Fluctuations, Higher Order Anharmonicities, and Phase Transitions in Barium Titanate

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- Ginzburg-Devonshire expansion for barium titanate
- Lattice model with eight-order anharmonicity
- Fluctuation contributions to fourth-order coefficients B_1 and B_2
- Temperature dependence of B_1 and B_2:

  theory *vs* experiment
- Fluctuation contributions ratio ♎B_1/♎B_2:

  theory *vs* experiment
- Summary

Ginzburg-Devonshire free energy expansion

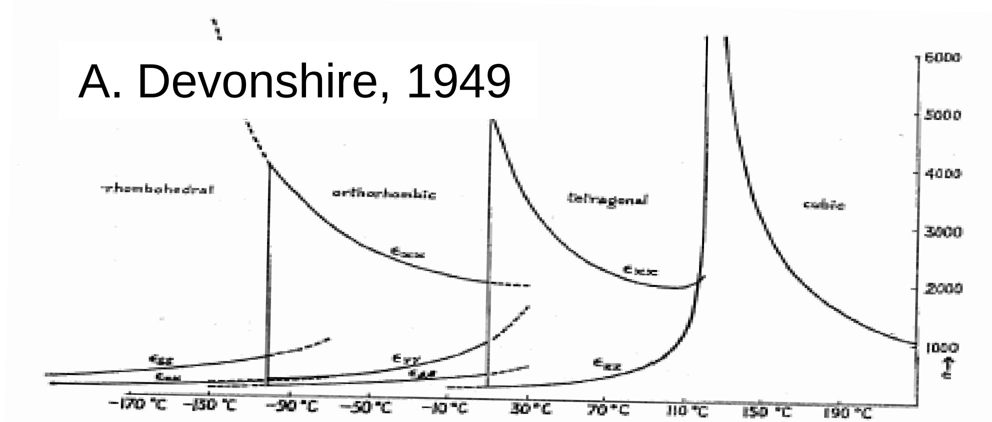
$$F = \frac{1}{2}A\left(P_x^2 + P_y^2 + P_z^2\right) + \frac{1}{4}B_1\left(P_x^4 + P_y^4 + P_z^4\right) + \frac{1}{2}B_2\left(P_y^2P_z^2 + P_z^2P_x^2 + P_x^2P_y^2\right)$$

$$+\frac{1}{6}\Gamma_1\left(P_x^6 + P_y^6 + P_z^6\right) + \frac{1}{2}\Gamma_2\left[P_x^4\left(P_y^2 + P_z^2\right) + P_y^4\left(P_z^2 + P_x^2\right) + P_z^4\left(P_x^2 + P_y^2\right)\right] + \frac{1}{2}\Gamma_3\left(P_x^2P_y^2P_z^2\right)$$

$$\mathrm{A} = \alpha(T - T_0)$$

- The expansion is sixth-order
- Anharmonic coefficients are constant

A. Devonshire, 1949



Principal dielectric constants of $BaTiO_3$ (theoretical).

Phenomenological theory *vs* experiment

- **strong temperature dependence of quartic (and sextic) anharmonic coefficients:**

M. E. Drougard, R. Landauer, D. R. Young, Phys. Rev. **98** (1955) 1010;
E. J. Huibregtse, D. R. Young, Phys. Rev. **103** (1956) 1705;
A. J. Bell, L. E. Cross, Ferroelectrics **59** (1984) 197;
A. J. Bell, J. Appl. Phys. **89** (2001) 3907.

- **presence of eighth-order terms in free energy expansion**

D. Vanderbilt, M. H. Cohen, PRB **63** (2001) 094108;
I. A. Sergienko, Yu. M. Gufan, S. Urazhdin, PRB **65** (2002) 144104;
Y. L. Li, L. E. Cross, L. Q. Chen, JAP **98** (2005) 064101;
Y. L. Wang, A. K. Tagantsev, D. Damjanovic, N. Setter, V. K. Yarmarkin, A. I. Sokolov, PRB **73** (2006) 132103; JAP **101** (2007) 104115.

For $BaTiO_3$ (Wang et al., 2006, 2007):

Both the temperature dependence of quartic coefficients and the presence of eighth order terms turn out to be essential for the adequate description of the $BaTiO_3$ dielectric behavior.

These essentialities attest to the unusually strong polarization anharmonicity of $BaTiO_3$, which is unexpected for classical displacive ferroelectrics.

The question is:

- Whether strong anharmonicity of $BaTiO_3$ ferroelectric subsystem and pronounced temperature dependence of coefficients of P_x^4 and $P_x^2 P_y^2$ terms in Ginzburg-Devonshire expansion are independent effects or they are related to each other?

Model of cubic displacive ferroelectric with strong anharmonicity

$$
\begin{aligned}
H_{anh} = {} & \frac{\beta_1}{4!}(\varphi_1^4+\varphi_2^4+\varphi_3^4)+\frac{\beta_2}{4}(\varphi_1^2\varphi_2^2+\varphi_2^2\varphi_3^2+\varphi_3^2\varphi_1^2)+\frac{\gamma_1}{6!}(\varphi_1^6+\varphi_2^6+\varphi_3^6) \\
& +\frac{\gamma_2}{48}\left[\varphi_1^2(\varphi_2^4+\varphi_3^4)+\varphi_2^2(\varphi_3^4+\varphi_1^4)+\varphi_3^2(\varphi_1^4+\varphi_2^4)\right]+\frac{\gamma_3}{8}\varphi_1^2\varphi_2^2\varphi_3^2 \\
& +\frac{\delta_1}{8!}(\varphi_1^8+\varphi_2^8+\varphi_3^8)+\frac{\delta_2}{6!2!}\left[\varphi_1^2(\varphi_2^6+\varphi_3^6)+\varphi_2^2(\varphi_3^6+\varphi_1^6)+\varphi_3^2(\varphi_1^6+\varphi_2^6)\right] \\
& +\frac{\delta_3}{(4!)^2}(\varphi_1^4\varphi_2^4+\varphi_2^4\varphi_3^4+\varphi_3^4\varphi_1^4)+\frac{\delta_4}{96}(\varphi_1^4\varphi_2^2\varphi_3^2+\varphi_1^2\varphi_2^4\varphi_3^2+\varphi_1^2\varphi_2^2\varphi_3^4)
\end{aligned}
$$

Eighth-order free energy expansion for cubic ferroelectrics (perovskites)

$$F = \frac{A}{2}(P_1^2 + P_2^2 + P_3^2) + \frac{B_1}{4!}(P_1^4 + P_2^4 + P_3^4) + \frac{B_2}{4}(P_1^2P_2^2 + P_2^2P_3^2 + P_3^2P_1^2)$$

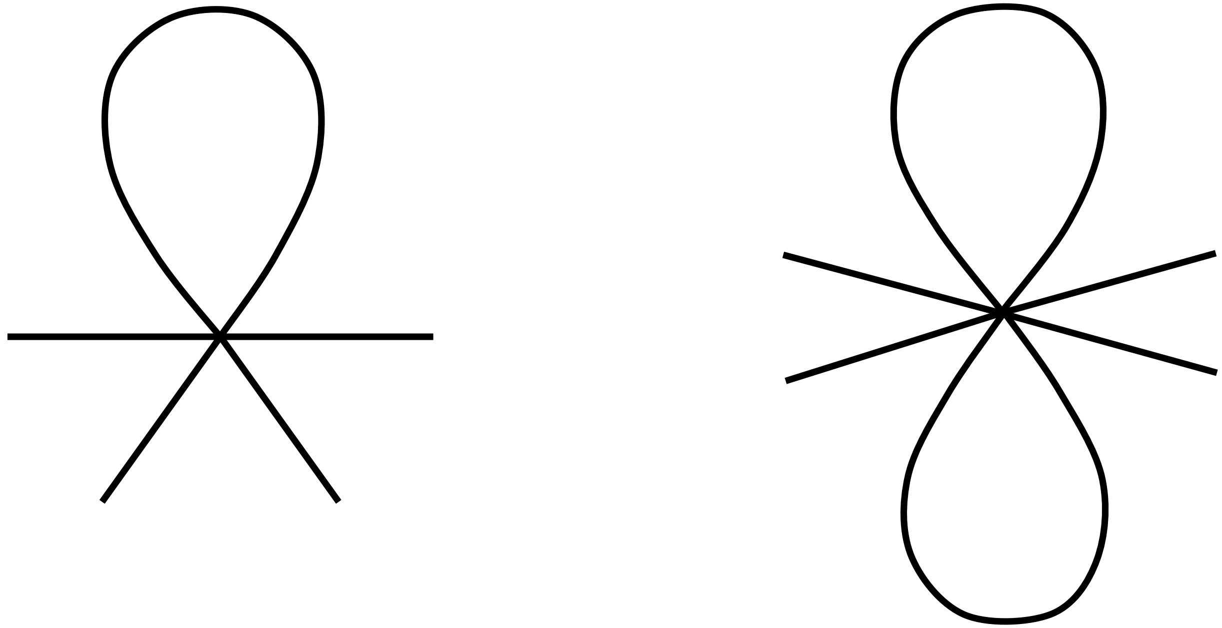
$$+ \frac{\Gamma_1}{6!}(P_1^6 + P_2^6 + P_3^6) + \frac{\Gamma_2}{48}\left[P_1^2(P_2^4 + P_3^4) + P_2^2(P_3^4 + P_1^4) + P_3^2(P_1^4 + P_2^4)\right]$$

$$+ \frac{\Gamma_3}{8}P_1^2P_2^2P_3^2$$

$$+ \frac{\Delta_1}{8!}(P_1^8 + P_2^8 + P_3^8) + \frac{\Delta_2}{6!2!}\left[P_1^2(P_2^6 + P_3^6) + P_2^2(P_3^6 + P_1^6) + P_3^2(P_1^6 + P_2^6)\right]$$

$$+ \frac{\Delta_3}{(4!)^2}(P_1^4P_2^4 + P_2^4P_3^4 + P_3^4P_1^4) + \frac{\Delta_4}{96}(P_1^4P_2^2P_3^2 + P_1^2P_2^4P_3^2 + P_1^2P_2^2P_3^4)$$

Fluctuation shift (anharmonic renormalization) of the fourth-order coefficients



$\varphi^6 \rightarrow \varphi^4 \langle\varphi\varphi\rangle \rightarrow \boldsymbol{P^4T}$

$\varphi^8 \rightarrow \varphi^4 \langle\varphi\varphi\rangle \langle\varphi\varphi\rangle \rightarrow \boldsymbol{P^4T^2}$

Green function (propagator) and one-loop integral *I*

$$\langle \varphi_\alpha(\vec{q})\varphi_\beta(-\vec{q})\rangle = G_{\alpha\beta}(\vec{q})$$

$$\approx \frac{kT}{\varepsilon^{-1}+s^2q^2+fs^2q_\alpha{}^2}\left[\delta_{\alpha\beta}-\frac{q_\alpha q_\beta}{s^{-2}\varepsilon^{-1}+q^2+fq_\beta{}^2}\left(\sum_{\gamma=1}^{3}\frac{q_\gamma{}^2}{s^{-2}\varepsilon^{-1}+q^2+fq_\gamma{}^2}\right)^{-1}\right]$$

$$I=\frac{1}{(2\pi)^3s^2}\int G_{11}(\vec{q})d\vec{q}\cong\frac{q_D}{3\pi^2s^2}\left(1-\frac{1}{5}f+\frac{1}{15}f^2-\frac{127}{5005}f^3\right)$$

Fluctuation contributions to coefficients B_1 and B_2

$$\delta B_1 = I\left(\frac{\gamma_1}{2}+\gamma_2\right)k_B T + I^2\left(\frac{\delta_1}{8}+\frac{\delta_2}{2}+\frac{\delta_3}{4}+\frac{\delta_4}{4}\right)(k_B T)^2$$

$$\delta B_2 = I\left(\gamma_2+\frac{\gamma_3}{2}\right)k_B T + I^2\left(\frac{\delta_2}{4}+\frac{\delta_3}{4}+\frac{5\delta_4}{8}\right)(k_B T)^2$$

Higher-order anharmonic constants – bare values of Γ_i and ☟$_j$

Let ♑$_i$ = ☝$_i$, ♎$_j$ = ☟$_j$. Then (Y. L.Wang et al., 2007)

♑$_1$ = $10.0 \cdot 10^{11}$ V m^9 C^{-5},   ♎$_1$ = $195 \cdot 10^{13}$ V m^{13} C^{-7},

♑$_2$ = $-1.06 \cdot 10^{11}$ V m^9 C^{-5},   ♎$_2$ = $36.4 \cdot 10^{13}$ V m^{13} C^{-7},

♑$_3$ = $4.41 \cdot 10^{11}$ V m^9 C^{-5},   ♎$_3$ = $16.1 \cdot 10^{13}$ V m^{13} C^{-7},

♎$_4$ = $0.9 \cdot 10^{13}$ V m^{13} C^{-7}

Fluctuation contributions and their signs – theory

♎👌$_1 = 3.49 \cdot 10^{11}\, I\, k_B T + 4.69 \cdot 10^{14}\, I^2 (k_B T)^2$,

♎👌$_2 = 1.14 \cdot 10^{11}\, I\, k_B T + 1.37 \cdot 10^{14}\, I^2 (k_B T)^2$

Since $I > 0$, ♎👌$_1$ and ♎👌$_2$ are positive and grow with temperature.

Temperature dependence of B_1, B_2 – experiment (Y.L.Wang et al., 2007)

👌$_1 = -4.39 \cdot 10^{10} + 9.60 \cdot 10^{7}\, T,$

👌$_2 = -0.896 \cdot 10^{10} + 2.68 \cdot 10^{7}\, T$

Both fourth-order coefficients
grow with temperature

Fluctuation contributions ratio ♎B$_1$/♎B$_2$ – theory *vs* experiment

Theory:

♎👌$_1^{(6)}$/♎👌$_2^{(6)}$ = **3.46**, ♎👌$_1^{(8)}$/♎👌$_2^{(8)}$ = **3.42**,

Experiment (Y. L.Wang et al., 2007):

♎👌$_1(T)$/♎👌$_2(T)$ = **3.58**

Alternative set of experimental values of Γ_i and 👎$_j$

Different set of bare values of sixth- and eighth-order couplings (Li-Cross-Chen experiments, 2005) results in alternative estimates:

♎👌$_1 = \quad 3.72\cdot10^{11}\ I\, k_B T + 2.16\cdot10^{14}\ I^2(k_B T)^2$,

♎👌$_2 = -\, 1.04\cdot10^{11}\ I\, k_B T + 0.123\cdot10^{14}\ I^2(k_B T)^2$

Here, the sign of ♎👌$_2$ is not fixed, but, for sure,
|♎👌$_2$| << ♎👌$_1$, in agreement with all known experiments.

Summary

- Lattice anharmonicities ♐^{6} и ♐^{8} give rise to fluctuation contribution to coefficients B_1 and B_2 of free energy expansion for $BaTiO_3$ that depend on temperature.
- Within the first perturbative order, fluctuation contributions ♎B_1 and ♎B_2 grow with temperature, in agreement with all known experimental data.
- The theory enables one to estimate, without adjusting parameters, the ratio ♎B_1/♎B_2 . Numerical value of this ratio turns out to be close to that found in experiment.

Fiz. Tverd. Tela. 51 (2009) 331; *arXiv: 0902.0516*