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Critical Behavior of the Spinodal

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The spinodal of ferroelectrics is a locus of vanishing inverse susceptibility in E-T space. Defining the spinodal exponent by $E \sim T^s$, the geometry has been studied by the static scaling hypothesis and the catastrophe theory. The scaling law $s=\beta\delta=\beta+\gamma$ and $2>s>1$ has been obtained. For higher order critical points of order O, $s=(2O\text{-}1)\tau/(2O\text{-}2)$, where τ is the transformation power of a control variable to temperature with the classical value of 1. Experiments of coercivity in TGS and DSP were compared with the theory.

§1. Introduction

The spinodal of a one-component system is defined by

$$\left(\frac{\partial^2 A}{\partial P^2}\right)_T = \frac{-1}{\left(\dfrac{\partial^2 G}{\partial E^2}\right)_T} = \frac{1}{\chi} = 0, \tag{1}$$

$A(P, T)$ and $G(E, T)$ being the Helmholtz free energy and the Gibbs function respectively. The variable P is polarization, and E electric field, and the response χ is susceptibility, in the case of ferroelectric systems. In the field space E-T, a phase becomes absolutely unstable in one side of the spinodal.

The Landau expansion up to the sixth power in a reduced form[1)] gives spinodals as shown in Fig. 1. When the specimen is swept in parallel to the E-axis, the spinodal gives the maximum value of coercivity, and to the T-axis the maximum thermal hysteresis.

In this paper, we study the geometry of the spinodal near the critical point, compare experimental results on TGS (triglycine sulfate) and DSP (dicalcium strontium propionate) with the theory, and criticize them.

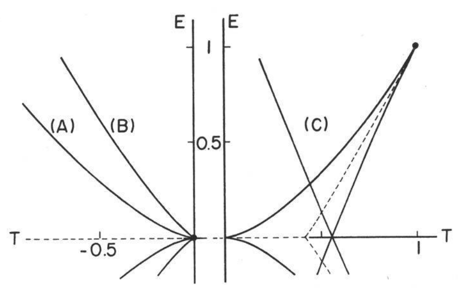

Fig. 1. Classical spinodals calculated by the Landau approximation. Broken lines are coexistence lines. Small circles are the ordinary critical point for (A) and (C), and the tricritical point for (B).

2. Theory

The static scaling hypothesis gives the Gibbs function of a generalized homogeneous function as

$$G(\lambda^{a_E}E, \lambda^{a_T}T) = \lambda G(E, T), \tag{2}$$

from which

$$\chi(\lambda^{a_E}E, \lambda^{a_T}T) = \lambda^{1-2a_E}\chi(E, T).^{2)} \tag{3}$$

Here we assume $a_E > a_T$; in other words, we take the direction in the field space with smaller scaling exponent of a path variable as the T-axis. Now we define the spinodal exponent s as

$$E \sim T^s, \tag{4}$$

representing the geometrical shape of the spinodal near the critical point. On the spinodal eq. (4), $\chi \to \infty$, therefore the left hand side of eq. (3) $\to \infty$. The arguments must satisfy

$$\lambda^{a_E}E \sim (\lambda^{a_T}T)^s.$$

From this

$$s = \frac{a_E}{a_T}. \tag{5}$$

Recalling the well-known relations of $\beta = (1-a_E)/a_T$, $\delta = a_E/(1-a_E)$ and $\gamma = (2a_E - 1)/a_T$, and the scaling law of the gap exponent $\Delta = \beta\delta$, we obtain the scaling law of the spinodal as

$$s = \beta\delta = \beta + \gamma = \Delta. \tag{6}$$

From the assumption $a_E > a_T$, it can be shown that the weak direction (larger exponent of any quantity) is the T-axis, and *any* other direction is the strong direction with smaller exponent. Since the T-axis is the unique direction, we can naturally expect that the coexistence line, of directional singularity, is on the T-axis, if it occurs at all. From eq. (5) and $a_E > a_T$, therefore, the spinodal goes to the critical point in parallel to the phase boundary. In other words, the spinodal is tapered off to the critical point.

Now we impose conditions plausible for our interest that the polarization $P = -(\partial G/\partial E)_T$ and anomalous entropy $S = -(\partial G/\partial T)_E$ converge to 0, the susceptibility $\chi = -(\partial^2 G/\partial E^2)_T$ diverges to ∞, and the anomalous specific heat divided by absolute temperature $c/T_{ab} = -(\partial^2 G/\partial T^2)_E$ does *not* converge to 0, at the critical point. That is, $1-a_E>0$, $1-a_T>0$, $1-2a_E<0$, and $1-2a_T \leqq 0$. These conditions give the limits

$$2 > s > 1. \tag{7}$$

In order to consider critical points of higher order, we utilize the catastrophe theory. It says that the singulalities of our critical points are topologically equivalent to the singulalities of the polynomial

$$V = u_1 x + \frac{1}{2} u_2 x^2 + \frac{1}{4} u_4 x^4 + \ldots + \frac{1}{k} u_k x^k + \frac{1}{k+2} x^{k+2}, \tag{8}$$

with the extreme condition of

$$\frac{\partial V}{\partial x} = u_1 + u_2 x + u_4 x^3 + \ldots + \mathrm{u}_k \mathrm{x}^{k-1} + x^{k+1} = 0, \tag{9}$$

where $k \geqq 2$ is even.[3~5] Here, $u_1 = u_2 = u_4 = \ldots = u_k = 0$, that is, the origin of the k-dimensional control space, gives the critical point of order

$$O = 1 + \frac{k}{2}.^{4,6)} \tag{10}$$

When $u_2 \neq 0$ and others are 0, x gives spontaneous x_s near the critical point from eq. (9) as

$$x_s = (-u_2)^{1/k}. \tag{11}$$

When $u_1 \neq 0$ and others are 0, eq. (9) gives

$$x = (-u_1)^{1/(1+k)}. \tag{12}$$

If we transform (u_1, u_2, x) to the physical variables (E, T, P), eq. (8) plays a roll of the Gibbs function. The transformation can be done by $u_1 \sim -E$, $u_2 \sim T^\tau$, and $x \sim P^\pi$, where τ, $\pi > 0$.[3,4] From eqs. (11) and (12),

$$P \sim (-T)^{\tau/k\pi}, \quad P \sim E^{1/(1+k)\pi},$$

that is,

$$\beta = \frac{\tau}{k\pi}, \quad \delta = (1+k)\pi. \tag{13}$$

The scaling exponents of the path variables a_E and a_T are obtained easily as

$$a_E = \frac{(1+k)\pi}{1+(1+k)\pi}, \quad a_T = \frac{k\pi}{1+(1+k)\pi} \cdot \frac{1}{\tau}. \tag{14}$$

The spinodal exponent is, from eq. (5),

$$S = \left(1 + \frac{1}{k}\right)\tau = \frac{2O-1}{2O-2}\tau. \tag{15}$$

The classical value of τ is 1, so that the spinodal exponent $s = 3/2, 5/4, 7/6, \ldots$ as $O = 2$ (ordinary critical point), 3 (tricritical point), 4,. . . . It tends to 1 for higher order critical points. The classical spinodals with $s = 3/2$ and 5/4 are those shown in Fig. 1(A) and (C), and (B) respectively.

§3. Experiments and Discussions

As mentioned earlier, the spinodal is the upper limit of coercivity. The experimental coercivity has been considered to be reduced greatly from the theoretical one by the mobility of the domain wall. Many of the coercivity experiments have shown convexed shape as a function of temperature. That is to say, the apparent exponent is less than 1. In fact, Gonzalo[7] observed it as 0.79. If $s > 1$, the coercivity may be truncated or compressed by the spinodal which goes to zero faster near the critical point. So the spinodal is expected to be obtained by coercivity experiments in a small temperature range.

For TGS, values of the critical exponents can be approximated by the classical values.[7~10] In the case of DSP, $\gamma = 1.33$ and $\beta = 0.31$,[11] giving $s = 1.64$. We measured coercivity of TGS from hysteresis loops of 0.3 Hz, as shown in Fig. 2. Falling short of the expectation, the exponent s seemed to be 1 near the critical point. Unpublished data of a well-annealed DSP crystal by Deguchi and Nakamura (60 Hz hysteresis loop)[12] is plotted for this purpose in Fig. 3.

As far as a value of electric field from the hysteresis loop concerned, we do have an ambiguity coming from the surface layer[13] and adiabaticity. If specific heat of the transition is

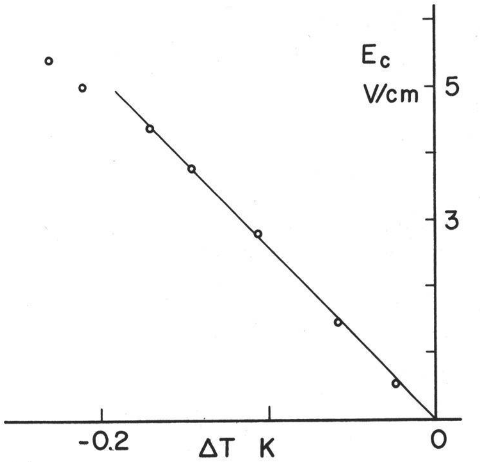

Fig. 2. Coercivity of TGS. From hysteresis loop, 0.3 Hz, 47.6 V/cm of amplitude.

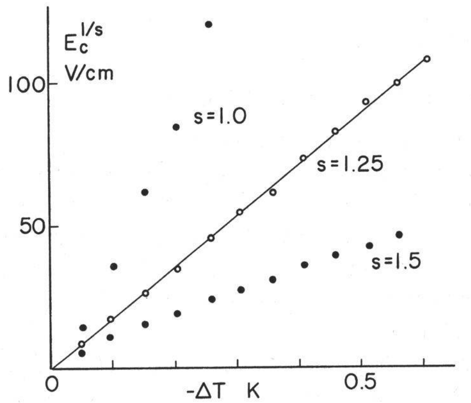

Fig. 3. Coercivity of DSP. From hysteresis loop, 60 Hz, 4.465 kV/cm of amplitude.

not very small compared with the normal one, the adiabaticity may give a considerable error. In addition, the domain wall motion may cause a reduction of the coercivity at very close to the critical point in some cases. We have presented here rather poor value of $s=1$ to be compared with 1.5 for TGS, and a pretty good value $s=1.25$ compared with 1.64 for DSP.

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References

1) K. Okada: Oyo Buturi **48** (1979) 645. The English translation is available on request.
2) E. H. Stanley: *Local Properties at Phase Transitions*, ed. K. A. Müller and A. Rigamonti (North-Holland, 1976) p. 45.
3) K. Keller, G. Dangelmayer, and H. Eikemeier: *Synergetics; Structural Stability in Physics*, ed. W. Güttinger and H. Eikemeier (Springer-Verlag, 1979) p. 186.
4) L. Benguigui and L. S. Schulman: Phys. Lett. **45A** (1973) 315.
5) L. S. Schluman: Phys. Rev. **B7** (1973) 1960.
6) T. S. Chang, A. Hankey and H. E. Stanley: Phys. Lett. **44A** (1973) 25.
7) J. A. Gonzalo: Phys. Rev. **144** (1966) 662.
8) J. A. Gonzalo: Phys. Rev. Lett. **21** (1968) 749.
9) E. Nakamura, T. Nagai, K. Ishida, K. Itoh and T. Mitui: *Proc. 2nd Int. Meeting Ferroelectricity, Kyoto, 1969*, J. Phys. Soc. Jpn. **28** (1970) Suppl. p. 271.
10) K. Deguchi and E. Nakamura: Phys. Rev. **B5** (1972) 1072.
11) K. Deguchi and E. Nakamura: Phys. Rev. Lett. **37** (1976) 1642.
12) K. Deguchi and E. Nakamura: private communication (1980).
13) T. Sekido and T. Mitsui: J. Phys. Chem. Solids **28** (1967) 967.