Weakly polar ferroelectricity: dielectric properties and possible nature

A. K. Tagantsev
A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

(Submitted 3 November 1986; resubmitted 25 February 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 7, 352–355 (10 April 1987)

A relationship has been established (for the first time) between the effective charge of a soft mode in a weakly polar ferroelectric and a component of the order parameter for the phase transition from a hypothetical "regular" phase into a paraphase. A temperature anomaly in the dielectric response of a weakly polar ferroelectric should have an unusual shape.

Ferroelectrics with anomalously small Curie-Weiss constants C have recently become the subjects of active research: $(CH_3NHCH_2COOH)_3CaCl_2$ (TSCC), $Li_2Ge_7O_{15}$ (LGO), and NH_4LiSO_4 (LAS). The values of C and of several other properties of these crystals can be explained on the basis that the charge of a soft mode

 0021-3640/87/070447-04$01.00

in them is anomalously small: 10^{-2}–10^{-3} of the charge of an electron (Smolenskiĭ *et al.*[1] have carried out a detailed analysis of the properties of TSCC from this standpoint). The nature of this small value, however, remains unresolved.

1. We believe that the small value of the effective charge of a soft mode of a weakly polar ferroelectric[1)] is a consequence of the circumstance that this mode has "arrived" at the Γ point from the boundary of the Brillouin zone upon a transition (real or hypothetical) which involves a doubling of the unit cell and which occurs at a temperature higher than that of the ferroelectric transition. We will illustrate these arguments in the particular case of TSCC. In the paraphase, TSCC crystals are broken up into three types of ferroelastic domains,[2] whose symmetry is orthorhombic (D_{2h}^{16}), or pseudohexagonal (D_{6h}^{3}). The paraphase structure can be reached from the hexagonal regular phase (which is not attainable experimentally) through an extrinsic ferroelastic transition involving condensation of the soft mode at the M point at the boundary of the Brillouin zone (a representation of the B_{1_u} group of the wave vector with the D_{2_h} point group).[2] To verify that the effective charge turns out to be small, as we wish it to, we can simply write out the invariant $\lambda E_y \eta_h \eta_1$ in the regular phase, where E_y is the component of the electric field along the ferroelectric axis, η_h is the normal coordinate corresponding to the representation B_{1_u} at point M (this coordinate is nonzero for the ferroelastic domain under consideration), and η_1 is the normal coordinate which corresponds to the mode from the M point. In the regular phase, this mode will play the role of a soft mode of the ferroelectric transition. Treating this term as an increment in the thermodynamic potential with the property of minimality at a fixed E_y, we find an additional contribution $-\lambda \eta_h \eta_1$ to the polarization component P_y. It follows immediately that in the paraphase the effective charge of the soft mode of the ferroelectric transition is $e_1 = -\lambda \eta_{h0}$ (here and below, the subscript 0 means a spontaneous value). The characteristic small values of the atomic displacements upon structural phase transitions make e_1 small at the atomic scale. We wish to point out that the presence of a paraphase with a structure close to a more highly symmetric structure in a crystal is not by itself a sufficient condition for the appearance of a weakly polar ferroelectric. Another necessary condition is that the mode η_1 which arrives from the boundary of the Brillouin zone must be soft.

Similar arguments can be made for LGO and LAS. Evidence in favor of this mechanism for the appearance of a weakly polar ferroelectricity is the correlation between the values of the Curie-Weiss constants in the paraphase $C \sim e_1^2 \sim \eta_{h0}^2$ and the parameters of the pseudohexagonal structure,[2] $h = (b/a - \sqrt{3})/2 \sim \eta_{h0}^2$ (a and b are constants of the orthorhombic unit cell), for these compounds:

TSCC $C = 30 - 58$ K (Ref. 3), $h = -0.016$ (Ref. 2),

LGO $C = 4.6$ (Ref. 4); 3.2 K (Ref. 5), $h = -0.0046$ (Ref. 5); 0.0027 (Ref. 4),

LAS $C = 5.6$ (Ref. 6); 2.75 K (Ref. 7), $h = -0.0015$ (Ref. 8); -0.0005 (Ref. 6).

2. We can show that, in addition to the anomalously small values of C and the nonstandard acoustic properties[1] when the effective charge of the soft mode is sufficiently small, the dielectric response in the ferroelectric phase and the spontaneous polarization of a weakly polar ferroelectric should depend on the temperature in an

unusual way. We write a Landau expansion of the thermodynamic potential in powers of η_1, taking into account the amplitude of the normal coordinate of the "hard" mode η_2, which provides the background dielectric constant in the direction of the polar axis, and the mixed invariant of fourth order which was introduced by Dvorak and Ishibashi[9] in a study of a two-sublattice model:

$$F = \frac{\alpha_1}{2}\eta_1^2 + \frac{\beta}{4}\eta_1^4 \frac{\alpha_2}{2}\eta_2^2 + \delta\eta_1^3\eta_2 - P_y E_y. \qquad (1)$$

Here $P_y = e_1\eta_1 + e_2\eta_2$; $\alpha_1 = A(T - T_c) \ll \alpha_2$; and e_2 is the effective charge (not small) of the hard mode ($e_1 \ll e_2$). Expression (1) does not have a term $\sim\eta_1\eta_2$, since η_1 and η_2 are, by definition, normal coordinates. Minimizing (1) with respect to η_1

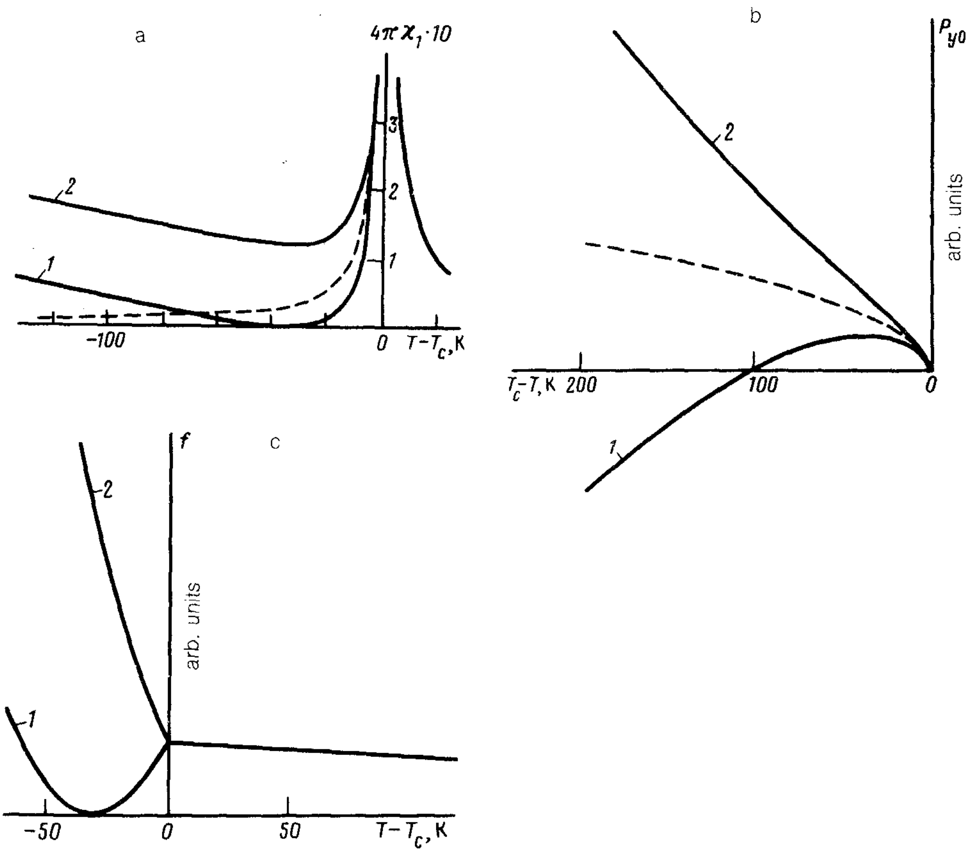

FIG. 1. Temperature dependence of (a) the anomalous part of the dielectric susceptibility, $4\pi\chi_1$, (b) the spontaneous polarization, and (c) the oscillator strength of the soft mode f, according to calculations for a weakly polar ferroelectric with a phase transition far from the tricritical point, with a Curie-Weiss constant $C = 2$ K, and $\beta\alpha_2 e_1/e_2 A\,|\delta| = 100$ K. 1—$\delta > 0$; 2—$\delta < 0$; dashed lines—temperature dependence of the values for a second-order phase transition in an ordinary ferroelectric. For f above T_C, the temperature dependence of η_{h0} has been taken into account.

and η_2, we find an expression for the spontaneous polarization: $P_{y0} = \eta_{10}(e_1 - e_2\delta\eta_{10}^2/\alpha_2)$. This expression is similar in structure to the result found in Ref. 9. In analyzing the dielectric response we note that because of the fourth term in (1), the variations in η_1' and η_2' near η_{10} and η_{20} are not normal coordinates. Rotating through an angle ϕ in the $(\eta_1' \eta_2')$ plane, we transform to normal modes in the ferroelectric phase: $\tilde{\eta}_1$ and $\tilde{\eta}_2$. This angle is $\phi \approx -3\delta\eta_{10}^2/\alpha_2$, and it is small to the extent that the parameter of the expansion in the Landau theory is small. The renormalizations of $-2\alpha_1$ and α_2 are small, in proportion to ϕ^2, and can be ignored. The renormalization of the charge of the soft mode, however, may be significant even if the expansion is valid, because of the small value of this charge. Expressing P_y in terms of $\tilde{\eta}_1$ and $\tilde{\eta}_2$, we find values for the charges of the normal modes in the ferroelectric phase: $\tilde{e}_2 \approx e_2$, $\tilde{e}_1 \approx e_1 + \phi e_2$. We then find the expression $\chi_1 \approx -(e_1 - e_2 3\delta\eta_{10}^2/\alpha_2)^2/2\alpha_1$ for the anomalous part of the dielectric susceptibility in the ferroelectric phase. Figure 1 shows the predicted temperature dependence of P_{y0}, χ_1, and the oscillator strength of the soft mode, $f \sim \tilde{e}_1^2$. The most interesting case is that with $\delta > 0$: a change in the sign of the spontaneous polarization (see also Ref. 9), a vanishing of the anomalous part of the dielectric susceptibility, and a quenching of the IR absorption line (but not of the Raman scattering!) associated with the soft mode at certain temperatures below the transition. These events should occur progressively closer to the transition as the charge of the soft mode in the paraphase is reduced. A calculation using standard estimates for the expansion parameters in (1) shows that for a displacive ferroelectric, with a second-order phase transition and a Curie-Weiss constant on the order of a few units with $\delta > 0$, we can expect χ_1 to vanish at a temperature a few tens of degrees below the transition.

3. Data[5] on the spontaneous polarization in LGO correspond to a weakly polar ferroelectric with a value $\delta > 0$. We are unaware of any optical or high-precision dielectric measurements which would make it possible to see a vanishing of the effective charge of the soft mode in this crystal. The unusual behavior of the spontaneous polarization[6] in LAS corresponds qualitatively to the case $\delta < 0$. Ammonium sulfate is a possible example of a weakly polar ferroelectric of the order-disorder type with $\delta > 0$.

I wish to thank E. L. Ivchenko and I. G. Sinem for useful discussions and S. A. Kizhaev for reading the manuscript and offering some useful comments.

[1)] "Weakly polar" here, as in Ref. 1, means a ferroelectric with an anomalously small charge for the soft mode.

[1] G. A. Smolenskiĭ, I. G. Siniĭ, A. K. Tagantsev, S. F. Prokhorova, V. D. Mikvabiya, and V. Vindsh, Zh. Eksp. Teor. Fiz. **88**, 1020 (1985) [Sov. Phys. JETP **61**, 599 (1985)].
[2] F. Sawada, Y. Makita, and Y. Takagi, J. Phys. Soc. Jpn. **42**, 1918 (1977).
[3] S. Sorge and U. Straube, Phys. Status Solidi **a51**, 117 (1979).
[4] M. Wada and Y. Ishibashi, J. Phys. Soc. Jpn. **52**, 193 (1983).
[5] A. A. Bush and Yu. N. Venevtsev, Fiz. Tverd. Tela (Leningrad) **28**, 1970 (1986) [Sov. Phys. Solid State **28**, 1101 (1986)].
[6] T. Mitsui, T. Oka, Y. Shiroishi, M. Takashige, K. Iio, and S. Sawada, J. Phys. Soc. Jpn. **39**, 845 (1975).
[7] V. N. Anisimova and N. R. Ivanov, Kristallografiya **31**, 1018 (1986) [Sov. Phys. Crystallogr. **31**, 605 (1986)].
[8] Y. Luspin, G. Hauret, and A. M. Gillet, Ferroelectrics **61**, 257 (1984).
[9] V. Dvorak and Y. Ishibashi, J. Phys. Soc. Jpn. **41**, 548 (1976).

Translated by Dave Parsons