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Conspicuous domination of polarization relaxation in kinetics of first-order phase transitions in perovskites

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We justify the application of the theory of the kink-type motion for interphase boundaries for perovskites at first-order phase transitions and obtain a criterion for separating two mechanisms for the front motion—the latent heat transfer and the relaxation of the order parameter. Calculations of the velocity of the interphase boundary motion caused by latent heat transfer at ferroelectric phase transitions show the domination of relaxation kinetics during the ferroelectric-paraelectric phase transitions in perovskites of the ABO_3 type. This allows us to conclude that the dynamics of interphase boundaries in perovskites are governed by the polarization evolution. [S0163-1829(96)04130-6]

The transition from a metastable phase to a thermodynamically stable phase takes place via fluctuations leading to the formation of nuclei of the new phase (large-scale heterophase fluctuations).[1] The description of systems which undergo a symmetry-breaking first-order phase transition must account for the nucleation and growth processes. The growth is associated with the propagation of interphase boundaries separating the high-temperature parent phase from the low-temperature product phase. In solid diffusionless transformations the growth may be slow enough for observation by the polarization microscope technique. In particular, in ferroelectrics sharp interphase boundaries can be observed.[2] Crystals with sharp interfaces most often have kinetically controlled rather than diffusion-limited growth. Usually the interphase dynamics are governed entirely by the time evolution of the order parameter (see, e.g., Ref. 3 and references therein), and the temperature can be considered a constant. Thus, the heat is assumed to be removed sufficiently rapidly and no temperature change occurs as the latent heat of the phase transition appears at the interphase boundary. However, as the interface moves it acts as a heat source with a strength proportional to the latent heat of fusion and the forward rate of motion, giving rise to a leap in the thermal gradient. The heat generated during the interphase boundary motion can accelerate the interface which, in turn, increases the heat production rate. A system involved in this avalanchelike process can be stabilized by heat removal via heat conductivity and heat exchange with the thermal bath. This problem is less significant in metallic systems. If one deals with substances which conduct heat very well, the temperature may be treated as a constant, so no kinetic equation additional to one for the order parameter is necessary. But for materials which do not conduct heat so well, we may need a second equation to determine the temperature distribution. The necessity to account for processes of dissipation of energy released (or additionally absorbed) during the time of transition has been discussed in Ref. 2.

In this paper we obtain a criterion that justifies the conditions when the heat transfer effect on the interphase boundary propagation has to be considered. We show here that at first-order phase transitions in ferroelectric semiconductors with perovskite structure the thermal conductivity is not a controlling process and the interface movement is governed by the kinetics of the phase transition.

The selection of the dominating process in the dynamics of phase transition fronts in ABO_3 perovskites demands, first of all, the development of the formalism for accounting for the heat transfer influence. The heat q flowing across the interphase boundary is

$$q = k \cdot \nabla T \cdot S \cdot \Delta t,$$

where k is the thermal conductivity coefficient, ∇T is the temperature gradient, S is the square of the area of the interface, and $\Delta t = \Delta R / v_T$, where ΔR is the change of size of the new phase during the interface motion with a velocity v_T. This heat per unit mass is the latent heat L: $L = (k \nabla T \Delta V)/(\Delta m v_T)$, where $\Delta m / \Delta V$ is the density ρ. Thus, the propagation rate of the phase transition front due to latent heat transport is given by

$$v_T = \frac{k \nabla T}{\rho L}. \tag{1}$$

Equation (1) represents the thermal balance between the heat generated by the system during the phase transition and that conducted away. The velocity v_T is determined by the rate at which heat is released at the advancing fronts, for example, paraelectric-ferroelectric fronts in the case of ferroelectrics.

The velocity of the interphase boundary movement caused by the relaxation kinetic process v may be derived from the time-dependent Ginzburg-Landau equation (TGLE).[4] For a moving phase transition front the TGLE holds at the interphase boundary provided the interphase boundary width Δ is considerably greater than the interatomic distances. The TGLE cannot be solved exactly in the three-dimensional case. Nevertheless, under the condition that the size of clusters of the new phase inside the old one R is much larger than the width of the interphase boundary Δ, $R \gg \Delta$, the exact solution can be obtained.[3] Thus, the theory works provided $R \gg \Delta \gg d$, where d is the lattice parameter.

The relation between a critical size R_c of the product transformed region and the growth rate v may be found, assuming that the spatial dependence of the polarization $P(r)$ is approximately given by

$$P = P_F \quad \text{at} \quad |r| \leqslant R,$$

$$P = P_F \sqrt{\frac{1}{2}\left[1 - \tanh\left(\frac{r-R}{2\Delta}\right)\right]} \quad \text{at} \quad R \leqslant r \leqslant R+\Delta,$$

$$P = 0 \quad \text{at} \quad |r| \geqslant R+\Delta, \tag{2}$$

$$P_F^2 = \frac{B}{2C}\left[1 + \left(1 - \frac{4AC}{B^2}\right)\right].$$

Here A, B, and C are coefficients of the Ginzburg-Landau functional (see below), $A = A'(T - T_0)$, T_0 is the temperature stability limit of the paraelectric phase, and A' is a constant. Equation (2) gives a radially symmetric cluster of the nucleating phase embedded in a spatially uniform, metastable background. The profile for the front applied here is obtained from the exact solution of the TGLE in the equilbrium limit (see Ref. 3). Using (2) with boundary conditions $\lim_{r\to\infty} P = 0$ and $\lim_{r\to 0} P = P_F$ and integrating over volume for $R \gg \Delta$ one obtains the free energy

$$F = -\frac{4\pi R^3 f(P_F)}{3} + \frac{\pi R^2 D P_F^2}{\Delta}. \tag{3}$$

D is the inhomogeneity coefficient, and the free energy density functional is

$$f(P) = \frac{1}{2}A(T)P^2 - \frac{1}{4}BP^4 + \frac{1}{6}CP^6.$$

This means that the surface tension $\sigma = DP_F^2/4\Delta$. In solids the volume change associated with the phase transition leads to the addition of the strain energy density Q to the free energy density f, so that we have the first term in (3) as $-(4\pi R^3/3)(f-Q)$. The strain energy reduces the effective driving force of the phase transition. Clearly, nucleation will not occur at all unless $f > Q$. The latter formula reflects the fact that at first-order phase transitions the volume and shape change associated with the transition cause a strain energy contribution to the free energy which can suppress the nucleation process.[5] According to the classical theory of nucleation, the new phase nucleus whose radius corresponds to the maximum of the free energy change is the critical nucleus with radius R_c. Then after maximization of (3) we derive

$$R_c = \frac{6D}{\Delta}\left(\left|4A - BP_F^2\right| - \frac{12Q}{P_F^2}\right)^{-1}. \tag{4}$$

Combining the interface velocity expression (see Ref. 3) and Eq. (4) we obtain

$$v = \frac{4\Gamma D}{R_c}\left(1 + \frac{Q}{\Delta p}\right), \tag{5}$$

where Γ is the Landau-Khalatnikov kinetic coefficient from the TGLE, which is independent of temperature, and $\Delta p = 2\sigma/R_c$ is the difference between pressures in two phases according to the Laplace formula.[4] Thus, the interface dynamics are controlled by competition of the polarization contribution to the free energy density and the relation between the strain energy density and the density of the energy stored at the front.

The propagation of the interphase boundary is determined by the kinetics of the order parameter, if $v_T \gg v$. Comparing the expression for the velocity of the interphase boundary mentioned above and Eq. (5) and supposing that $\nabla T \approx \Delta T/R_c$ (ΔT is supercooling or superheating), we obtain the criterion of domination of the kinetics of polarization over the thermal conduction-driven mechanism:

$$\frac{k\Delta T}{4\rho L\Gamma D}\left(\frac{1}{1 + Q/\Delta p}\right) \gg 1. \tag{6}$$

Now we can check criterion (6) for ferroelectric perovskite semiconductors with ABO_3 stoichiometry. Many measurements of the interphase boundary dynamics have been carried out for these ferroelectrics.[2] We take necessary material parameters from the data of Ref. 6–11. The elastic coefficients for Q are taken from Ref. 12. The deformations accompanying the phase transformation are taken from Ref. 13: $\epsilon_{xx} = \epsilon_{yy} = -0.001\,59, \epsilon_{zz} = -0.003\,66$. For estimations of the strain energy the essential decrease of the stiffness coefficients c_{ij} caused by softening the lattice near the phase transition should be taken into account.[14] Then the required ratio is about 5×10^4. Γ should be estimated from the slower dynamics leading to central peaks.[9] They result from the highly anharmonic terms in the free energy expressions which are responsible for the formation of the product phase.[9] The nuclei near first-order phase transitions have long lifetimes. The appearance of a long-range order is caused by thermal hopping in the metastable states. The width of the central peak in this case is controlled by the time required for the formation and collapse of the clusters. Therefore one can suppose that Γ is determined by the width of the central peak caused by nuclei of the product phase. Their dynamics are much slower than those analyzed in Ref. 6. The central peak width is about three to four orders of magnitude smaller than the width of other modes. This leads to the value of Γ about 10^7 Hz.[9] For Γ used in Ref. 6 ($\Gamma = 1.61 \times 10^{10}$ sec^{-1}) the criterion (6) is also fulfilled. Thus, after inserting the presented experimental values into (6) we conclude that the heat transfer process is more rapid than the kinetics of the order parameter relaxation. For this reason, the latter process determines the interface propagation in the above ferroelectric semiconductors. Consequently, the release of the latent heat of the phase transition does not play an important part in the dynamics of interphase boundaries in the perovskites under consideration. However, if $(k\Delta T/4\rho L\Gamma D)[1/(1+Q/\Delta p)]\approx 1$, the two processes must be taken into account. The theory of the kink-type motion for interphase boundaries[3] is therefore suitable for perovskite ferroelectric semiconductors because it fulfills criterion (6). The latter is caused by the comparatively high thermal conductivity and comparatively low latent heat.

Additional evidence in favor of the conspicuous domination of polarization relaxation in kinetics of first-order phase transitions in perovskites is the following.

(1) The kinetics observed in the review[2] are not described by the Arrhenius law as is seen from the temperature dependence of the front velocity.[3]

(2) The same value of superheating and supercooling leads to different velocities of the interphase boundary. The velocity in the heating process is larger than in the cooling one[6] as follows from the exact solution of the time-dependent Ginzburg-Landau equation.[3]

(3) The temperature dependence of the interface velocity is characteristic of the overdamped motion described by the relaxational kinetics of the order parameter.[3]

(4) The values of velocity calculated using (5) are in good agreement with the measured ones.[2]

The most attractive feature of the suggested mean-field consideration of the delicate balance between the relaxation kinetics and the heat transfer in the phase growth process of perovskites is the possibility of avoiding any analysis of the influence of major defects of crystals on the growth. The parameters of our approach were extracted from the experimental measurements, which are produced on real crystals with a polycrystalline structure and a rather high density of defects. Thus the parameters of our estimations already include the information on the different types of defects as well as polycrystallinity. A high density of defects is an inherent property of perovskites and any kind of atomistic consideration immediately leads to the necessity of consideration of many types of defects: point, planar, linear, etc.

The consideration is valid for finite and polycrystalline solids provided the sample or grain size is much larger than the interphase boundary width. This condition is fulfilled in the experimental studies of the interphase boundary motion in the perovskites $PbTiO_3$ and $BaTiO_3$,[2] and even in the nanocrystalline $Pb(Sr/Ti)O_3$ system.[15] The ferroelectric phase transition disappears when the grain size decreases, approaching some critical value.[15] Under these conditions our approach is inapplicable. Thus, our approach is suitable for quite a wide range of sample and grain sizes.

The suggested analysis leads to an answer to the question of the dominating process in the phase growth of ferroelectric perovskites. The obtained result was not obvious and the modern review[2] left this question open.

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[1] V. I. Yukalov, Phys. Rep. **208**, 395 (1991).

[2] J. Dec, Phase Transitions **45**, 35 (1993).

[3] A. Gordon and S. Dorfman, Phys. Rev. B **51**, 9306 (1995); A. Gordon, S. Dorfman, and P. Wyder, J. Phys. Condens. Matter **7**, 9905 (1995).

[4] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, 3rd ed. (Pergamon Press, Oxford, 1980), Part I.

[5] H. E. Cook, Phys. Rev. B **15**, 1477 (1977).

[6] J. Dec, Ferroelectrics **89**, 193 (1989).

[7] G. Shirane and A. Takeda, J. Phys. Soc. Jpn. **7**, 1 (1952).

[8] D. D. Glower and D. C. Wallace, J. Phys. Soc. Jpn. **18**, 679 (1963).

[9] R. Blinc, Ferroelectrics **20**, 121 (1978).

[10] R. Ramirez, M. F. Lapeña, and J. A. Gonsalo, Phys. Rev. B **42**, 2604 (1990).

[11] G. A. Samara, Ferroelectrics **2**, 277 (1971).

[12] W. L. Bond, W. P. Mason, and H. J. McSkimin, Phys. Rev. **82**, 442 (1951).

[13] H. F. Kay and P. Vouzden, Philos. Mag. **40**, 1019 (1949).

[14] E. J. Huibregtse, W. H. Bessey, and M. E. Drougard, J. Appl. Phys. **30**, 899 (1959).

[15] J. Meng, G. Zou, Y. Ma, X. Wang, and M. Zhao, J. Phys. Condens. Matter **6**, 6549 (1994).