Національна академія наук України

ІНСТИТУТ ФІЗИКИ КОНДЕНСОВАНИХ СИСТЕМ

ICMP–96–17E

I.V.Stasyuk, K.O.Trachenko

Structural Phase Transition in "$\varphi^3 + \varphi^4$" Model.

ЛЬВІВ

УДК: 537.226.33, 537.312.62

PACS: 64.60.Cn, 63.20.Ry, 74.25.Kc

Структурний фазовий перехід в моделі "$\varphi^3 + \varphi^4$"

І.В.Стасюк, К.О.Траченко

Анотація. Для опису структурного фазового переходу ангармонічний потенціал, що діє на іон кристалічної гратки, вибирається у найбільш загальному, несиметричному вигляді, в якому, на доданок до четвертого, присутній ангармонізм третього порядку; взаємодія між іонами в різних комірках враховується в наближенні середнього поля. Отримані залежності параметра порядку, вільної енергії та діелектричної сприйнятливості від зовнішнього поля і залежності параметра порядку та вільної енергії від температури для різних параметрів моделі. Отримана фазова діаграма (зовнішнє поле, температура) і досліджений вплив кубічного ангармонізму на форму фазової діаграми та положення критичної точки. Досліджений фазовий перехід першого роду як при зміні зовнішнього поля, так і температури.

Structural Phase Transition in "$\varphi^3 + \varphi^4$" Model.

I.V.Stasyuk, K.O.Trachenko

Abstract. In the context of description of structural phase transition, the anharmonic potential effecting on the ion in the crystal lattice is selected in the form that, in addition to quadric, includes cubic anharmonicity, thus possessing the most general non-symmetrical form; the interaction among ions in different cells is accounted in the mean field approximation. The dependencies of the order parameter, free energy and dielectric susceptibility on the externally applied field and the order parameter and free energy on the temperature are derived for various model parameters. The phase diagram (external field, temperature) is derived and the influence of cubic anharmonicity on the form of the phase diagram and location of the critical point is studied. The first order phase transition, occuring as the external field varies as well as the temperature, is studied.

1. Introduction

While studying the mechanism of the structural phase transitions in crystals, the problem of choosing the type of the model potential V(q) in the Hamiltonian

$$H = \sum_i (\frac{p_i^2}{2M} + V(q_i)) - \frac{1}{2}\sum_{ij} \varphi_{ij} q_i q_j \qquad (1)$$

describing an ion in the lattice cell is raised.

As is mentioned in a number of papers, including [1], in the harmonic approximation $V(q) = \frac{\alpha}{2}q^2, \alpha = M\omega_0^2$, the crystal lattice may become unstable in the case of the negative value of α. In [1] the simplest stabilizing interaction is chosen in the form

$$V(q_i) = -\frac{\alpha q_i^2}{2} + \frac{\beta q_i^4}{4}. \qquad (2)$$

As is shown in [1], in this model the system undergoes a structural phase transition which in two limit cases can be displacive or order-disorder in character, depending on the parameters in the inititial Hamiltonian.

In a number of papers (see, for example, 2), the exact numerical calculations were carried out, based on (2). Accounting for the interaction among ions in different cells in the mean-field approximation, it was shown that the system undergoes a structural order phase transition. Studying the behavior of the order parameter, it was concluded that approximate methods lead to the results which do not comply with the results of exact nimerical approach (according to [1], even self-consistent approach is not satisfactory when considerinig systems described by (2); this approach describes the behavior of the soft mode properly only beyond the critical area described by the temperature of the first order phase transition).

In addition to the description of ion motion in ferroelectrics, the model anharmonic potential is applied to the description of the lattice anharmonicity in the high temperature superconductors. As is shown in [4], such an anharmonicity is inherent to the motion of the apex oxygen in YBaCuO and other superconductive compounds. In [3] the model potential possessing the most general non-symmetric form

$$V(q_i) = \frac{\alpha q_i^2}{2} - \frac{\beta q_i^3}{3} + \frac{\gamma q_i^4}{4}, \qquad (3)$$

was applied to describe the motion of the apex oxygen in $YBa_2Cu_3O_{7-\delta}$ compound. Basing on (3) and applying the method of self-consistent

phonons it was shown that the behaviour of the apex oxygen is bistable. The dependence of the order parameter on the temperature was shown to be of a hysteresis character. However, the question of the applicability of the method of self-consistent phonons to the description of the phase transition in the systems described by (3), including critical areas arises (see [1]).

In addition to the studies of YBaCuO series, structural phase transitions in Hg-based superconductors have been recently of wide consideration, in the context of reported connection between the lattice softening in these compounds and transition to the superconducting state. Particlularly, in [5] it was mentioned that near the transition point an anomalous abrupt mode softening was observed.

In this paper we assume that the model potential acting on the ion posesses the most general form (3). Secondly, we propose to account for the anharmonic character of the ion motion by the exact numerical treatment of (1), in which the interaction among ions in different cells we account for in the mean-field approximation, assuming the long-range character of the intercell interaction. Basing on this approach, we derive the dependencies of the order parameter, free energy and dielectric susceptibility on the externally applied field and the order parameter and free energy on the temperature for various model parameters. Analysing these dependencies we conclude that the system undergoes the first order phase transition, as the external field varies as well as the temperature; we note the anomalous behavior of the dielectric susceptibility near the phase transition point. In addition to that, we construct the phase diagram (external field, temperature) and study the influence of the cubic anharmonicity on the form of the phase diagram and the location of the critical point.

2. Model Hamiltonian

Accounting for the last term in (1) in the mean-field approximation leads to

$$-\frac{1}{2}\sum_{ij} \varphi_{ij} q_i q_j \to \varphi \langle q \rangle q - \frac{1}{2}\varphi \langle q \rangle^2, \qquad (4)$$

$$\varphi = -\sum_i \varphi_{ij}.$$

Before writing the Hamiltonian used for the calculations we comment on the interaction of the ion and conductivity electrons which is beleived

to play a crucial role in the mechanism of the high temperature superconductivity. In case of the symmetric form of the anharmonic potential (2) the anharmonic mode can be described in terms of the pseudospin variables (see, for example, [6]). Furthemore, in the Muller's model the interaction of the CuO-plane electrons and the local anharmonic mode has the form $g(n_{i\uparrow}+n_{i\downarrow})S_i^z$, where S_i^z is the pseudospin variable, $gn_{i\sigma}$ represents the energy change of the electron of spin σ in site i due to the apex oxygen transition from one minimum ($S_i^z=+\frac{1}{2}$) of the anharmonic potential to the other one ($S_i^z=-\frac{1}{2}$) (see [6]). In case of the non-symmetric form of the anharmonic potential (3) the interaction between the ion and conductivity electrons can be chosen in the Holstein-type form Dnq, where n - electrons concentration. However, in the considerations below we assume that $n=const$, $d=n*D$, thus interpreting d as externally applied field acting on the ion.

This leads to the following form of H:

$$H=\sum_i H_i;$$
$$H_i=\frac{p_i^2}{2M}+\frac{M\omega_0^2}{2}q_i^2-\frac{\beta q_i^3}{3}+\frac{\gamma q_i^4}{4}+dq_i+\varphi\langle q\rangle q_i-\frac{1}{2}\varphi\langle q\rangle^2 \tag{5}$$

We introduce the phonon creation and annihilation operators:

$$q=\sqrt{\frac{\hbar}{2M\omega_0}}(b^+ +b),\ p=i\sqrt{\frac{M\hbar\omega_0}{2}}(b-b^+). \tag{6}$$

In matrix representation these operators have the form of infinite matrices:

$$(b^+)_{ij}=\delta_{(i+1)j}\sqrt{i},\quad (b)_{ij}=\delta_{i(j+1)}\sqrt{i}. \tag{7}$$

After substituting q and p in (5), according to (6), the Hamiltonian matrix has the following form (all terms are divided by $\hbar\omega_0$):

$$H=\hat{\alpha}-C_1\hat{\beta}+C_2\hat{\gamma}+C_3\hat{\sigma}(d+\varphi\langle q\rangle)-C_4\langle q\rangle, \tag{8}$$

where

$$C_1=\frac{\beta}{3}\left(\frac{\hbar}{2M\omega_0}\right)^{\frac{3}{2}}\frac{1}{\hbar\omega_0},\ C_2=\frac{\gamma}{4}\left(\frac{\hbar}{2M\omega_0}\right)^{2}\frac{1}{\hbar\omega_0}, \tag{9}$$
$$C_3=\left(\frac{\hbar}{2M\omega_0}\right)^{\frac{1}{2}}\frac{1}{\hbar\omega_0},\ C_4=\frac{\varphi}{2}\frac{1}{\hbar\omega_0},$$

and

$$\begin{aligned}
\alpha_{ij}&=\delta_{ij}\frac{2i-1}{2},\\
\beta_{ij}&=\delta_{i(j+1)}3i\sqrt{i}+\delta_{j(i+1)}3j\sqrt{j}+\delta_{i(j+3)}\sqrt{i(i+1)(i+2)}+\\
&\quad\delta_{j(i+3)}\sqrt{j(j+1)(j+2)},\\
\gamma_{ij}&=\delta_{ij}3(i^2+(i-1)^2)+\delta_{i(j+2)}2(2i+1)\sqrt{i(i+1)}+\\
&\quad\delta_{j(i+2)}2(2j+1)\sqrt{j(j+1)}+\delta_{i(j+4)}\sqrt{i(i+1)(i+2)(i+3)}+\\
&\quad\delta_{j(i+4)}\sqrt{j(j+1)(j+2)(j+3)},\\
\sigma_{ij}&=\delta_{i(j+1)}\sqrt{i}+\delta_{j(i+1)}\sqrt{j}.
\end{aligned} \tag{10}$$

As the calculation of dependencies of thermodynamical functions on model parameters shows, accounting for the finite number of harmonic oscillator levels, i.e., limiting the size of the Hamiltonian matrix to $N=25$ is sufficient when $\frac{kT}{\hbar w}\le 5$. All calculations below are made within this range of model parameters.

3. Dependence of order parameter and free energy on the external field. Phase diagram

For calculation of order parameter we use the expression

$$\langle q\rangle=\frac{Sp(qe^{-\beta H})}{Spe^{-\beta H}} \tag{11}$$

After the unitary transformation is made

$$H_d=V^{-1}HV, \tag{12}$$

which diagonilizes the Hamiltonian matrix, we get

$$\langle q\rangle=\frac{Sp(\tilde{q}e^{-\beta H_d})}{Spe^{-\beta H_d}},\ \tilde{q}=V^{-1}qV \tag{13}$$

Note that $\langle q\rangle$ is contained in the Hamiltonian (5). Denoting

$$f=d+\varphi\langle q\rangle \tag{14}$$

we derive the self-consistent system of equations:

$$\begin{cases}\langle q\rangle=\langle q\rangle(f,T)\\ f=d+\varphi\langle q\rangle.\end{cases} \tag{15}$$

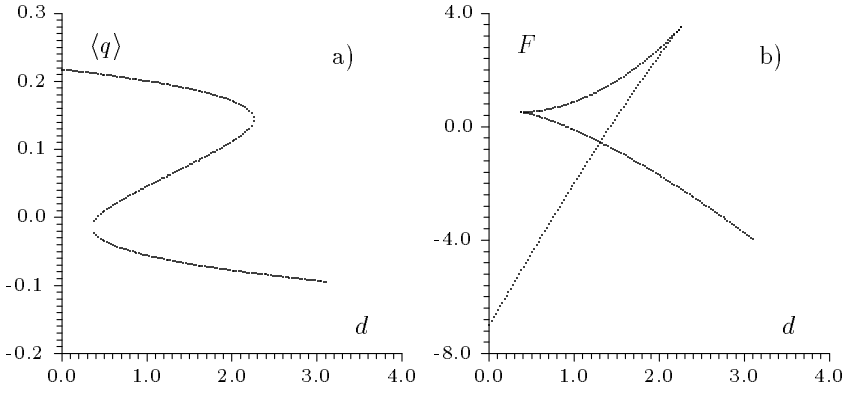

Figure 1: Dependencies of the order parameter and free energy on the external field, $\frac{kT}{\hbar\omega_0}$=0.17.

Numerical solution of this system allows to obtain the dependence $\langle q\rangle = \langle q\rangle(d)$ (Fig.1a) for various values of kT/hw (in all calculations below, φ=-20; C_1=0.157 and C_2=0.025). Using this dependence in the Hamiltonian (5) we calculate the dependence of the free energy on the external field, according to the expression below:

$$F(d,T) = -T\ln Sp\; e^{-\beta\varepsilon} - \frac{1}{2}\varphi\langle q\rangle^2 \qquad (16)$$

Fig. 1b represents the dependence F=F(d).

The dependencies shown on Fig.1 are typical for the first order phase transition. The abscissa of the self-crossing of the curve F corresponds to the value d^* at which the phase transition occurs, causing a jump-like change of the order parameter on Fig.1a. Raising the temperature leads to vanishing of hysteresis-type of this dependence, i.e., to vanishing of phase transition.

Temperature increase results in decrease of d^*. Finding numerically d^* for each value of the temperature, we construct phase diagram (d^*, T) which is shown on Fig.2a.

The left end of this curve corresponds to the value $\frac{kT}{\hbar\omega} = 4.6$ at which the phase transition vanishes, having a meaning of the critical point. The same diagram is presented on Fig. 2b for the higher value of $C_1 = 0.197$. It shows that increasing of cubic anharmonism leads to the higher value of the temperature at which the phase transition disappears, i.e., to the higher value of the critical temperature.

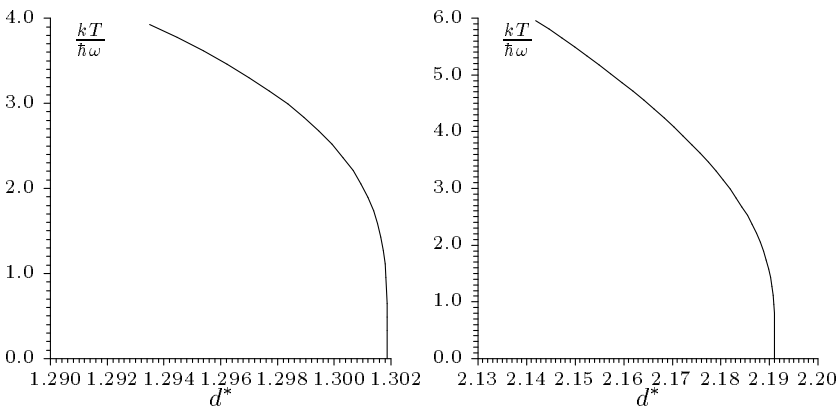

Figure 2: Phase diagram for different values of cubic anharmonicity: $C_1 = 0.157$ (a) and $C_1 = 0.197$ (b).

Having the dependence $\langle q\rangle = \langle q\rangle(d)$, one can calculate the dielectric susceptibility function $\chi \sim -\frac{\partial\langle q\rangle}{\partial d}$. The dependencies $\chi^{-1} = \chi^{-1}(d)$ are shown on Fig. 3a - 3b. While the behavour of χ (or χ^{-1}) is finite at the value $\frac{kT}{\hbar\omega_0} = 1.4$ (Fig. 3a) which corresponds to the middle of the phase diagram on Fig.2a, it has an infinite point as $\frac{kT}{\hbar\omega_0} = \simeq 3.9$, (correspondingly, χ^{-1} reaches zero on Fig. 3b), i.e. as it approaches the critical point at the phase diagram.

4. Dependence of the order parameter and free energy on the temperature

Solving numerically system (15) for certain values of d we derive the dependence $\langle q\rangle = \langle q\rangle(T)$. Using this dependence in the Hamiltonian (5) and diagonilizing it we obtain the dependence of the free energy on the temperature, according to (16). The dependencies of the order parameter and free energy are shown in Figs. 4-6 for three values of d: d=1.4, d=1.3, and d=1.2, which fall, respectively, to the right of, on, and to the left of the phase diagram in Fig. 2a. The value of $d \simeq 1.293$ corresponds to the critical point (left end of the phase diagram in Fig.2a); the dependence of the order parameter on the temperature for this value of d is shown in Fig. 7.

The analysis of the free energy dependence on the temperature in the range $d > 1.3$ (Fig. 4), i.e., to the right side of the phase diagram

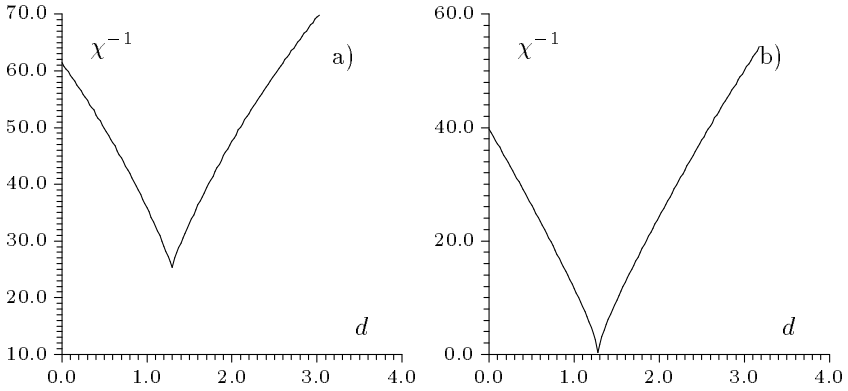

Figure 3: Inverse dielectric susceptibility as function of the external field, for the values of $\frac{kT}{\hbar\omega_0}$=1.4 and $\frac{kT}{\hbar\omega_0}$=3.9 which correspond to the middle and the left end of Fig. 2a.

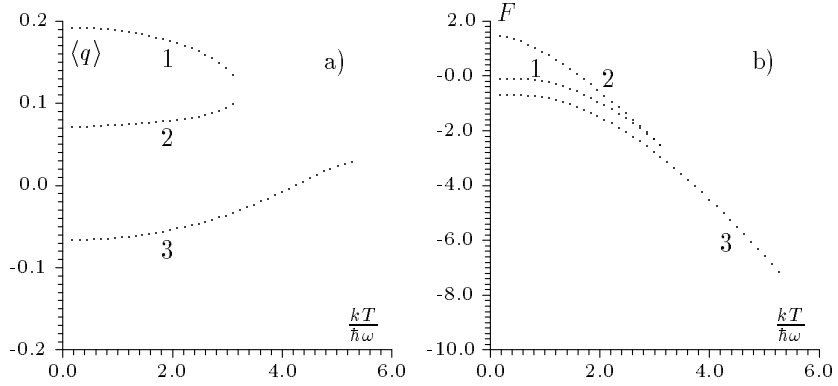

Figure 4: Plots of the order parameter and the free energy as functions of the $\frac{kT}{\hbar\omega_0}$ at d=1.4 (to the right of the phase diagram shown in Fig. 2a).

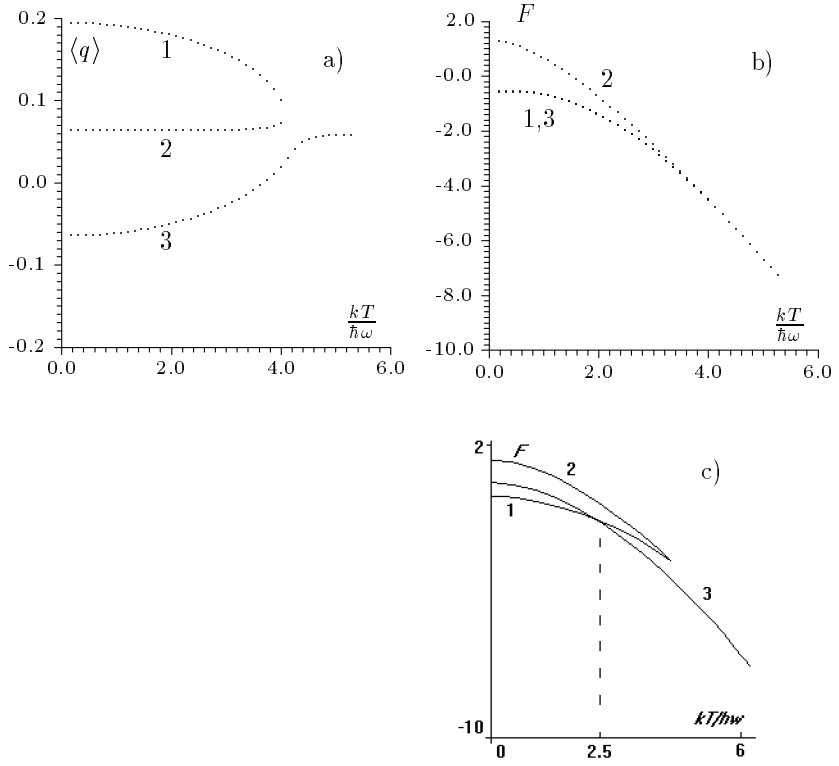

Figure 5: Plots of the order parameter and the free energy as functions of the $\frac{kT}{\hbar\omega_0}$ at d=1.3 (on the phase diagram shown in Fig.2a). Since branches 1 and 3 in Fig. b) are very close to each other and can not be visually resolved, we also plot in Fig. c) the schematic representation of the same dependence.

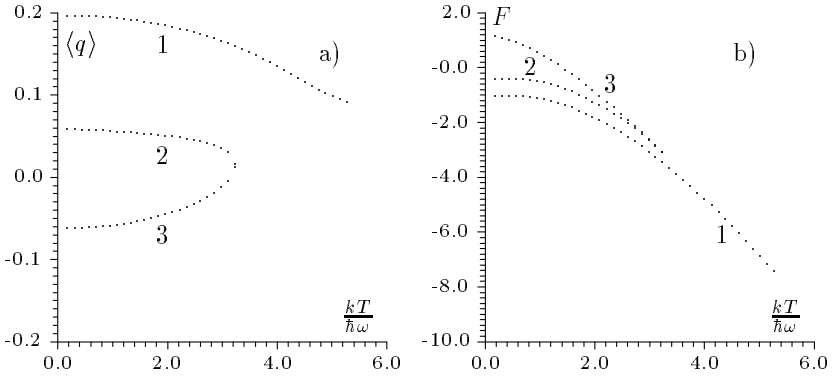

Figure 6: Plots of the order parameter and the free energy as functions of the $\frac{kT}{\hbar\omega_0}$ at d=1.2 (to the left of the phase diagram shown in Fig. 2a).

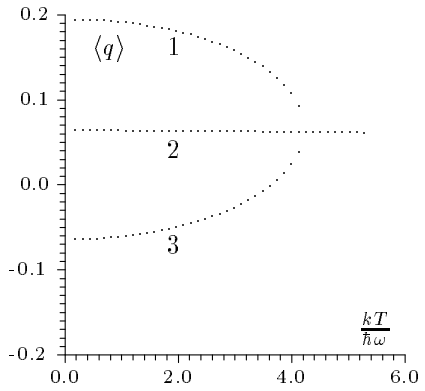

Figure 7: Plot of the order parameter as function of the $\frac{kT}{\hbar\omega_0}$ at the critical point of the phase diagram in Fig. 2a, d=1.293.

curve in Fig. 2a shows that branch 3 of the $\langle q\rangle = \langle q\rangle(\frac{kT}{\hbar\omega})$ dependence corresponds to the minimal value of the free energy, which means that the order parameter varies smoothly in this range of values of d. In the range $1.293 < d < 1.302$, i.e. on the phase diagram curve, the minimal free energy corresponds to the jump of the order parameter from branch 3 to branch 1 (Fig. 5) at the value $\frac{kT}{\hbar\omega} = 2.5$, which corresponds to the first order phase transition. When $d < 1.293$, or to the left of the phase diagram, the order parameter varies smoothly, by the branch 1 in Fig.6; no phase transition occurs in this range of d.

There is an another way which allows to determine the range of d where the phase transition occurs. We calculate the dependence of the free energy on order parameter, according to (16), for the fixed value of $\frac{kT}{\hbar\omega} = 0.2$, and three different values of d =1.4, 1.3, 1.2 which fall, respectively, to the right of, on, and to the left of the phase diagram shown in Fig. 2a. These dependencies are shown in Fig.8a - 8c.

Comparing Fig. 8a and the dependence of the order parameter on the temperature shown in Fig. 4a (case $d = 1.2$) one concludes that the minimal value of the free energy at $\langle q\rangle \simeq -0.07$ corresponds to the branch 3 of the Fig. 4a, therefore the order parameter varies smoothly along this branch. The same smooth behaviour of the order parameter in case d=1.4 can be concluded by comparing Fig. 8c and Fig.6a; in this case the order paramater varies along branch 1 of the Fig. 6a which corresponds to the minimal value of the free energy at $\langle q\rangle \simeq 0.2$.

However, if $d = 1.3$, the minimal value of the free energy in Fig. 8b corresponds to the value of the order parameter $\langle q\rangle \simeq 0.2$, or the branch 1 of the Fig. 5a. Therefore, if $d = 1.3$, a jump like transition of the order parameter from branch 1 to branch 3 occurs (Fig.5a), confirming the conclusion resulting from the analysis of the dependencies of the order parameter and free energy on the temperature.

5. Conclusions

The approach which is based on the exact numerical solution of the single ion problem in the crystal lattice allows to consider the most general non-symmetrical form of the potential which effects on this ion. Accounting for the long-range interaction in the mean-field approximation, the dependencies of the dynamic and thermodynamic functions on the external field and the temperature are derived. These dependencies testify that the system undergoes the first order phase transition, with the jump-like change of the order parameter $\langle q\rangle$, as the external field varies as well as the temperature. It is established that the increase of the cu-

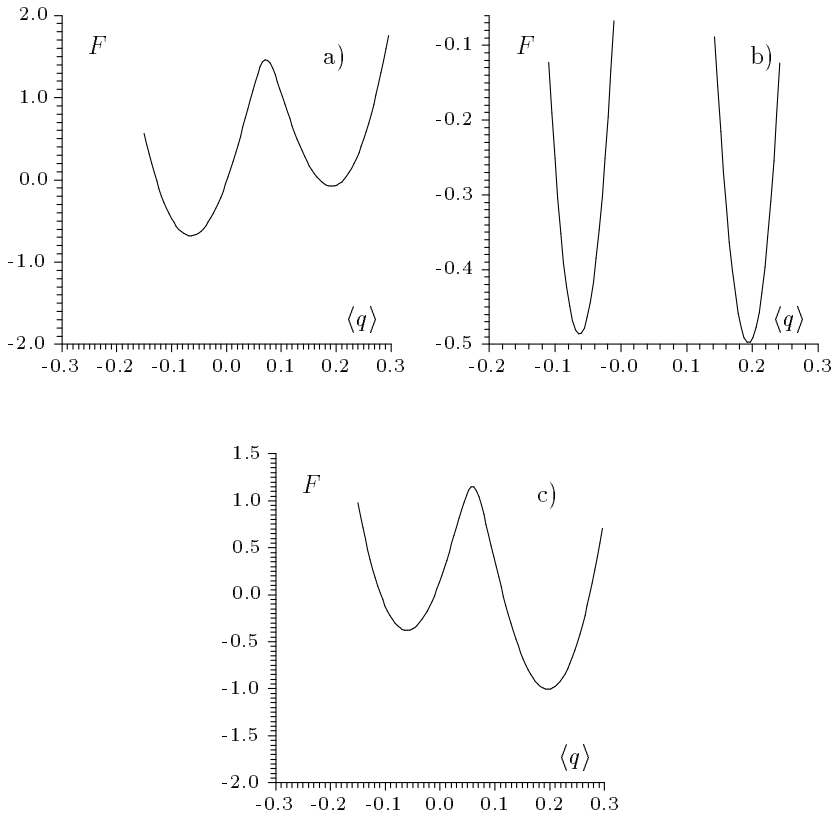

Figure 8: Dependencies of the free energy on the order parameter: d=1.4 (a), d=1.3 (b), and d=1.2 (c), $\frac{kT}{\hbar\omega_0}$=0.2.

bic anharmonicity leads to the increase of the critical temperature. The phase diagram (d,T) of the model is built.

References

[1] В.Л. Аксенов, Н.М. Плакида, С. Стаменкович. Рассеяние нейтронов сегнетоелектриками. - Москва: Енергоатомиздат. - 1984. - с.55-71.

[2] N. Gillis, T. Koehler. Phase transitions in a simple model ferroelectric - comparison of exact and variational treatments of a molecular-field Hamiltonian. // Phys. Rev. B. - 1973. - 9, No 9. - P. 3806-3818.

[3] А. Сайко, В. Гусаков, В. Кузьмин. О влиянии бистабильного поведения апексного атома кислорода на сверхпроводящий переход в $YBa_2Cu_3O_{7-\delta}$. // Письма в ЖЭТФ. - 1992. - 56, N 8. - С.425-428.

[4] A. Bishop, R.Martin, K. Muller, Z. Tesanovic. Superconductivity in oxides: toward a unified picture. // Z. Phys. B - Condensed Matter. - 1989. - 76, No 1. - P.17-24.

[5] M. Krantz, C. Thomson, Hj. Mattausch, M. Cardona. Raman-active phonons and mode softening in superconducting $HgBa_2CuO_{4+\delta}$. // Phys. Rev. B. - 1994. - 50, No 2. - P.1165-1170.

[6] I.V. Stasyuk, A.M.Shvaika. On the electron spectrum of the Hubbard model including interactions with local anharmonic vibrations. // Physica C. - 1993. - 213, No 1. - P.57-70.

Препринти Інституту фізики конденсованих систем НАН України розповсюджуються серед наукових та інформаційних установ. Вони також доступні по електронній комп'ютерній мережі на WWW-сервері інституту за адресою http://www.icmp.lviv.ua/

The preprints of the Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine are distributed to scientific and informational institutions. They also are available by computer network from Institute's WWW server (http://www.icmp.lviv.ua/)

Ігор Васильович Стасюк
Костянтин Олексійович Траченко

Структурний фазовий перехід в моделі "$\varphi^3 + \varphi^4$"

Роботу отримано 26 липня 1996 р.

Затверджено до друку Вченою радою ІФКС НАН України

Рекомендовано до друку семінаром відділу квантової статистики

Виготовлено при ІФКС НАН України