

Comment on: “Intrinsic Ferroelectric Coercive Field”

In their recent Letter [1] Ducharme *et al.* have claimed that they observed for the first time an “intrinsic coercive field” E_c in ultrathin Langmuir-Blodgett (LB) films of vinylidene fluoride copolymer (VDF-TrFE), as predicted by the Landau-Ginzburg theory of ferroelectricity. The term “intrinsic coercive field” stands here for the field which is necessary to reverse the spontaneous polarization *homogeneously* over the sample, without the domain nucleation and growth processes. Experimentally the coercive field is usually much smaller than its intrinsic value. Thus, if the claim [1] were right, this would be a very interesting result. However, we show below that this is not the case and the observation of the intrinsic coercive field yet remains a task for the future.

The switching time in Ref. [1] was 1–10 sec in a strong field of about 10 MV/cm in PVDF-TrFE films 2–30 ML thick. It is astronomically long compared to the relevant order parameter relaxation time, which is at most 10^{-8} sec in usual solid state ferroelectrics. The observed standard switching times in ferroelectrics are less than 60 ns in KNO_3 films in the field 1 MV/cm, and less than 10 ns in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ [2]. This is a domain-assisted switching, which, in fact, must be much *slower* in comparison with the (hypothetical) homogeneous switching. We see that the claim of Ducharme *et al.* is off the scale by at least 8 orders of magnitude.

The identification of the observed coercive field with the intrinsic one is based on comparison of its value and temperature dependence with that given by the Landau-Ginzburg theory for weak first-order phase transitions. However, it does *not* apply to the system in question, which is a ferroelectric composite (mixture of amorphous and crystalline phases). The transition is *strong* first order even in every PVDF crystallite [3], as, e.g., follows from $\sim 10\%$ change in lattice spacing during the transition in thin films [3,4]. This change is huge in comparison with a mere 0.25% lattice spacing change in BaTiO_3 . Even if we approximate the discontinuity by the low-temperature value of polarization, $\approx 0.1 \text{ C/m}^2$ [5], we find that the (overestimated) spontaneous deformation in PVDF should be just 2%, i.e., about 5 times smaller than the observed value [6].

Moreover, we conclude that in the ferroelectric phase the lattice spacing is halved compared to paraelectric phase, and this violates the fundamental group-subgroup relation for *space* groups of paraelectric and ferroelectric phases, required by the Landau theory of second-order or weak first-order phase transitions. The halving of the period is found in the literature for the bulk PVDF see, e.g., [7]) and for the surface ferroelectric transition in thin films [4], which is qualitatively similar to the bulk transition accord-

ing to the same group [4,5]. In the Landau theory, however, there is either no change in translational symmetry at the second-order phase transition, or it *only* consists in the *increase* of some lattice periods by 2, 4, or 3 times at transition from symmetric phase [8]. Note that it would be misleading to compare only the corresponding point groups to check the group-subgroup relation.

The ultrathin films of PVDF are poorly ordered too: in published data the distance between the neighboring chains fluctuates within about 20%, coherence length in the films is about 30 nm, and it *reduces* down to 10 nm in ferroelectric phase [4]. Thus, the coherence in LB films is even worse than in bulk samples [3]. This may be pretty regular for a polymer material but is a complete disaster compared to standard ferroelectric crystals. The plateau in E_c for thicknesses less than 10 nm may be related to some surface effects, which become progressively more important.

The fabrication of the fairly perfect ultrathin films of vinylidene fluoride copolymer ferroelectric [5] is a significant experimental achievement. But the interpretation [1] of their results is not tenable. More generally, it is hard to imagine the system less suitable to serve as a benchmark model for studying the intrinsic ferroelectric properties than PVDF (co)polymers [1,5].

A. M. Bratkovsky¹ and A. P. Levanyuk^{1,2}

¹Hewlett-Packard Laboratories
1501 Page Mill Road
Palo Alto, California 94304

²Facultad de Ciencias, C-III
Universidad Autónoma de Madrid
28049 Madrid, Spain

Received 3 May 2000; published 18 June 2001

DOI: 10.1103/PhysRevLett.87.019701

PACS numbers: 77.80.Dj, 64.70.Kb

- [1] S. Ducharme, V. M. Fridkin, A. V. Bune, S. P. Palto, L. M. Blinov, N. N. Petukhova, and S. G. Yudin, *Phys. Rev. Lett.* **84**, 175 (2000).
- [2] J. F. Scott, *Ferroelectr. Rev.* **1**, 1 (1998).
- [3] J. F. Legrand, *Ferroelectrics* **91**, 303 (1989).
- [4] J. Choi *et al.*, *Phys. Rev. B* **61**, 5760 (2000).
- [5] L. M. Blinov *et al.*, *Usp. Fiz. Nauk* **170**, 247 (2000).
- [6] With the electrostriction constant $k_{33} = -2.3 \text{ m}^4/\text{C}^2$ for the bulk material which is expected to be larger than that for a thin film; see A. V. Bune *et al.*, *J. Appl. Phys.* **85**, 7869 (1999).
- [7] K. Tashiro, in *Ferroelectric Polymers*, edited by H. S. Nalwa (Dekker, New York, 1995).
- [8] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I* (Butterworth Heinemann, Oxford, U.K., 1980), Sec. 145.