

General Features of the Intrinsic Ferroelectric Coercive Field

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The value of the intrinsic ferroelectric coercive field is obtained independently from general energy considerations and from the predictions of several models of the ferroelectric state. All predictions yield a value of order of the depolarization field, which is equal to the spontaneous polarization divided by the dielectric permittivity, and are consistent with the recent measurements of the intrinsic ferroelectric coercive field in ultrathin Langmuir-Blodgett films of copolymers of polyvinylidene fluoride with trifluoroethylene. Prior studies had succeeded only in measuring the much smaller extrinsic coercive fields, which are limited by nucleation processes and domain motion.

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The defining characteristic of a ferroelectric is the ability repeatedly to reverse, or switch, the polarization by application of a sufficiently large external electric field as illustrated by the hysteresis loops in Fig. 1. Yet since the discovery of ferroelectricity eighty years ago by Valasek, few published reports have considered the value of the intrinsic coercive field connected with collective polarization reversal, a consequence of the instability of the macroscopic polarization state in an opposing electric field. This is because the measured value of the ferroelectric coercive field has been invariably much smaller than the intrinsic value predicted by theory, such as the Landau-Ginzburg (LG) mean field model [1] or by ferroelectric Ising model [2,3]. The low extrinsic coercive field observed in real ferroelectric crystals and films is caused by nucleation of domains with reversed polarization, which then grow and coalesce by domain wall motion [2,4,5]. Nucleation can occur at fixed defects in the crystal or due to a passive (nonferroelectric) surface layer [6]. Nucleation mechanisms and domain wall dynamics must be arbitrarily inserted into these models in order to explain the experimental observations of switching kinetics with much lower coercive fields in real ferroelectric materials [2]. In fact, the study and modeling of extrinsic switching is a great industry in the field and is central to the application of ferroelectric films to nonvolatile random-access memories [7].

It has proven difficult to prevent extrinsic switching by eliminating defects or pinning domain walls. Another way to achieve intrinsic switching is to make a particle small enough or a film thin enough to inhibit nucleation [5,8–10]. Several mechanisms for this finite-size effect have been proposed, including reduction of nucleation volume, introduction of space charge near the electrodes, elimination of passive layers, and domain-wall pinning [4,6,10,11]. Even in the thinnest ferroelectric films obtained previously, the measured extrinsic coercive field is much smaller than the expected intrinsic value calculated from theoretical models, and con-

sequently there has been relatively little published discussion of intrinsic switching, except to note that it remained out of reach. The thin ferroelectric films have indeed shown the nucleation-inhibition finite site effect, an increase of the coercive field with the decrease of thickness, but the value of the measured coercive field was still much lower than the intrinsic one and correspondingly the switching is still controlled by the nucleation and domains. Recently [12], we succeeded in finding the limiting intrinsic coercive field in films as thin as 1 nm made by Langmuir-Blodgett (LB) deposition of a two-dimensional ferroelectric copolymer [13].

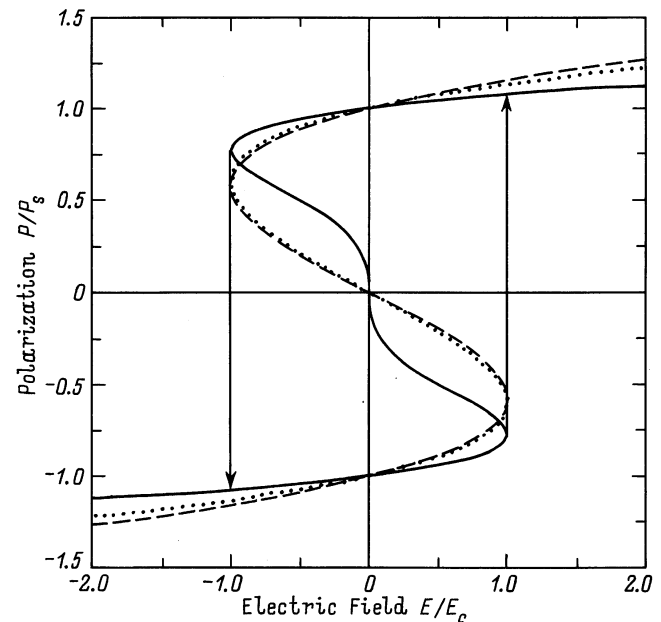


Figure 1. Theoretical ferroelectric hysteresis loops from the first-order Landau-Ginzburg model (solid line), second-order Landau-Ginzburg model (dashed line), Ising-Devonshire model (dotted line).

The measured values of the intrinsic coercive field were in good agreement with the predictions of the LG mean-field theory [1,14]. Here, we analyze the calculation of the intrinsic coercive field from a more general perspective and from several specific models of ferroelectricity.

We can estimate the intrinsic ferroelectric coercive field E_c by calculating the external electric field necessary to overcome the depolarization field $P_S/\varepsilon\varepsilon_0$, where P_S is the spontaneous polarization, ε is the dielectric constant (More precisely, the contribution to the dielectric constant from ferroelectricity. The total dielectric constant of the medium $\varepsilon_T = \varepsilon_B + \varepsilon$ contains contributions from the background polarizability and the ferroelectric polarizability) along the direction of spontaneous polarization and ε_0 is the permittivity of free space. The energy density associated with the spontaneous polarization is $u_P = (1/2)P_S^2/\varepsilon\varepsilon_0$. Application of an external field E in a direction opposite to the spontaneous polarization, would contribute to energy density $u_E = \mathbf{E} \cdot \mathbf{P}_S = -EP_S$. (This contribution applies to all kinds of ferroelectrics, whether displacive, order-disorder, or other. For example, in ferroelectric materials consisting of fixed dipoles, with the dipole moment μ and density N , that form macroscopic polarization $\mathbf{P}_S = -N\langle\mu\rangle$, as in ferroelectric polymers, the energy density of the dipoles in the applied field is $u_E = -N\langle\mathbf{E} \cdot \mu\rangle$, leading to the same result). The intrinsic coercive field E_c is then approximately the value of the applied field that produces an energy comparable to the polarization energy, $u_E \approx u_P$, so that the intrinsic coercive field is approximately half the depolarization field,

$$E_c \approx \frac{1}{2} \frac{P_S}{\varepsilon\varepsilon_0} \quad (\text{from energy}). \quad (1)$$

The intrinsic coercive field for a ferroelectric-paraelectric phase transition of the first order (close to second order) can be calculated from the Landau–Ginzburg phenomenology (LG1) [15,16]. The LG1 Gibbs free energy in a uniaxial material is $G = G_0 + (1/2)\alpha P^2 + (1/4)\beta P^4 + (1/6)\gamma P^6 - PE$, where the first coefficient is the Curie–Weiss form $\alpha = (T - T_0)/(\varepsilon_0 C)$, T_0 is the Curie temperature, C is the Curie constant, the second coefficient obeys the condition $\beta < 0$, whereas that for the necessary third coefficient is $\gamma > 0$. The parameters T_0 , β , and γ are assumed independent of temperature and electric field. From the minima of the free energy density, it is possible to calculate the properties of the ferroelectric phase that exists just below the zero-field transition temperature $T_C = T_0 + (3/16)\varepsilon_0 C \beta^2/\gamma$. In the ferroelectric phase, the spontaneous polarization is $P_S = \pm\sqrt{-\beta(1 + \sqrt{1-t})/2\gamma}$, where $t = 4\alpha\gamma/\beta^2$, and the ferroelectric contribution to the dielectric constant is given by $1/\varepsilon\varepsilon_0 = -8\alpha + (9/4)(\beta^2/\gamma)$. The LG1 intrinsic coercive field from just below $T_0(t = 0)$ up to $T_C(t = 3/4)$ is well approximated by $E_c \approx 2\beta(3|\beta|/5\gamma)^{3/2}(1 - (25/24)t)$ [12,17], so the coer-

cive field can be written as

$$E_c \approx \frac{3\sqrt{3}}{25\sqrt{5}} \frac{P_S}{\varepsilon\varepsilon_0} \left(1 - \frac{1}{6}t\right) \quad (\text{from LG1}). \quad (2)$$

The value of the intrinsic coercive field E_c near the Curie temperature T_0 is about 1/10 of the depolarization field.

The Landau–Ginzburg continuous ferroelectric phase transition of the second order (LG2) [1] is modeled with a free energy $G = G_0 + (1/2)\alpha P^2 + (1/4)\beta P^4 - PE$, where the first coefficient is again $\alpha = (T - T_0)/(\varepsilon_0 C)$, and the second coefficient $\beta > 0$. The ferroelectric phase in zero electric field exists below the transition temperature $T_C = T_0$, where the spontaneous polarization $P_S = \pm\sqrt{-\alpha/\beta}$ and the ferroelectric contribution to the dielectric permittivity is given by $1/\varepsilon\varepsilon_0 = -2\alpha$. The intrinsic coercive field $E_c = 2\beta(-\alpha/3\beta)^{3/2}$ calculated from the LG2 free energy can be written [17]

$$E_c = \frac{1}{3\sqrt{3}} \frac{P_S}{\varepsilon\varepsilon_0} \quad (\text{from LG2}). \quad (3)$$

Devonshire [16] applied the Ising model to ferroelectrics consisting of electric dipoles with dipole moment p_0 , which can achieve a collective ordered state. The two-level (spin-1/2) Ising–Devonshire (ID) model describes a uniaxial ferroelectric with an order-disorder phase transition with the an order parameter equal to the normalized spontaneous polarization $S = P_S/P_{S0}$, where $P_{S0} = Np_0$. The order parameter is obtained from the transcendental equation [2,3,16] $S = \tanh[(J_0 S + Ep_0)/kT]$, where k is the Boltzmann constant and J_0 is the pseudospin Ising interaction constant.

In the ferroelectric phase near (but below) $T_C = T_0 = J_0/k$, the zero-field spontaneous polarization follows a simple 1/2 power scaling $S \approx \pm\sqrt{3(1 - T/T_C)}$, and the dielectric constant is given by $1/\varepsilon\varepsilon_0 \approx [(kT_0)/(Np_0^2)][1 - T/T_0]$. The ID intrinsic coercive field near T_C is approximately $E_c \approx [(2kT_0)/(3p_0)][1 - T/T_0]^{3/2}$, so the coercive field near T_C can be written

$$E_c \approx \frac{1}{3\sqrt{3}} \frac{P_S}{\varepsilon\varepsilon_0} \quad (\text{ID}). \quad (4)$$

Note that the ID and LG2 models are equivalent near T_0 , predicting the same temperature dependencies for spontaneous polarization, dielectric constant, and coercive field, because near T_C the ID order parameter S is small and the free energy of the ID model can be expanded in powers of P_S , to reproduce the LG2 free energy.

The value of the coercive field near the Curie temperature T_0 obtained from the three mean-field models (Eqs. 2–4) ranges from 10 to 20% of the depolarization field $P_S/\varepsilon\varepsilon_0$, a little less than the value 50% estimated from basic energy considerations (Eq. 1), even as the spontaneous polarization and dielectric constant vary strongly with temperature. The predictions hold well near T_0 for all models, as shown in Fig. 2. Therefore, the essential existence and approximate value of the intrinsic coercive field does not

Typical experimental values of the coercive field E_C^{exp} compared to the depolarization field E_d for BaTiO₃, TGS and BL copolymer films (all values obtained near T_0)

Material	ϵ	$P_S, \text{C/m}^2$	$E_C^{\text{exp}}, \text{MV/m}$	$E_d = P_S/\epsilon\epsilon_0, \text{MV/m}$	$E_C^{\text{exp}}/(1/2)E_d$
BaTiO ₃ [18]	150	0.26	0.20	196	0.0020
triglycine sulphate (TGS) [19]	43	0.028	0.011	74	0.00030
KD ₂ PO ₄ [20]	43	0.062	0.34	163	0.0042
PZr _{0.25} Ti _{0.75} O ₃ (PZT)100 nm thin film [21]	200	0.38	10	215	0.093
polyvinylidene fluoride (PVDF) [22]	11	0.065	55	667	0.16
# P(VDF:TrFE 65:35) [23]	9.3	0.080	45	972	0.093
# P(VDF:TrFE 75:25) 60 nm thin film [24]	10	0.10	125	1129	0.22
P(VDF-TrFE 70:30) ≤ 15 nm thin films [13,17]	8	0.10	480	1412	0.68
Ratio $E_C / (1/2)E_d$ (at T_0) predicted by				Model	
				LG1	0.18
				LG2	0.38
				ID	0.38

depend on the nature of the ferroelectric transition, whether it is first order or second order, displacive or order-disorder, from permanent dipoles or induced dipoles. However, the measured dielectric constant includes the background contribution and near T_C the ferroelectric contribution is typically larger than the equilibrium value due to thermal hysteresis (especially in first-order ferroelectrics), particularly in ferroelectrics with a first-order phase transition. Therefore, the value of the depolarization field $P_S/\epsilon\epsilon_0$ obtained from direct measurements near T_C will likely be somewhat less than the intrinsic value.

Measurements of the coercive field in bulk ferroelectric crystals has invariably yielded values much smaller than the intrinsic value, as summarized in the Table. While the traditional ferroelectrics extremely low coercive fields, the ferroelectric polymer polyvinylidene fluoride (PVDF) and its copolymers showed considerably higher coercive fields, typically 50 MV/m in "bulk" films, approaching the intrinsic value predicted by the various models. By 1986, Kimura

and Ohigashi [24] reported that copolymer films thinner than 1 μm showed increasing coercive fields with decreasing thickness (Fig. 3), down to a then-record coercive field of 125 MV/m in a copolymer film 60 nm thick [24]. But the solvent-spinning techniques used would not yield thinner films of sufficient quality and dielectric strength, so the measurement of the intrinsic coercive field lay just beyond reach.

The successful fabrication by LB deposition of ultra-thin films of PVDF and copolymers with trifluoroethylene (TrFE) beginning in 1995 [25–27] presented us with highly crystalline films with the polymer chains lying in the film plane and polarization axis perpendicular to the film. These films, ranging in thickness from 1 nm to over 100 nm, allowed us to study ferroelectricity down to the monolayer level [12,13,25–29]. One of the surprising results from these studies was the existence of two-dimensional ferroelectricity [13], as the ferroelectric phase persisted in the thinnest films, with no significant decrease in the transition temperature, contrary to the common expectation that finite-size scaling would suppress ferroelectricity. But finite-size effects did appear to suppress nucleation in films thinner than 1 μm [24,28]. As Fig. 3 shows, the rising coercive field with decreasing thickness d observed by Kimura and Ohigashi continues with the thinner LB films to follow a $d^{-0.7}$ power law scaling down to a thickness of 15 nm [28], consistent with a finite-thickness suppression of nucleation or domain wall motion.

The films of thickness 15 nm (30 monolayers) or less, on the other hand, had coercive fields of about 500 MV/m at 25°C, comparable to the theoretical intrinsic value [12] calculated with the LG1 model with free-energy coefficients determined in prior studies [30,31]. Because of uncertainties in the LG1 parameters the good coincidence between the measured and expected coercive field did not ensure that it was indeed the intrinsic value. But, cessation of finite-size scaling below 15 nm implies that polarization reversal longer initiated by nucleation, that is, nucleation

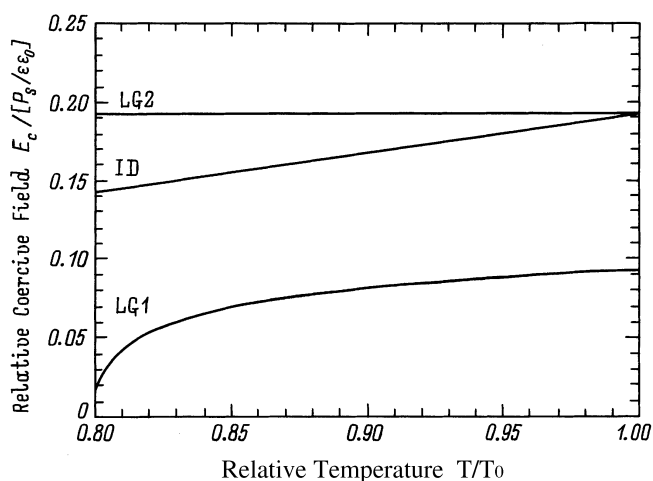


Figure 2. Intrinsic coercive field E_C , normalized to the depolarization field $P_S/\epsilon\epsilon_0$ calculated from LG2 model, LG1 model, and ID model.

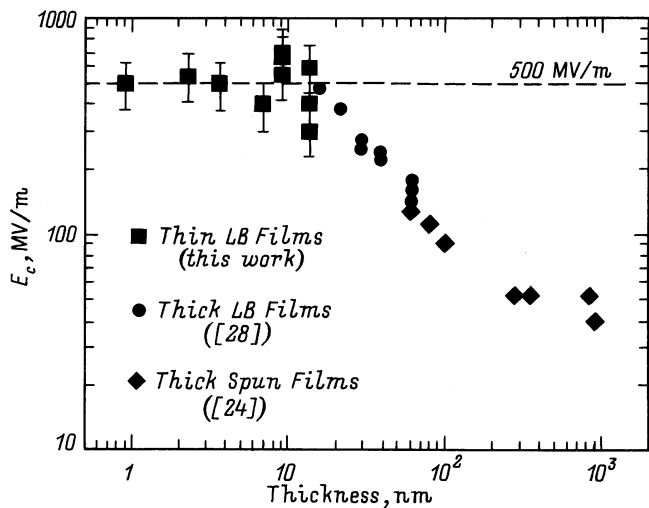


Figure 3. Scaling with thickness of the coercive field, measured at or near at 25°C, of ferroelectric vinylidene fluoride-trifluoroethylene copolymer films. Adapted from [12].

is inhibited, and polarization reversal depends only on the intrinsic ferroelectric properties. Detailed measurements of the temperature dependence of the coercive field confirmed the specific predictions of the LG1 model [12] and thus established that the intrinsic measurements coincided with the intrinsic coercive field. Though nucleation and domains do not limit the value of the coercive field, they should play a key role in switching dynamics. Preliminary imaging of the polarization through pyroelectric scanning microscopy has not revealed domains larger than the 2 μm resolution of our current system, but further study is necessary before any can be said about domain and crystallite properties.

It is not clear whether or not the two-dimensional nature of ferroelectricity in the vinylidene fluoride copolymers was essential for this achievement. There may soon be results bearing on this question as several groups have reported making good films with thickness less than 10 nm from several known bulk ferroelectric materials [21,32–34]. Recent improvements in the quality of solvent-crystallized of vinylidene fluoride copolymers should help elucidate the effects nucleation and domain-wall motion in bulk crystals [35–37].

References

- [1] V. Ginzburg. Zh. Eksp. Teor. Fiz. **15**, 739 (1945).
- [2] M.E. Lines, A.M. Glass. Principles and Applications of Ferroelectrics and Related Materials. Clarendon, Oxford (1977). 680 p.
- [3] B.A. Strukov, A.P. Levanyuk. Ferroelectric Phenomena in Crystals. Springer Verlag, Berlin (1998).
- [4] W.J. Merz. Phys. Rev. **95**, 690 (1954).
- [5] W.J. Merz. J. Appl. Phys. **27**, 938 (1956).
- [6] A. M. Bratkovsky, A.P. Levanyuk. Phys. Rev. Lett. **84**, 3177 (2000).
- [7] O. Auciello, J.F. Scott, R. Ramesh. Phys. Today **51**, 22 (1998).
- [8] K. Dimmler, M. Parris, D. Butler, S. Eaton, B. Pouligny, J.F. Scott, Y. Ishibashi. J. Appl. Phys. **61**, 5467 (1987).
- [9] J.F. Scott. Phase Transitions **30**, 107 (1991).
- [10] Y. Ishibashi. In: Ferroelectric Thin Films: Synthesis and Basic Properties / Ed. by C. Paz de Araujo, J.F. Scott, G.W. Taylor. Gordon and Breach, Amsterdam (1996). P. 135.
- [11] A.K. Tagantsev. Integrated Ferroelectrics **16**, 237 (1997).
- [12] S. Ducharme, V.M. Fridkin, A. Bune, S.P. Palto, L.M. Blinov, N.N. Petukhova, S.G. Yudin. Phys. Rev. Lett. **84**, 175 (2000).
- [13] A.V. Bune, V.M. Fridkin, S. Ducharme, L.M. Blinov, S.P. Palto, A. Sorokin, S. G. Yudin, A. Zlatkin. Nature **391**, 874 (1998).
- [14] V. Ginzburg. Zh. Eksp. Teor. Fiz. **10**, 107 (1946).
- [15] V. Ginzburg. Zh. Eksp. Teor. Fiz. **19**, 39 (1949).
- [16] A.F. Devonshire. Advances in Physics **3**, 85 (1954).
- [17] L.M. Blinov, V.M. Fridkin, S.P. Palto, A.V. Bune, P.A. Dowben, S. Ducharme. Physics Uspekhi **170**, 243 (2000).
- [18] F. Jona, G. Shirane. Ferroelectric Crystals. Macmillan, N. Y. (1962).
- [19] P.J. Lock. Appl. Phys. Lett. **19**, 390 (1971).
- [20] G.A. Samara. Ferroelectrics **5**, 25 (1973).
- [21] T. Maruyama, M. Saitoh, I. Sakai, T. Hidaka, Y. Yano, T. Noguchi. Appl. Phys. Lett. **73**, 3524 (1998).
- [22] M.A. Marcus. Ferroelectrics **40**, 29 (1982).
- [23] T. Fukukawa. Ferroelectrics **57**, 63 (1984).
- [24] K. Kimura, H. Ohigashi. Jpn. J. Appl. Phys. **25**, 383 (1986).
- [25] S. Palto, L. Blinov, A. Bune, E. Dubovik, V. Fridkin, N. Petukhova, K. Verkhovskaya, S. Yudin. Ferro. Lett. **19**, 65 (1995).
- [26] A. Bune, S. Ducharme, V.M. Fridkin, L. Blinov, S. Palto, N. Petukhova, S. Yudin. Appl. Phys. Lett. **67**, 3975 (1995).
- [27] S. Palto, L. Blinov, E. Dubovik, V. Fridkin, N. Petukhova, A. Sorokin, K. Verkhovskaya, S. Yudin, A. Zlatkin. Europhys. Lett. **34**, 465 (1996).
- [28] L.M. Blinov, V.M. Fridkin, S.P. Palto, A.V. Sorokin, S.G. Yudin. Thin Solid Films **284–285**, 474 (1996).
- [29] S. Ducharme, S.P. Palto, L.M. Blinov, V.M. Fridkin. In: Proceedings of the Fundamental Physics of Ferroelectrics / Ed. by R. Cohen, K. Rabe. American Institute of Physics, Aspen, CO (2000). P. 354.
- [30] S. Ducharme, A.V. Bune, V.M. Fridkin, L.M. Blinov, S.P. Palto, A.V. Sorokin, S. Yudin. Phys. Rev. **B 57**, 25 (1998).
- [31] A.V. Bune, C. Zhu, S. Ducharme, L.M. Blinov, V.M. Fridkin, S.P. Palto, N.G. Petukhova, S.G. Yudin. J. Appl. Phys. **85**, 7869 (1999).
- [32] T. Tybell, C.H. Ahn, J.-M. Triscone. Appl. Phys. Lett. **75**, 856 (1999).
- [33] E.D. Specht, H.-M. Christen, D.P. Norton, L.A. Boatner. Phys. Rev. Lett. **80**, 4317 (1998).
- [34] J.F.M. Cillessen, M.W.J. Prins, R.M. Wolf. J. Appl. Phys. **81**, 2777 (1997).
- [35] H. Ohigashi, K. Omote, H. Abe, K. Koga. Jpn. J. Appl. Phys. **68**, 1824 (1999).
- [36] H. Ohigashi, K. Omote, T. Gomyo. Appl. Phys. Lett. **66**, 3281 (1995).
- [37] M. Hikosaka, K. Sakurai, H. Ohigashi, T. Koizumi. Jpn. J. Appl. Phys. **32**, 2029 (1993).