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S. STAMENKOVIĆ
N.M. PLAKIDA
V.L. AKSIENOV
T. SIKLÓS

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by

S. Stamenković
"Boris Kidrič" Institute for Nuclear Sciences, Vinča
YU-11001 Belgrade, POB 522, Yugoslavia

N.M. Plakida and V.L. Aksienov
Joint Institute for Nuclear Research, Dubna,
SU-101000 Moscow, Head Post Office, POB 79, USSR

T. Siklós
Central Research Institute for Physics,
H-1525 Budapest, POB 49, Hungary

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ABSTRACT

In the framework of the general theory of ferroelectrics displacive type phase transitions are investigated in the T=OK quantum limit, when the phase transition is due to the zero-point fluctuations. The critical value of the zero point energy is evaluated in the case of the completaly ordered and disordered lattices, not taking into account tunnelling.

АННОТАЦИЯ

В рамках обобщенной теории сегнетоэлектриков исследован фазовый переход типа смещения в квантовом предельном случае нулевой температуры, когда фазовый переход определяется энергией нулевых колебаний. Получены оценки для критического значения энергии нулевых колебаний - без учета эффекта туннелировки - для предельных случаев полностью упорядоченной и полностью разупорядоченной решетки.

KIVONAT

A ferroelektromos anyagok általános elmélete keretei között vizsgáltuk a rácstorzulással járó fázisátalakulásokat a T=O K kvantum határesetben, amikor is a fázisátalakulást a nullponti rezgések okozzák. Megbecsültük a nullponti energia kritikus értékét - az alagut-effektust nem véve figyelembe - a teljesen rendezett és a teljesen rendezetlen rácsok esetében.

In reference [1] an unified model for ferroelectric phase transitions has been presented, which took into account both the statistical disordering of the ions in the cells and the dynamic instability of the fluctuations of the lattice leading to displacive phase transitions. The solution of the self-consistent system of equations for the two order parameters, $\sigma_\alpha = \langle\sigma_i^\alpha\rangle$, the average number of ions in the state $\alpha = \pm 1$, and $\vec{b}_\alpha = \langle\vec{S}_i^\alpha\rangle$, the average displacement of ions in the cell in the state α has been obtained in [1] and subsequently in [2], in the classical limit of high temperatures, $kT \gg \hbar\omega_D$.

It is also interesting to investigate the quantum limit of zero temperature when the phase transition is determined by the quantum fluctuations and the energy of the zero point fluctuations and not by thermal excitations. Displacive phase transitions in the model of ferroelectrics in the quantum case has been investigated also in reference [3].

1. Self-consistent system of equations

The model of ferroelectrics [1] is described by a system of harmonically coupled ions, each of which can occupy one of the two minima ($\alpha = \pm 1$) of a one-particle potential well:

$$H = \sum_{i,\alpha} \sigma_i^\alpha \{\frac{1}{2m} (\vec{P}_i^\alpha)^2 - \frac{A}{2} (\vec{S}_i^\alpha)^2 + \frac{B}{4} (\vec{S}_i^\alpha)^4\} + \qquad /1/$$

$$+ \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \sigma_i^\alpha \sigma_j^\beta \varphi_{ij} (\vec{S}_i^\alpha - \vec{S}_j^\beta)^2 ,$$

where the projection operators $\sigma_i^+ = 1$ or 0 /accordingly $\sigma_i^- = 1 - \sigma_i^+ = 0$ or 1/ if at the i-th lattice point the ion is in the state $\alpha = +1$ or $\alpha = -1$ respectively. $\vec{P}_i^\alpha$ and $\vec{S}_i^\alpha$ are the moments and the coordinate of the ion, A and B are parameters of the one-particle potential well, φ_{ij} is the coupling constant between the ions in the three dimensional lattice.

From the condition of equilibrium $d\langle P_i^\alpha(t)\rangle/dt = 0$ in [1] the following equation has been obtained

$$\eta_\alpha^3 - (1-3y_\alpha)\eta_\alpha + (\eta_+ + \eta_-)f_o\sigma_{-\alpha} = 0 \qquad /2/$$

which relates the equilibrium position of ions $\eta_\alpha = (B/A)^{1/2} \langle S_i^\alpha\rangle$ to the average number of ions $\sigma_\alpha = \langle\sigma_i^\alpha\rangle$ in the state α. Here $f_o = \sum_j \varphi_{ij}/A = \varphi_o/A$ is the dimensionless coupling constant.

The quantity y_α is the average squared displacement of ions from the equilibrium position in the state α. It has been determined by the help of the phonon Green's function in the form

$$y_\alpha = \frac{B}{A}\langle(S_i^\alpha - b_i^\alpha)^2\rangle = \frac{B}{A}\langle(u_i^\alpha)^2\rangle =$$

$$= \frac{B}{NA^2}\sum_q \int_0^\infty d\omega \coth\frac{\omega}{2\Theta}\left[-\frac{1}{\pi}\,\mathrm{Im}\,D_{\vec{q}}^\alpha(\omega+i\varepsilon)\right], \qquad /3/$$

$$D_{\vec{q}}^\alpha(\nu) = \frac{\nu^2-(\Delta_{-\alpha}^2 + f_o)}{(\nu^2-\nu_{\vec{q}+}^2)(\nu^2-\nu_{\vec{q}-}^2)-\sigma_+\sigma_- f_{\vec{q}}^2} = \frac{\nu^2-(\Delta_{-\alpha}^2 + f_o)}{(\nu^2-\nu_{q_1}^2)(\nu^2-\nu_{q_2}^2)} \qquad /4/$$

where $\nu^2 = \omega^2/(A/m)$; $\nu_{\vec{q}\alpha}^2 = \Delta_\alpha^2 + (f_o - \sigma_\alpha f_{\vec{q}})$;

$$\nu_{q(1,2)}^2 = \frac{1}{2}(\nu_{q_+}^2 + \nu_{q_-}^2) \pm \frac{1}{2}\{(\nu_{q_+}^2 - \nu_{q_-}^2)^2 + 4\sigma_+\sigma_- f_q^2\}^{1/2};$$

$$\Delta_\alpha^2 = -1 + 3(\eta_\alpha^2 + y_\alpha); \quad f_{\vec{q}} = (1/A)\sum_j \varphi_{ij}\, e^{i\vec{q}(\vec{\ell}_i - \vec{\ell}_j)}.$$

Performing the integration in /3/ in the case of zero temperature, when coth($\omega/2\Theta$)=1, taking into account /4/ one obtains:

$$y_\alpha = \frac{\lambda}{N}\sum_q \frac{1}{2(\nu_{q_1}+\nu_{q_2})}\left(1+\frac{\Delta^2_{-\alpha}+f_o}{\nu_{q_1}\nu_{q_2}}\right) , \qquad /5/$$

where $\lambda=(A/m)^{1/2}/(A^2/B)$ is a quantum parameter, proportional to the ratio of the energy of zero point fluctuations, $\hbar\omega_o=(A/m)^{1/2}$ and the height of the barrier in the one-particle potential well, $U_o=(A^2/4B)$.

For the determination of the average population σ_α or the pseudospin variable $\sigma=\langle\sigma_i^z\rangle=(2\sigma_+-1)(1-2\sigma_-)$, an effective pseudospin Hamiltonian has been introduced:

$$\tilde{H}_s = \sum_i h_i\sigma_i^z - \frac{1}{2}\sum_{i,j}\tilde{I}_{ij}\,\sigma_i^z\,\sigma_j^z , \qquad /6/$$

where $\sigma_i^z=\pm1$, h_i and $\tilde{I}_{ij}$ are the average effective field and the "exchange integral" which depend on the state of phonon subsystem [1].

In the Hamiltonian /1/ and /6/ the tunnelling between states $\alpha=\pm1$ is not taken into account and therefore in the limit $\Theta\to0$ an unique solution, $\sigma=1$ appears /if $\tilde{I}_{ij}>0$, $h_i\geq0$/. The effect of tunnelling, suggested in [4], makes it possible to generalize the Hamiltonian /1/ and to introduce in /6/ the transverse field, $\Omega\sum_i\sigma_i^x$, which in turn may lead to the solution $\sigma\to0$ in the case $\Theta\to0$. In the present work we will not discuss the solution of the self-consistent system of equations for the phonon system and the pseudospin system in the range $0<\sigma<1$; instead we will investigate only two cases, namely the case of the completely ordered, $\sigma=1$ lattice and the case of the completely disordered, $\sigma=0$ lattice. Doing so, we will assume that the right choice of the value of the transverse field Ω, can ensure the transition from $\sigma=1$ to $\sigma=0$ in the case of zero temperature, $\Theta=0$.

2. Displacive type phase transition in ordered lattices

In the completely ordered lattice all the ions are in the same state, for example $\alpha=+1$ and $\sigma=1$. In this case the equation of selfconsistency /5/ takes the following form:

$$y_+ = \frac{\lambda}{2N}\sum_q \frac{1}{\sqrt{\Delta_+^2 + f_o - f_q}} = \frac{\lambda}{2}\int_o^{\omega_D} \frac{g(\omega^2)d\omega^2}{\sqrt{\Delta_+^2+\omega^2}} , \qquad /7/$$

where the density of the phonon frequencies

$$g(\omega^2) = \frac{1}{N}\sum_q \delta(f_o - f_q - \omega^2), \qquad \omega<\omega_D , \qquad /8/$$

has been introduced.

Taking into account the condition of equilibrium /2/, in the case of $\sigma=1(\sigma_-=0)$ we obtain one equation for the self--consistent determination of the equilibrium displacement η or the gap in the spectrum of the frequencies $\Delta_+^2=2\eta^2$, in the ferroelectric phase:

$$\eta^2 = 1 - \frac{3}{2}\lambda\int_o^{\omega_D} \frac{g(\omega^2)d\omega^2}{\sqrt{2\eta^2+\omega^2}} . \qquad /9/$$

As it can be seen the solution of this equation for the ferroelectric phase with $\eta\neq 0$ exist only if $\lambda<\lambda_{c(1)}$, where the critical value $\lambda_{c(1)}$ is determined by

$$\lambda_{c(1)} = \frac{2}{3}\left\{\int_o^{\omega_D} \frac{g(\omega^2)d\omega^2}{\omega}\right\}^{-1} = \frac{2}{3}\frac{\sqrt{f_o}}{\mu_{-1}} . \qquad /10/$$

Here $\mu_{-1}=\overline{\omega^{-1}}$ is the average of the inverse of the frequency; for the Debye spectrum $g(\omega^2)=3\omega/2\omega_D^3$; $\mu_{-1}=3/2\sqrt{2}\sim 1$ if $\omega_D^2=2f_o$.

Consequently, displacive type transition in ordered lattices can take place only if the lattice consists of sufficiently heavy ions, that is if

$$m > \left(\frac{2}{3}\frac{\sqrt{\varphi_o}}{\mu_{-1}}\frac{A}{B}\right)^{-2} \qquad /11/$$

for a given coupling constant φ_o between the ions and a given width $S_o=\sqrt{A/B}$ of the one-particle potential well in accordance with reference [3].

3. Displacive type phase transition in disordered lattices

Let us discuss the effect of disordering on the displacive type phase transition. Putting in /2/ and /3/ $\sigma=0$, corresponding to equal number of ions in the states $\alpha=+1$ and $\alpha=-1$ and consequently meaning that $\Delta_+^2=\Delta_-^2\equiv\Delta_o^2$; $\eta_+=\eta_-\equiv\eta$ we get the following system of equations

$$\eta^2 = 1-f_o-3y \qquad /12/$$

$$y = \frac{\lambda}{2}\int_0^{\omega_D}\frac{g(\omega^2)d\omega^2}{\sqrt{\Delta_o^2+\omega^2}} . \qquad /13/$$

Therefore the self-consistent equation for the determination of the gap, $\Delta_o^2>0$ in the phonon spectrum in the case of $\sigma=0$ and $\eta>0$ takes the following form

$$\Delta_o^2 = 2\eta^2-f_o = 2-3f_o-3\lambda\int_0^{\omega_D}\frac{g(\omega^2)d\omega^2}{\sqrt{\Delta_o^2+\omega^2}} \qquad /14/$$

Displacive type phase transition, $\eta>0$, can take place if $\lambda<\lambda_{c(o)}$, where the critical value of λ is determined by the condition $\Delta_o^2(\lambda_{c(o)})=0$, that is

$$\lambda_{c(o)} = \frac{2}{3} \frac{\sqrt{f_o}}{\mu_{-1}} (1-\frac{3}{2} f_o) = \lambda_{c(1)}(1-\frac{3}{2} f_o) \qquad /15/$$

Consequently, the occurence of the disordering decreases both the limiting value of the allowed energy of the zero--point fluctuations and the limiting value of the temperature of the phase transition in the classical limit of high temperatures: $\tau_c^{(o)}=\tau_c^{(1)}\{1-(3/2)f_o\}$ [1]. However it has to be mentioned that the transition into the state σ=O can take place only if $f_o \ll 1$, and therefore formula /15/ is valid only if f_o<<1. In the case f_o>1, in accordance with [1], only the state with σ=1 is possible and formula /10/ is valid.

The explicit effect of tunnelling and the evaluation of the limiting value of the quantum parameter λ in this case will be done in a separate paper.

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