung method.

2. LINEAR BRAVAIS LATTICE

We consider a linear Bravais lattice of period a along the x axis with lattice points in the positions $x_l = la$ (l , integer) and a point (x, r) , a distance r from the line of the lattice ($r > 0$). To evaluate the sum

$$S_n(x, r) = \sum_{l=-\infty}^{+\infty} \frac{1}{[(x - x_l)^2 + r^2]^{n/2}}, \quad (1)$$

² J. Hove and J. A. Krumhansl, *Phys. Rev.* **92**, 569 (1953).

¹ See, e.g., M. Born, *Atomtheorie des festen Zustandes* (B. G. Teubner, Leipzig, 1923), Sec. 37 and G. Leibfried, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. VII/1, p. 104, Sec. 26.

³ B. M. E. van der Hoff and G. C. Benson, *Can. J. Phys.* **31**, 1087 (1953); G. C. Benson and H. P. Schreiber, *Can. J. Phys.* **33**, 529 (1955); H. P. Schreiber and G. C. Benson, *Can. J. Phys.* **33**, 534 (1955); F. van Zeggeren and G. C. Benson, *J. Chem. Phys.* **26**, 1077 (1957).