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# Critical Behaviour of Tetragonal Ferroelectric Undergoing Phase Transition into Incommensurate Phase

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The static behaviour of an "easy-plane" tetragonal ferroelectric near the incommensurate phase transition point is considered. It is shown that the critical fluctuations may turn the continuous transition into the first-order one provided the crystal anisotropy is sufficiently large. It is also found that the dipolar interaction and the coupling of the order parameter to elastic strains suppress the critical fluctuations extending the region of validity of the Landau theory results (modified by some logarithmic factors).

In this report we consider the critical behaviour of the model describing the phase transition in a tetragonal crystal having no center of symmetry. This model has been introduced first by Levanyuk and Sannikov[1] to explain the dielectric anomalies in $(NH_4)_2BeF_4$. The corresponding Landau-Wilson Hamiltonian reads:

$$H=\int_V d\boldsymbol{r}\left\{\frac{\kappa_0^2}{2}(\varphi_x^2+\varphi_y^2)+\frac{1}{2}[(\nabla\varphi_x)^2+(\nabla\varphi_y)^2]\right. -\sigma\left(\varphi_x\frac{\partial\varphi_y}{\partial z}-\varphi_y\frac{\partial\varphi_x}{\partial z}\right)+\frac{\beta_1^{(0)}}{8}(\varphi_x^4+\varphi_y^4) \left.+\frac{\beta_2^{(0)}}{4}\varphi_x^2\varphi_y^2\right\}, \tag{1}$$

where two-component field $(\varphi_x, \varphi_y)$ describes the order parameter fluctuations, inverse bare correlation length squared $\kappa_0^2$ being the linear measure of distance from the phase transition line, and bare coupling constants are defined in such a way that for $\beta_1^{(0)}=\beta_2^{(0)}$ the system is isotropic in $(x, y)$-plane. For the sake of simplicity the anisotropic gradient term is neglected in eq. (1) although it is relevant in the renormalization group (RG) sense.* When expressed in terms of Fourier-transformed fields

$$\varphi_\alpha(\boldsymbol{q})=\frac{1}{V}\int_V e^{-i\boldsymbol{qr}}\varphi_\alpha(\boldsymbol{r})d\boldsymbol{r},\quad \varphi_\alpha(\boldsymbol{q})=\varphi_\alpha^*(-\boldsymbol{q}), \tag{2}$$

the Hamiltonian (1) takes the form:

$$H=\sum_{\boldsymbol{q}}\left\{\frac{1}{2}(\kappa_0^2+q^2)[\varphi_x(\boldsymbol{q})\varphi_x(-\boldsymbol{q})\right. +\varphi_y(\boldsymbol{q})\varphi_y(-\boldsymbol{q})]+i\sigma q_z[\varphi_x(\boldsymbol{q})\varphi_y(-\boldsymbol{q}) -\varphi_x(-\boldsymbol{q})\varphi_y(\boldsymbol{q})]+\sum_{\boldsymbol{q}+\boldsymbol{q}'+\boldsymbol{q}''+\boldsymbol{q}'''=0}\left\{\frac{\beta_1^{(0)}}{8}\right. \times[\varphi_x(\boldsymbol{q})\varphi_x(\boldsymbol{q}')\varphi_x(\boldsymbol{q}'')\varphi_x(\boldsymbol{q}''') +\varphi_y(\boldsymbol{q})\varphi_y(\boldsymbol{q}')\varphi_y(\boldsymbol{q}'')\varphi_y(\boldsymbol{q}''')] \left.+\frac{\beta_2^{(0)}}{4}\varphi_x(\boldsymbol{q})\varphi_x(\boldsymbol{q}')\varphi_y(\boldsymbol{q}'')\varphi_y(\boldsymbol{q}''')\right\}. \tag{3}$$

Equation (3) is inconvenient to be dealt with since its harmonic part is non-diagonal in the field variables. To remove this shortcoming we replace two real fields $\varphi_x$ and $\varphi_y$ by single complex field $\psi(\boldsymbol{q})$ related to the original ones by following equations:

$$\varphi_x(\boldsymbol{q})=\frac{1}{\sqrt{2}}[\psi(\boldsymbol{q})+\psi^*(-\boldsymbol{q})],$$

$$\varphi_y(\boldsymbol{q})=\frac{i}{\sqrt{2}}[\psi(\boldsymbol{q})-\psi^*(-\boldsymbol{q})]. \tag{4}$$

Although the field $\psi(\boldsymbol{q})$ doesn't possess any symmetry properties with respect to the inversion $\boldsymbol{q}\to-\boldsymbol{q}$ the fields $\varphi_x$ and $\varphi_y$ given by Eq. (4) obey the symmetry relation (2) as a result of the proper structure of eq. (4). Substituting eq. (4) into (3) one gets:

$$H=\sum_{\boldsymbol{q}}(\kappa_0^2+q^2-2\sigma q_z)\psi(\boldsymbol{q})\psi^*(\boldsymbol{q}) +\sum_{\boldsymbol{q}+\boldsymbol{q}'+\boldsymbol{q}''+\boldsymbol{q}'''=0}\left\{\frac{\gamma_1^{(0)}}{4}\psi(\boldsymbol{q})\psi(\boldsymbol{q}')\right.$$

* The anisotropy of spatial dispersion may be shown to produce here just the same effects as in the case of centrosymmetric crystal. In particular, it may cause the splitting of continuous phase transition into two first-order transitions close together in temperature.[2]

$$\times \psi^*(-\boldsymbol{q}'')\psi^*(-\boldsymbol{q}''')+\frac{\gamma_2^{(0)}}{8}[\psi(\boldsymbol{q})\psi(\boldsymbol{q}')$$

$$\left.\times \psi(\boldsymbol{q}'')\psi(\boldsymbol{q}''')+\text{c.c.}]\right\}, \qquad (5)$$

where

$$\gamma_1^{(0)}=(3\beta_1^{(0)}+\beta_2^{(0)})/2,\ \gamma_2^{(0)}=(\beta_1^{(0)}-\beta_2^{(0)})/2. \qquad (6)$$

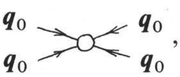
The expression obtained looks like the Hamiltonian of interacting Bose-gas. This similarity is, however, far from to be complete. Indeed, eq. (5) contains not single but two interaction terms of essentially different nature. The first one generated by the isotropic (O(2)) quartic interaction of fields $\varphi_x$ and $\varphi_y$ conserves the number of particles, while the second one originating from the anisotropic term of initial Hamiltonian describes the simultaneous creation and annihilation of four "$\psi$-fluctuons." Moreover, the propagator of $\psi$-fluctuons

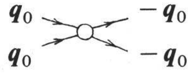
$$G_0(\boldsymbol{q})=\langle\psi(\boldsymbol{q})\psi^*(\boldsymbol{q})\rangle_0=\frac{1}{\kappa_0^2+q^2-2\sigma q_z} \qquad (7)$$

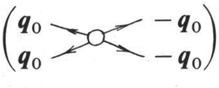
is "shifted" by the vector $\sigma\boldsymbol{e}_z$ in momentum space since the critical fluctuations are condensed at the finite wave vector in the case discussed.

We put first $\gamma_2^{(0)}=0$, i.e. consider the simplest, isotropic regime of critical behaviour. In this case the Hamiltonian (5) is precisely identical to that of the XY model (Bose-gas) provided the trivial replacement $\psi(\boldsymbol{q}+\sigma\boldsymbol{e}_z)\to\tilde{\psi}(\boldsymbol{q})$ is performed. The critical behaviour of the XY model is well known.[3] It undergoes the continuous phase transition, and the critical exponents displayed are $\gamma\cong1{,}32$, $\beta\cong0{,}35$, $\alpha\approx0$.

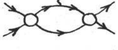
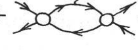
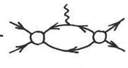
Let's further take into account the crystal anisotropy. To clear up the role played by the anisotropy in the problem considered the RG equations for effective coupling constants $\gamma_1$ and $\gamma_2$ are to be derived and solved. Since the critical fluctuations are centred in $\boldsymbol{q}$-space near the wave vector $\boldsymbol{q}_0=\sigma\boldsymbol{e}_z$ we define the renormalized coupling constants in a following, somewhat unconventional way:

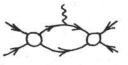
$\gamma_1=\Gamma_1(\boldsymbol{q}_0,\boldsymbol{q}_0,\boldsymbol{q}_0)=$  ,

$\gamma_2=\Gamma_2(\boldsymbol{q}_0,\boldsymbol{q}_0,-\boldsymbol{q}_0)=$  (8)

(  ).

The derivatives of $\gamma_1$ and $\gamma_2$ with respect to the dressed inverse correlation length squared $\kappa^2$ are determined within the one-loop approximation by the graphs:

$\dfrac{\partial\gamma_1}{\partial\kappa^2}=$  +  +  , (9)

$\dfrac{\partial\gamma_2}{\partial\kappa^2}=$  , (10)

while the RG equations themselves take the form:

$$\frac{\partial g_1}{\partial t}=g_1-g_1^2-\frac{9}{5}g_2^2$$

$$\frac{\partial g_2}{\partial t}=g_2-\frac{6}{5}g_1g_2 \qquad (11)$$

where $t=-\ln\kappa$, $g_i=5\gamma_i/16\pi\kappa$, $i=1,2$.

Equations (11) possess four fixed points: $g_1=5/6$, $g_2=\pm5/18$ (saddle points), $g_1=g_2=0$ (unstable knot), and $g_1=1$, $g_2=0$ (stable knot). If the initial values of $g_1$, $g_2$ lie within the sector $|g_2|<g_1/3$ constituting the domain of attraction of the stable knot then the system becomes isotropic under $T\to T_c$, and it behaves like the XY model mentioned above; the tetragonal anisotropy is renormalized away by the critical fluctuations in this case. On the contrary, in strongly anisotropic crystals whose critical behaviour is governed by the saddle fixed points the fluctuations cause further increase of the anisotropy until the Landau-Wilson Hamiltonian becomes unstable that is known to indicate the first-order phase transition.[2] Thus, the incommensurate transitions in such crystals should be first-order.

In addition to the crystal anisotropy long-range dipolar and elastic interactions influence considerably upon the critical behaviour of ferroelectrics. To take into account the dipolar forces one can add to the Hamiltonian (3) the term

$$H_{\mathrm{D}}=\frac{1}{2}\sum_{\boldsymbol{q}}\sum_{\alpha,\beta=x,y}(\varDelta^2+hq^2)n_\alpha n_\beta\varphi_\alpha(\boldsymbol{q})\varphi_\beta(-\boldsymbol{q}),$$

$$n_\alpha=q_\alpha/q. \qquad (12)$$

Non-centro-symmetric ferroelectrics possess the piezoelectric coupling of the order parameter fluctuations to elastic strains in disordered phases. The corresponding contribution to the Hamiltonian for crystals of the $\mathrm{D}_4$ class considered below is as follows:

$$H_s=d\int(\varphi_x u_{yz}-\varphi_y u_{xz})\mathrm{d}\boldsymbol{r}+\frac{1}{2}\int c_{\alpha\beta\gamma\delta}u_{\alpha\beta}u_{\gamma\delta}\mathrm{d}\boldsymbol{r},$$

$$c_{\alpha\beta\gamma\delta}=\left(\kappa-\frac{2}{3}\mu\right)\delta_{\alpha\beta}\delta_{\gamma\delta}+\mu(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}), \quad (13)$$

where the elastic crystal anisotropy is neglected. The piezoelectric coupling which may be treated exactly by calculation of functional integrals over the elastic degrees of freedom results in the additional interaction of the critical fluctuations described by the term:

$$-\sum_{\boldsymbol{q}} W_{\alpha\beta}(\boldsymbol{q})\varphi_\alpha(\boldsymbol{q})\varphi_\beta(-\boldsymbol{q}),$$

$$W_{xx}(\boldsymbol{q})=D(1-n_x^2-4\gamma n_y^2 n_z^2),$$

$$W_{xy}(\boldsymbol{q})=W_{yx}(\boldsymbol{q})=-Dn_x n_y(1-4\gamma n_z^2),$$

$$W_{yy}(\boldsymbol{q})\rightleftarrows W_{xx}(\boldsymbol{q}),\quad D=\frac{d^2}{\mu},$$

$$\gamma=\frac{K+\mu/3}{K+4\mu/3}\, x\rightleftarrows y. \quad (14)$$

The Green function $G_{\alpha\beta}(\boldsymbol{q})$ in the case considered takes the form:

$$G_{xx}(\boldsymbol{q})=[\kappa^2-D+n_y^2(\Delta^2-D)+4\gamma Dn_x^2 n_z^2]\det{}^{-1}A,$$

$$G_{xy}(\boldsymbol{q})=G_{yx}^*(\boldsymbol{q})=[i\sigma q_z-n_x n_y(\Delta^2+D+4\gamma Dn_z^2)]\det{}^{-1}A,$$

$$\det A=(\kappa^2-D+q^2)[\kappa^2-D+q^2+(1-n_z^2)(\Delta^2+D+4\gamma Dn_z^2)]+4\gamma D(\Delta^2+D)n_z^2(1-n_z^2)^2-\sigma^2 q_z^2,$$

$$G_{yy}(\boldsymbol{q})\underset{x\rightleftarrows y}{\rightleftarrows}G_{xx}(\boldsymbol{q}). \quad (15)$$

It can be seen that corrections to the results of Landau theory calculated on the base of eq. (15) diverge logarithmically for $\sigma^2<\kappa^2<D$. Hence, the dipolar forces and the coupling to elastic strains suppress the critical fluctuations making the results of Landau theory valid, apart from the logarithmic corrections, within the region mentioned. However, for $\kappa^2<\sigma^2$, i.e. very near $T_c$ the effect of two factors discussed becomes negligible, and the system displays the power-law behaviour or the fluctuation-induced first-order phase transition. If the continuous transition occurs, then the incommensurate superstructure should turn into right (undistorted) helix under $T\to T_c-0$ because of the critical decay of crystal anisotropy shown above. This prediction may be verified in experiments on neutron diffraction or second harmonic generation.

## References

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