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Entropic jump of aorder-disorder transition

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Résumé. — Cette communication fait le point des conclusions simples relatives aux mécanismes microscopiques dans les matériaux ferroélectriques, mécanismes du type ordre-désordre ou du type déplacement. Le premier implique l'existence de noyaux critiques et de fluctuations. Pour le dernier on ne possède pas une connaissance essentielle et détaillée de l'anharmonicité, et en particulier dans le cas des ferroélectriques à modes couplés.

Abstract. — This paper reviews the present status of the original simple inferences about the microscopic mechanism of ferroelectrics, order-disorder or displacive mechanisms. The former involves critical nuclei and fluctuations. For the latter, essential detailed knowledge of the anharmonicity is lacking, and especially in coupled-mode ferroelectrics.

I. Introduction. — This paper discusses the microscopic significances of the change of polarization, \( \Delta P \), at the ferroelectric transition in general, and the coupled-mode model for KDP-type ferroelectrics. In ferroelectrics, the microscopic mechanisms are: (a) an ordering mechanism among « permanent » microscopic dipoles \( p_0 \), (b) a cooperative displacive mechanism of induced microscopic dipoles \( P \), (c) a coupled Kobayashi mechanism, in which co-operative ordering of protons on hydrogen bonds triggers motions of ions along the polarization axis. In KDP-type ferroelectrics, the value of \( \Delta P \) has remained ambiguous in the models proposed, right from the early Slater model. In general, ferroelectrics with a finite \( P \)-drop will have a finite entropy jump, provided only that \( \text{d}(\mathbf{r})/\text{d}T \) is not zero, where \( 1/\lambda' \) is the electric susceptibility. The question to be answered is whether the entropy jump implies an ordering mechanism, or more generally, it is correct to tabulate as in lines A and B of the table, and how should line C be completed? Some of the available evidence is surveyed and it is concluded that there is no justification for the correlation B, and that we must await a fuller understanding of the macroscopic implications of the coupled-mode mechanism before completing C.

II. Macroscopic. — 1. Entropy Jump at Transition. — Using Devonshire's free-energy \( G \), the relation entropy \( S = -\partial G/\partial T \) leads to

\[
\Delta S \approx \frac{1}{2} (\Delta P)^2 \frac{\text{d}x'}{\text{d}T}
\]

so that finite \( P \) jump implies finite \( S \) jump. In such cases, transition proceeds inhomogeneously, and the author has shown [1] that it can be nucleated, with a critical nucleus volume which we may expect to be proportional to \( (\Delta T)^{-2} \) where \( \Delta T \) is the extent of superheating. Demjanov et al. [2] have used a different approach in which polar nuclei above \( T_0 \) each evolve into a domain wall and its associated domains below \( T_0 \) and their curve relating the volume of a nucleus to the temperature seems qualitatively similar to the relation expressed above. Their nuclei above \( T_0 \) may be regarded as polarization fluctuations, and fluctuations large compared with \( \Delta P \) will invalidate the field description we are using.

Under what circumstances will the simple description become invalid? Ginzburg [3] has made the estimate as follows. For nonuniform \( P \), write \( G = \int g(\mathbf{r}) \, dV \) with \( g = c(\text{grad} \, P)^2 + g_0 + aP^2 + bP^4 \), where \( g_0, a, b, c \) are functions of \( T \). At a point \( \mathbf{r} \), \( P \) deviates from the mean \( \bar{P} \) by \( \Delta P \), which may be Fourier analysed into « wavelengths » \( 1/k, \Delta = \sum P_k \exp(i\mathbf{k}.\mathbf{r}) \). The corresponding \( G \) deviation is written down; the probability of an individual fluctuation is proportional to \( \exp(-\Delta G/kT) \). It is interesting to note that Raman scattering also measures this \( \bar{P}^2 \). For the mean square fluctuation one gets [4] the correlation function \( < [P_1 - \bar{P}_1][P_2 - \bar{P}_2] > \) between fluctuations at different points \( r_1, r_2 \) in terms of the coherence length \( L \) for the fluctuation; \( L = (c/a)^{1/3} \). At \( T = T_0 + \Delta T \), if the mean \( P \) fluctuation over distance \( L \) is to be appreciably less than \( \Delta P \), one finds that \( \Delta T \) must exceed an expression which has been estimated as \( T_0/10^4 \) for barium titanate. At this critical value for fluctuations, I estimate [1] that the nucleus volume is \( 10^8 \) cu Å. Closer than that to \( T_0 \), or for larger nuclei, the fluctuations will invalidate the field description.
II. Macroscopic. — 2. « SOFT » behaviour of polarization. — Whether or not AP at transition is finite, is not determined by the electrostatic co-operation $\beta P$, but by the curve $P(F, T)$. In a supposedly displacive ferroelectric, that involves the macroscopic polarizability $A$, as a function of $F$ and of $T$. Or one may look at the soft-mode description taken at wavenumber $k = 0$, which is exactly equivalent. A simple potential energy $\Phi = \frac{1}{2} fu^2 - qu$ corresponds to $\omega_0^2 f = 1 - \beta N a$. Here the microscopic polarizability $\alpha = q^2 f, F = \beta P$, and $P = N a u$. This frequency $\omega_T$ vanishes at the temperature where $Na$ reaches $1/\beta$. These soft-mode fluctuations of $P$ become unstable as $T$ decreases through $T_0$ but this harmonic description is unphysical so that there is no indication of whether a new stable situation corresponds to a $P_c$ value which is finite. For that we need the form of the anharmonic terms in $\Phi$. The distinction which is of interest is between forms such as $\Phi = \frac{1}{2} fu^2 - a u^4 + bu^6$ and $\Phi = \frac{1}{2} fu^2 + bu^4$.

The dynamical behaviour is to be derived from Lagrangian equations after writing down potential energy-density $U = \frac{1}{2} N f u^2 + \cdots$ and kinetic energy-density expression which involves an effective inertial mass. But it is $U$ which is substantially identical to $G$, and $G$ also must include the terms beyond the term in $P^2$. We conclude that the nature of $\Delta P$, as to whether it is finite or not, does not correspond one-to-one with the division permanent-dipole $u$ induced-dipole.

For the coupled mode, the ionic movements of $K$ and $P$ are coupled through $\eta$. We conclude that the nature of AP, as to whether $\eta$ is finite or not, does not correspond one-to-one with the division permanent-dipole $u$ induced-dipole. 

The finite $\Delta P$ is then related to $\eta$, to the well flattens is not along the $\eta$ axis. The $\eta$ section would become flat at $T_0$ but before $T$ decreases to $T_0$, the other section becomes flat, at temperature $T_0$, indicating that when $\eta$ becomes unstable, $P$ and $x$ go with it, and the extra anharmonic knowledge as before is required to predict whether or not the changes are infinitesimal at $T_0$.

IV. Microscopic considerations. — The finite $\Delta S$ accompanying $\Delta P$ could result from configurational entropy of disordering of dipoles, which must surely continue to exist above $T_0$, so that they should be permanent dipoles $p_0$. The perovskites have traditionally been regarded as cases of non-permanent dipoles, but diffuse X-ray scattering has raised doubts. Neutron scattering from barium titanate above $T_0$ also can be interpreted as due to atoms which tunnel between six potential minima [8]. In barium titanate, the $\Delta P$ at transition is reduced linearly by hydrostatic pressure and is expected to become zero above 20 kbars. It then should become second-order. In KDP and isomorphs, model calculations [9] show that hydrostatic pressure should move the double-well separation to zero at a bond length of 2.40 Å. The relation of $p_0$ to the well separation is not a simple one, but it has been calculated [10] that $\ln p_0$ will decrease at 0.9 % per kbar in KD*P. The order-disorder mechanism must then disappear.

In cases which are supposedly displacive, the macroscopic polarizability $A$ used presumably corresponds to an induced dipole $p$ with microscopic polarizability $\alpha$, where $A \equiv N a$. The finite $\Delta P$ is then related to the nature of the anharmonicity in the microscopic potential energy $\Phi$, corresponding to a non-permanent dipole $p = qu$. Thus the nature of $\Delta P$ does not correspond one-to-one with the division permanent-dipole $u$ induced-dipole.

For the coupled mode, the ionic movements of $K$...
and of PO₄ have not yet been described in sufficient detail to know whether one may speak of a co-operative mechanism among the ions, or whether their correlated displacements are to be regarded as «accidental», due to the co-operation among the trigger protons. The thermodynamics given above [7] assumes that these ionic displacements in themselves could not give a displacive ferroelectric mechanism and Kobayashi [6] assumes similarly. What is needed is an ionic view of the coupling term \(-F_2 QS\) in the Hamiltonian.

References