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Institute of Semiconductor Physics, Academy of Sciences of the Lithuanian SSR, Vilnius[1])

On the Theory of Isostructural Phase Transitions in Crystals

By

V. E. SCHNEIDER and E. E. TORNAU

The thermodynamics of two types of isostructural phase transitions (IPT) is investigated in the framework of the Mitsui model using the molecular field approximation. The first type of IPT is obtained including four-particle interaction members into the Hamiltonian. The consideration dealing with the temperature dependence of the asymmetry parameter explains IPT of the second type. It is shown that the maximum of dielectric constant may appear either in the point of IPT or above it. The investigation carried out gives a qualitative explanation of the experimental facts in numerous crystals undergoing IPT.

В рамках модели Мицуи в приближении молекулярного поля исследуется термодинамика двух типов изоструктурных фазовых переходов. Для возникновения одного из них необходимо присутствие в гамильтониане четырехчастичных взаимодействий, для другого наличие температурной зависимости параметра асимметрии. Показано, что максимум диэлектрической проницаемости может появиться как в самой точке изоструктурного перехода, так и выше её. Проведенное исследование позволяет качественно объяснить экспериментальные данные в большом классе кристаллов, испытывающих изоструктурные переходы.

1. Introduction

Phase transitions occurring without any change in the symmetry of the crystalline lattice are called isostructural phase transitions (IPT; see, e.g. Barma et al. [1]). Now a rather large quantity of crystals showing IPT are known, e.g. some superionic conductors [2], $(NH_4)_3H(SO_4)_2$ [3], $Ca_2Pb(C_2H_5COO)_6$ and $Ca_2Sr(C_2H_5COO)_6$ [4], $SnCl_2 \cdot 2\,H_2O$ [5]. Near the IPT point T_i various thermodynamic properties — specific heat, dielectric constant, etc. — show an anomalous behaviour. However, the appearance of these anomalies may be different going from crystal to crystal. So in $(NH_4)_3H(SO_4)_2$ during IPT from the VI to the VII phase the dielectric constant shows a weak bend [3] only. But in $SnCl_2 \cdot 2\,H_2O$ near T_i ε increases by three orders [6]. The character of the behaviour of the order parameter P near T_i is one of the main reasons leading to the qualitative difference of one IPT from another.

It is well known that during the usual second-order phase transition $P = 0$ at temperatures $T > T_c$ and $P \neq 0$ at $T < T_c$ and when $T \to 0$, $P \to 1$ [7]. In IPT case we may distinguish two essentially different kinds of $P(T)$ behaviour.

First, at T_i the parameter P performs a jump from the value $0 < P_1 < 1$ to $P_1 < P_2 \leqq 1$ — (Fig. 1a). The jump value $\Delta P = P_2 - P_1$ may be $\Delta P \leqq 1$ and $\Delta P \ll 1$ as well. $\Delta P = 0$ is also possible but then the $P(T)$ dependence shows a bend at the T_i point. These transitions are called isostructural phase transitions of the first type — IPT-1. They are specific to the largest part of the crystals mentioned above [2 to 5].

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[1]) 52 K, Pozhelos, Vilnius 232600, USSR.

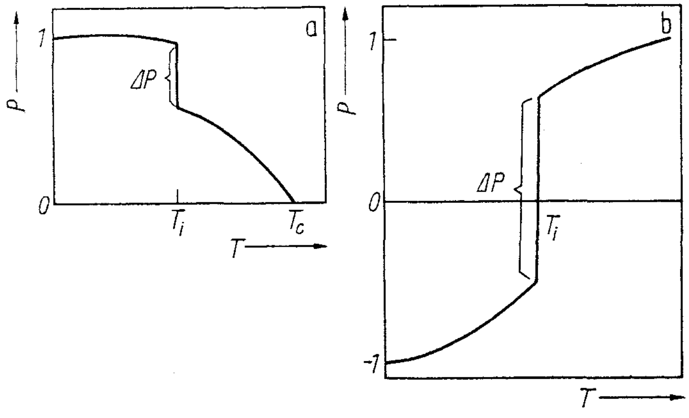

Fig. 1. Schematic representation of two types of $P(T)$ dependences undergoing IPT. T_i is the IPT point, T_c is the point of the usual phase transition

Second, it may occur that P at $T = T_i$ performs a jump from the value $P_1 > 0$ to $P_2 < 0$ — Fig. 1b. The best example, showing such $P(T)$ behaviour is the crystal $SnCl_2 \cdot 2\,H_2O$ [5]. This type of isostructural transitions will be called IPT-2.

Further we shall show that the behaviour of the thermodynamic properties for these two types of IPT is quite different.

A change of $P(T)$ sign was observed, e.g. in $(NH_4)_2SO_4$ [8] and in a number of ferrites [9]. However, the appearance of $P(T_k) = 0$, where T_k is the so-called compensation point, is not related with IPT. Around T_k no singularities in the behaviour of the macroscopic properties occur, while in $SnCl_2 \cdot 2\,H_2O$ specific heat and dielectric constant show great anomalies [6, 10].

In this paper the thermodynamics of both types of IPT will be studied in the framework of Mitsui's [11] model using the molecular field approximation (MFA) quite sufficient for the qualitative explanation of IPT.

There are several papers (see [3, 4, 12, 13]) devoted to the IPT problem. However, in these works the analysis was made on the basis of a phenomenological free energy expansion [7] with addition of some new members. But it appeared rather difficult to understand the nature of IPT on the phenomenological level. More consecutive would be the addition of extra interactions to the microscopic Hamiltonian and the calculation of the particle function with this energy. This would allow to describe the variety of IPT to a rather full extent.

2. The Model Hamiltonian

We consider the Hamiltonian of a two-sublattice model,

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2\,, \tag{1}$$

$$\mathcal{H}_1 = -\frac{1}{2}\sum_{ij} J_{ij}(s_i s_j + \sigma_i \sigma_j) - \sum_{ij} K_{ij} s_i \sigma_j - \Delta \sum_i (s_i - \sigma_i) - H \sum_i (s_i + \sigma_i)\,, \tag{1a}$$

$$\mathcal{H}_2 = -\frac{1}{2}\sum_{ijkl} v^{(1)}_{ijkl}(\sigma_i \sigma_j \sigma_k \sigma_l + s_i s_j s_k s_l) - \sum_{ijkl} v^{(2)}_{ijkl} \sigma_i \sigma_j s_k s_l\,, \tag{1b}$$

where the variables $s_i = \pm 1$, $\sigma_i = \pm 1$ are related to two different sublattices, J_{ij} and K_{ij} are the potentials of pair interactions among the spins in the same and different sublattices, respectively, Δ is a parameter characterizing the asymmetry of the two-minima potential, H the external field, $v_{ijkl}^{(1)}$ and $v_{ijkl}^{(2)}$ are the potentials of four-particle interactions. The Hamiltonian (1 a) was proposed by Mitsui [11] to characterize the phase transition in Rochelle salt and later was often used in the investigations of transitions in various ferroelectrics [14 to 16]. The Hamiltonian (1 a) may be also used to describe ordering in superionic conductors [2]. If one assumes $n_i = \frac{1}{2}(1 + \sigma_i)$, $p_i = \frac{1}{2}(1 + s_i)$, then the Hamiltonian of a superionic conductor of type [17]

$$\mathcal{H}_s = - \sum_{ij} [J_{ij}^{(1)} n_i n_j + J_{ij}^{(2)} p_i p_j + J_{ij}^{(3)} n_i p_j] - \varepsilon_1 \sum_i n_i - \varepsilon_2 \sum_i p_i$$

obtains the form (1 a).

In MFA the free energy $F = -T \ln \operatorname{Sp} \exp(-\mathcal{H}/T)$ may be written

$$\begin{aligned} F &= J \frac{s^2 + \sigma^2}{2} + K s \sigma + \frac{3}{2} v_1 (s^4 + \sigma^4) + 3 v_2 s^2 \sigma^2 - \\ &\quad - T (\ln 2 \operatorname{ch} H_1/T + \ln 2 \operatorname{ch} H_2/T)\,, \\ H_1 &= J s + K \sigma + 2 v_1 s^3 + 2 v_2 s \sigma^2 + \Delta + H\,, \\ H_2 &= J \sigma + K s + 2 v_1 \sigma^3 + 2 v_2 s^2 \sigma - \Delta + H\,, \end{aligned} \tag{2}$$

where $\sigma \equiv \langle \sigma_i \rangle$, $s \equiv \langle s_i \rangle$ are the average values of spins, $J = \sum_{ij} J_{ij}$, $K = \sum_{ij} K_{ij}$, $v_1 = \sum_{ijkl} v_{ijkl}^{(1)}$, $v_2 \equiv \sum_{ijkl} v_{ijkl}^{(2)}$. Convenient for further analysis the notations

$$a = \frac{K - J}{K + J}, \quad \gamma = \frac{\Delta}{K + J}, \quad t = \frac{T}{K + J}, \quad \beta = \frac{1}{t}, \quad \xi = \frac{s + \sigma}{2},$$

$$\eta = \frac{s - \sigma}{2}, \quad g_1 = \frac{v_1 + v_2}{K + J}, \quad g_2 = \frac{3 v_1 - v_2}{K + J}, \quad h = \frac{H}{K + J}$$

transform expression (2) into

$$\begin{aligned} F &= \xi^2 - a \eta^2 + 3 g_1 (\xi^4 + \eta^4) + 6 g_2 \xi^2 \eta^2 - \\ &\quad - t (\ln 2 \operatorname{ch} \beta H_1' + \ln 2 \operatorname{ch} \beta H_2')\,, \\ H_1' &= \xi - a \eta + 2 g_1 (\xi^3 + \eta^3) + 2 g_2 \xi \eta (\xi + \eta) + \gamma + h\,, \\ H_2' &= \xi + a \eta + 2 g_1 (\xi^2 - \eta^3) - 2 g_2 \xi \eta (\xi - \eta) - \gamma + h\,. \end{aligned} \tag{3}$$

The equilibrium values of ξ and η can be obtained from the condition $\partial F / \partial \xi = = \partial F / \partial \eta = 0$,

$$\xi = \tfrac{1}{2} (\operatorname{th} \beta H_1' + \operatorname{th} \beta H_2')\,, \qquad \eta = \tfrac{1}{2} (\operatorname{th} \beta H_1' - \operatorname{th} \beta H_2')\,. \tag{4}$$

The thermodynamics of transitions (3), (4) in the case $g_1 = g_2 = 0$ and $\Delta = \text{const}$ is well known [18]. There are several regions (depending on the ratio between the parameters a and γ) where the phase transition to the state with $\xi \neq 0$ can occur [11, 14]. However, the influence of the members g_1, g_2 on transition thermodynamics was never consecutively investigated. It is interesting to mention that four-particle interaction terms in (3) may have deformation origin as well.[2]) We may assume that the interaction potentials J_{ij} and K_{ij} in (1 a) depend on distance and, correspondingly, on deformation (in MFA, only on homogeneous deformation),

$$J_{ij} = J + J' u_{\alpha\alpha}\,, \qquad K_{ij} = K + K' u_{\alpha\alpha}\,, \tag{5}$$

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[2]) For this remark we are thankful to Dr. E. V. Kholopov.

where the dash means differentiation with respect to the coordinate, $u_{\alpha\alpha}$ is the volume deformation tensor. Putting (5) into (1 a) and finding the free energy in MFA as in [19] we obtain the former free energy expression (3), with $g_1 \approx (J' - K')^2$.

The influence of g_1, g_2 on the thermodynamic properties of IPT-1 is presented in Section 3. The temperature dependence of Δ qualitatively explaining IPT-2 is shown in Section 4.

3. The First Type of Isostructural Phase Transition (IPT-1)

For simplicity we limit our investigation to the region $a + 1 > 2\gamma$, $|a| < 1$, and take $h = 0$. When $g_1 = g_2 = 0$ a second-order phase transition to the state $\xi \neq 0$ occurs. Our aim is to show how the four-particle interactions lead to IPT. The necessary condition for IPT-1 to occur is

$$F_2(\xi_2 \to 1, \eta_2 \to 0, T_i) = F_1(\xi_1 \neq 0, \eta_1 \neq 0, T_i)\,, \tag{6}$$

where F_1, F_2 are the free energies determined by (3), ξ_1, η_1 the equilibrium values of the order parameters at $T = T_i + 0$, ξ_2, η_2 at $T = T_i - 0$. With the aim of investigating the temperature dependence of ξ near T_c ($T_c \gtrsim T_i$) we expand equation (4) with respect to $\xi' = \xi + 2g_1\xi^3$ while neglecting the constant g_2 which makes no contribution to the present consideration. The $\beta\xi'$ value can be obtained from (4)

$$\left.\begin{aligned}
&(\beta\xi')^2 \approx \frac{A(\zeta)}{B(\zeta)}\,,\\
&A(\zeta) = a \operatorname{th}\zeta + \frac{\zeta}{\operatorname{ch}^2\zeta} - \gamma\,,\\
&B(\zeta) = \frac{\zeta}{\operatorname{ch}^2\zeta}\left(\frac{1}{3} - \operatorname{th}^2\zeta + \frac{a\operatorname{th}\zeta}{\zeta}\right),\\
&\zeta = (\gamma - a\eta + 2g_1\eta^3)/t\,.
\end{aligned}\right\} \tag{7}$$

We can also expand the free energy F_1 from (6) near T_c with respect to the parameter $\beta\xi'$. Limiting ourselves to the second-order term in $\beta\xi'$ we obtain

$$F_1 \approx -A(\zeta)\,(\beta\xi')^2 = -\frac{A^2(\zeta)}{B(\zeta)}\,. \tag{8}$$

On the other hand, F_2 at $T = T_i - 0$, when T_i is sufficiently low, can be written as

$$F_2 \approx -1 - g_1\,. \tag{9}$$

The comparison of (8) and (9) yields that at

$$g_1 \approx -1 + \frac{A^2(\zeta)}{B(\zeta)} \tag{10}$$

PT is possible. Thus, $g_1 < 0$, because considering (10), the assumptions $\big(A(\zeta)/B(\zeta)\big) \ll 1$ and $A(\zeta) \ll 1$ were made.

Some tendencies of the $\xi(T)$ behaviour were established solving the exact equations (4) with a computer.

The dependence of order parameter ξ on $\tau = (T_c - T)/T_c$ for various values g_1 and fixed $a = 0.5$, $\gamma = 0.1$, and $g_2 = 0$ is shown in Fig. 2. IPT-1 is not observed at low $|g_1|$, but beginning from $g_1 \approx -0.17$ a small jump $\Delta\xi$ on the $\xi(\tau)$ dependence appears. It indicates the occurrence of IPT-1. A further increase of $|g_1|$ causes the decrease of the difference $(T_c - T_i)/T_c$ and the increase of the jump value $\Delta\xi$.

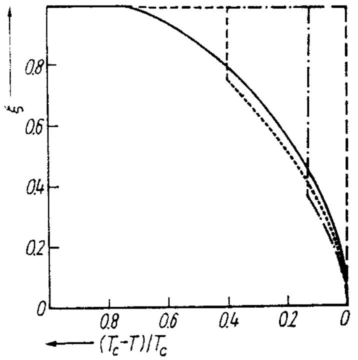

Fig. 2

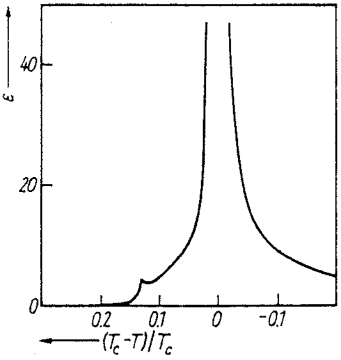

Fig. 3

Fig. 2. The behaviour of the order parameter ξ on $(T_c - T)/T_c$ for various values of g_1. ——— $g_1 = -0.16$, ---- -0.2, —·— -0.24, — — — -0.27

Fig. 3. The dependence of the dielectric constant ε on $(T_c - T)/T_c$ for $g_1 = -0.24$

Beginning from $g_1 \approx -0.265$ IPT-1 vanishes ($T_i \to T_c$) and the system jumps abruptly from the state $\xi = 0$ to the fully ordered one $\xi = 1$. It resembles the analogous $\xi(T)$ behaviour in the Slater model [20] for KDP. A further advance of $|g_1|$ gives no account on the transition order. It should be noted that the variation of other parameters a, γ, and g_2 (in permissible limits) qualitatively does not change IPT-1.

Therefore, four-particle interactions or deformation effects mentioned in (5) are the main parameters responsible for IPT-1 occurrence.

The analysis of the temperature dependence of the dielectric constant $\varepsilon = (\mathrm{d}\xi/\mathrm{d}h)_{h=0}$ and specific heat $C = -T\,(\partial^2F/\partial T^2)$ shows that the behaviour of $C(T)$ and $\varepsilon(T)$ near T_i qualitatively differs. In Fig. 3 the dependence $\varepsilon(\tau)$ for $g_1 = -0.24$ is presented. When $\tau \to 0$, the Curie-Weiss law $\varepsilon(\tau) \sim \tau^{-1}$ is valid. At $T \to T_i$ the $\varepsilon(\tau)$ dependence shows a small bend. A similar $\varepsilon(\tau)$ behaviour was observed in $(NH_4)_3H(SO_4)_2$ at the pressure $p \approx 5.2$ to 5.4 kbar [3]. In Table 1 the ratios of specific heat jumps ΔC at T_c and T_i points due to g_1 at $a = 0.5$, $\gamma = 0.1$, $g_2 = 0$ are presented. The values $\Delta T = (T_c - T_i)/T_c$ and $\Delta\xi = \xi(T_i + 0) - \xi(T_i - 0)$ are also presented there. Table 1 shows that the jump (ΔC) at $T = T_i$ can be both of the same order as (ΔC) at $T = T_c$ and considerably exceed it, contrary to $\varepsilon(T)$ where $\varepsilon(T_c) \gg \varepsilon(T_i)$ for all g_1.

The above results qualitatively describe the experimental facts in several crystals. E.g. in superionic conductor $RbAg_4I_5$ two transitions were observed. One of them (at low temperature) is an isostructural phase transition of first type [2]. The experimental value $\Delta T \approx 0.42$ in $RbAg_4I_5$. Then according to our theory $(\Delta C)_{T_i} \approx 1.5(\Delta C)_{T_c}$

Table 1

g_1	-0.2	-0.22	-0.24	-0.26
$(T_c - T_i)/T_c$	0.41	0.27	0.14	0.02
$\Delta\xi$	0.25	0.43	0.61	0.88
$(\Delta C)_{T_i}/(\Delta C)_{T_c}$	1.5	4.5	11.5	12.5

and the jump of the order parameter $\Delta\xi \approx 0.25$ in the T_i point. According to Johnston et al. $(\Delta C)_{T_i} \gtrapprox (\Delta C)_{T_c}$ in $RbAg_4I_5$ [21]. However, the value of $\Delta\xi$ at T_i is unknown to us. In ferroelectric $(NH_4)_3H(SO_4)_2$ at pressure $p = 5.2$ kbar, $\Delta T \approx 0.11$. Our theory at $\Delta T \approx 0.11$ gives $\Delta\xi \approx 0.6$. According to Gesi [3] $\Delta\xi = (P_S - P_i)/P_S \approx \approx 0.64$, where P is the polarization, $P_S = P(T_i - 0)$ and $P_i = P(T_i + 0)$. For these ΔT and $\Delta\xi$ the specific heat jump $(\Delta C)_{T_i}$ must exceed $(\Delta C)_{T_c}$ by approximately ten times. However, the experimental data on the specific heat in $(NH_4)_3H(SO_4)_2$ at $p = 5.2$ kbar are unknown.

4. The Second Type of Isostructural Phase Transition (IPT-2)

Comparing the energies $U = \langle\mathcal{H}\rangle$ of various ordered phases from (1) ($T \to 0$) we obtain

$$\left.\begin{aligned} U_{F1} &= -J - K - v_1 - v_2 - 2H\,, \\ U_{F2} &= -J - K - v_1 - v_2 + 2H\,, \\ U_{AF1} &= -J + K - v_1 - v_2 - 2\Delta\,, \\ U_{AF2} &= -J + K - v_1 - v_2 + 2\Delta\,. \end{aligned}\right\} \tag{11}$$

In F1 phase $\langle s\rangle = \langle\sigma\rangle = 1$, in F2 $\langle s\rangle = \langle\sigma\rangle = -1$, in AF1 $\langle s\rangle = 1$, $\langle\sigma\rangle = -1$, and in AF2 $\langle s\rangle = -1$, $\langle\sigma\rangle = 1$; (11) shows that when $H = 0$, $K < 0$, $\Delta > 0$, the AF1 state is more favourable and when $K < 0$, $\Delta < 0$, the AF2 state appears. The symmetry of AF1 and AF2 phases will coincide if not only s_i and σ_i but also Δ simultaneously change sign.

Now it would be useful to remember the six-vertex Baxter model in external staggered field S [23]. The field S acting on every one of six vertices changes the energy of only two "antiferroelectric" ones, while the action of direct fields does not change their energies. It can be seen from (1), (11) that the asymmetry parameter Δ influences only the energies of antiferroelectric states. Therefore, the asymmetry parameter Δ in Mitsui's model (1) is analogous to Baxter's stepped field S (if to make no difference between internal and external fields).

The thermodynamics of the transition described by Hamiltonian (1a) at $\Delta = \text{const}$ was investigated in various approximations [14, 23, 24]. It is interesting to consider the case $\Delta = \Delta(T)$ assuming that near the temperature T_i Δ turns to zero in agreement with the simplest linear rule

$$\Delta = \Delta_0(T - T_i)\,, \tag{12}$$

where $\Delta_0 > 0$, $\Delta > 0$ at $T > T_i$ and $\Delta < 0$ at $T < T_i$. The introduction of the T dependence of Δ permits to describe qualitatively the thermodynamic properties of IPT-2. It is noteworthy that a dependence analogous to (12) was assumed in Baxter's staggered field S model when describing the transition in $SnCl_2 \cdot 2\,H_2O$ [5]. We consider the case $K < 0$ or $|a| > 1$. Then $\xi \equiv 0$, and (3) can be written

$$F = a\eta^2 - 2t \ln 2 \operatorname{ch} \beta(\Delta_0\tau_i + a\eta)\,, \tag{13}$$

where $\tau_i = t - t_i$. Here and further a will mean $|a|$. Besides, in (3) we took $g_1 = 0$, $g_2 = 0$, because these terms have no influence on IPT-2. It follows from (13) that at $\Delta_0 \equiv 0$ the phase transition point $t_c = a$. Equation (4) for the definition of the equilibrium value η becomes

$$\eta = \operatorname{th} \beta(\Delta_0\tau_i + a\eta) \equiv \operatorname{th} \varkappa\,. \tag{14}$$

Expressions (13), (14) are invariant with respect to a simultaneous change of signs $\eta \to -\eta$, $\tau_\mathrm{i} \to -\tau_\mathrm{i}$. Therefore,

$$F(\eta, \tau_\mathrm{i}) = F(-\eta, -\tau_\mathrm{i}) \neq 0\,, \tag{15}$$

and the symmetry of the system on both sides of $\tau_\mathrm{i} = 0$ is the same. At $\tau_\mathrm{i} = 0$ and $\tau = t - a = 0$, when $\eta = 0$, the symmetry of the system differs from (15). This may be easily noticed if one compares (15) and $F(\eta = 0, \tau_\mathrm{i} = 0) = -2t \ln 2$. From (13), (14) we obtain the values of specific heat C, dielectric constant ε, and "staggered" susceptibility $\tilde{\varepsilon} = 1/(\partial\Delta/\partial\eta)$

$$\begin{gathered} C = \frac{2t(q\Delta_0 - \alpha)^2}{t \operatorname{ch}^2 \alpha - a}, \\ \varepsilon = \frac{1}{t \operatorname{ch}^2 \alpha - 1}, \qquad \tilde{\varepsilon} = \frac{1}{t \operatorname{ch}^2 \alpha - a}, \end{gathered} \tag{16}$$

where $q = 1$ if $\tau_\mathrm{i} > 0$ and $q = -1$ if $\tau_\mathrm{i} < 0$. Expressions (13), (14), (16) determine the thermodynamics of IPT-2. However, before discussing the results which can be obtained from (13), (14), (16) with the help of a computer, we tried to solve the problem analytically in various limiting cases.

4.1 The thermodynamics of the transition for low η

In order to investigate analytically the singularities of IPT-2 thermodynamics we studied the case $\tau_\mathrm{i} \ll 1, \tau \ll 1$ and $b = a - 1 \ll 1$. Then $\eta \ll 1$ and we can expand (12) in a series with respect to η. Leaving only linear terms in τ and τ_i and the terms of fourth order in η, we obtain

$$F = \tau\eta^2 - 2\Delta_0\tau_\mathrm{i}\eta + \tfrac{1}{6}\eta^4\,. \tag{17}$$

Then the equation describing η may be written

$$\eta\tau - \Delta_0\tau_\mathrm{i} + \frac{\eta^3}{3} = 0\,. \tag{18}$$

The specific heat C, $\chi = 1/\varepsilon$ and $\tilde{\chi} = 1/\tilde{\varepsilon}$ are

$$C = 2t\frac{(q\Delta_0 - \eta)^2}{\tau + \eta^2}, \qquad \tilde{\chi} = \tau + \eta^2\,, \qquad \chi = \tau + b + \eta^2\,. \tag{19}$$

We shall investigate the dependences of η, C, χ at different τ, τ_i, Δ_0 and for simplicity consider $\chi \approx \tilde{\chi}$. We introduce $\tau_\mathrm{i} = \tau + \mu$, where $|\mu| \ll a$. Then, depending on, the sign of μ, three regions with qualitatively different behaviour of thermodynamic functions can appear.

(i) $\mu = 0$

In this case $\tau = \tau_\mathrm{i}$ and (18), (19) at $|\tau| \to 0$ and $|\tau| \ll \Delta_0^2$, give

$$\left.\begin{aligned} \eta &= \pm(3\Delta_0\,|\tau|)^{1/3}\left[1 \mp \frac{|\tau|^{1/3}}{(3\Delta_0)^{2/3}}\right], \\ \chi &= (3\Delta_0\,|\tau|)^{2/3} \mp |\tau|\,, \\ C(\tau > 0) &= \frac{2\Delta_0^{4/3}a}{(3\tau)^{2/3}}\left[1 - \frac{5\tau^{1/3}}{(3\Delta_0)^{2/3}}\right], \\ C(\tau < 0) &= \frac{2\Delta_0^{4/3}a}{(3\,|\tau|)^{2/3}}\left[1 - \frac{7\,|\tau|^{1/3}}{(3\Delta_0)^{2/3}}\right]. \end{aligned}\right\} \tag{20}$$

Here the upper sign corresponds to the region $\tau > 0$, and the lower $-\tau < 0$. It may be seen that at the point of IPT-2 $\tau_i = 0$ the order parameter η changes its sign and ε and C become infinite in accordance with the rule $\tau^{-2/3}$. This was noticed in [4, 12, 13]. However, contrary to their results, it follows from (20) that even at $\tau = \tau_i$ the dependences $\eta(\tau)$, $C(\tau)$, and $\chi(\tau)$ are not fully symmetric with respect to the point $\tau = 0$.

(ii) $\mu > 0$.

We investigate first the temperature region $|\tau| \to 0$, but $\tau_i \neq 0$ and suppose that $\tau_i \gg |\tau|$ or more strictly $\tau_i \gg |\tau|^{3/2}\,\varDelta_0^{-1}$. Then, solving equation (18) we obtain

$$\left.\begin{aligned}
\eta &= (3\varDelta_0\tau_i)^{1/3}\left[1 \mp \frac{|\tau|}{(3\varDelta_0\tau_i)^{2/3}}\right],\\
\chi &= (3\varDelta_0\tau_i)^{2/3} \mp \tau\,,\\
C &= \frac{2}{(3\varDelta_0\tau_i)^{2/3}}\Big\{[\varDelta_0 - (3\varDelta_0\tau_i)^{1/3}]^2\,(a \pm\\
&\qquad \pm |\tau|) \pm a\,|\tau|\left(\frac{\varDelta_0^2}{(3\varDelta_0\tau_i)^{2/3}} - 1\right)\Big\},
\end{aligned}\right\} \tag{21}$$

where the upper sign corresponds to the region $\tau > 0$ and the lower to $\tau < 0$.

Now we consider $|\tau_i| \to 0$, but $|\tau| \neq 0$. Then at $|\tau_i| \ll |\tau|^{3/2}\,\varDelta_0^{-1}$ as in (21) we obtain

$$\left.\begin{aligned}
\eta &= \pm(3\,|\tau|)^{1/2}\left[1 \pm \frac{\varDelta_0\,|\tau_i|}{2\sqrt{3}\,|\tau|^{3/2}}\right],\\
\chi &= \pm\frac{3\varDelta_0\,|\tau_i|}{(3\,|\tau|)^{1/2}} + 2\,|\tau|\,,\\
C &= \frac{1}{|\tau|}\Big\{(a+\mu)\,[\varDelta_0 - (3\,|\tau|)^{1/2}]^2\left(1 \mp \frac{9\varDelta_0\,|\tau_i|}{(3\,|\tau|)^{3/2}}\right) \pm\\
&\qquad \pm |\tau_i|\,[\varDelta_0 - (3\,|\tau|)^{1/2}]^2 \pm \varDelta_0\,|\tau_i|\left(\frac{3}{(3\,|\tau|)^{1/2}} - \frac{\varDelta_0}{|\tau|}\right)\Big\},
\end{aligned}\right\} \tag{22}$$

where the upper sign notes $\tau_i > 0$ and the lower $\tau_i < 0$.

It follows from (21), (22) $\eta(\tau = 0) = (3\varDelta_0\mu)^{1/3}$. When $\tau_i \to 0 + 0$, $\eta \to (3\mu)^{1/2}$, and when $\tau_i \to 0 - 0$, $\eta \to -(3\mu)^{1/2}$. Thus, in the point of IPT-2 $\tau_i = 0$ the order parameter η performs a jump $\varDelta\eta = 2(3\mu)^{1/2}$. It is of interest to note that the maxima of the specific heat $C_{\max}$ and dielectric constant $\varepsilon_{\max}$ may be reached at different temperatures. It follows from (21), (22), that $C = C_{\max}$ at $\tau_i = 0$ only. Comparing $\chi_1 = \chi(\tau = 0) = (3\varDelta_0\mu)^{2/3}$ and $\chi_2 = \chi(\tau_i = 0) = 2\mu$ we obtain that at $\gamma_c = \frac{2}{3}(2\mu)^{1/2} > \varDelta_0$, $\chi = \chi_{\min}$ (or $\varepsilon = \varepsilon_{\max}$) when $\tau \to 0$. If $\gamma_c < \varDelta_0$, then $\chi = \chi_{\min}$ near $\tau_i \to 0$. Moreover, the χ minimum at $\gamma_c > \varDelta_0$ appears in the point τ obtained from (18), (19),

$$\tau \approx \tfrac{1}{4}\,(\tau_i - \tfrac{8}{3}\,\varDelta_0^2) > 0 \tag{23}$$

but at $\gamma_c < \varDelta_0$, $\chi = \chi_{\min}$ is always at $\tau_i = 0$.

Thus, during IPT-2 χ may become minimum not in the point of the isomorphic transition $\tau_i = 0$, but in the region $T > T_i$, while $C = C_{\max}$ at $T = T_i$ only. This fact found experimentally in $SnCl_2 \cdot 2\,H_2O$ was discussed from another viewpoint in the work of Salinas and Nagle [25].

(iii) $\mu < 0$

This case can be investigated similarly to $\mu > 0$. At $|\tau_i| \to 0$ and $|\tau_i| \ll \tau^{3/2}\varDelta_0^{-1}$ we obtain

$$\eta = \pm\frac{\varDelta_0\,|\tau_i|}{\tau}\left(1 - \frac{\varDelta_0^2\tau_i^2}{3\tau^3}\right), \qquad \chi = \tau + \frac{\varDelta_0^2\tau_i^2}{\tau^2}. \tag{24}$$

At $|\tau| \to 0$, $|\tau| \ll (\Delta_0 |\tau_i|^{3/2})$, η and χ are expressed as

$$\eta = -(3\Delta_0 |\tau_i|)^{1/3} \left[1 \mp \frac{|\tau|}{(3\Delta_0|\tau_i|)^{2/3}}\right],$$
$$\chi = (3\Delta_0 |\tau_i|)^{2/3} \mp \tau\,. \tag{25}$$

In (24) the upper sign corresponds to the region $\tau_i > 0$ and in (25) to $\tau > 0$. For simplicity we excluded the expressions of C in (24), (25).

Contrary to the case $\mu > 0$, the order parameter η near $\tau_i \approx 0$ approaches zero linearly $\eta \sim |\tau_i|$. The behaviour of all thermodynamic functions is symmetric with respect to the point $\tau_i = 0$. The maximum of specific heat as previously appears in the point $\tau_i = 0$. However, $\chi = \chi_{\min}$ may occur at $\tau_i \neq 0$. If $\Delta_0 > \frac{1}{3}\mu^{1/2}$, then $\chi = \chi_{\min}$ at $\tau_i = 0$, but if $\Delta_0 < \frac{1}{3}\mu^{1/2}$, then $\chi = \chi_{\min}$ only at $\tau_i < 0$.

Thus, the analytical investigation shows that the assumption (12) allows to explain qualitatively the occurrence of IPT-2. Moreover, various temperature dependences $\eta(T)$, $\chi(T)$, and $C(T)$ are described mainly by two parameters: "closeness" $t_c - t_i = \mu$ and Δ_0.

4.2 *Numerical analysis*

Here we present the results of the numerical investigations of expression (13), (14), and (16) obtained with the help of a computer.

In Fig. 4 to 7 the calculated dependences of η, ε, C on $\tau = t - a$ and $\tau_i = t - t_i$ at $a = 1.2$ and various values of μ and Δ are shown. As seen from Fig. 4 the character of $\eta(T)$ essentially depends on Δ_0 and $\mu > 0$. Thus, for low Δ_0 and $\mu > 0$ with τ decrease, $\eta(\tau)$ increases till the IPT point ($\tau_i = 0$), while at large Δ_0, $\eta(\tau)$ (τ decreasing) decreases itself. Here, the case is possible, when $\eta(\tau) \approx$ const in a broad enough temperature region $\tau_i > 0$ (Fig. 4, curve 2). The value of the order parameter jump $\Delta\eta$ ($\tau_i = 0$) decreases while μ decreases, but does not depend on Δ_0.

Fig. 5 shows that the maximum of specific heat for all values of the model parameters occurs in the point $\tau_i = 0$ but $\varepsilon = \varepsilon_{\max}$ can be either at $\tau > 0$ or $\tau_i = 0$ as well.

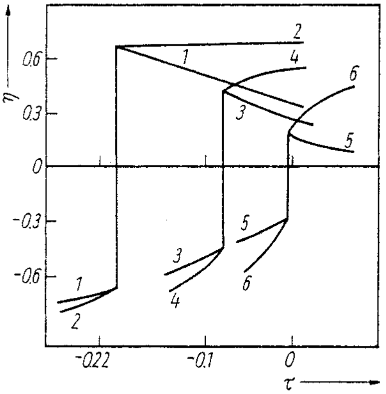

Fig. 4

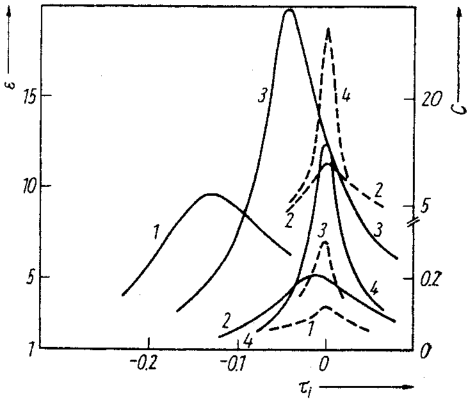

Fig. 5

Fig. 4. The dependence of the order parameter η on $\tau = t - a$ at $\mu > 0$ and $a = 1.2$. (1) $\mu = a/6$, $\Delta_0 = 0.1$; (2) $a/6$, 1.0; (3) $a/15$, 0.1; (4) $a/15$, 1.0; (5) $a/120$, 0.1; (6) $a/120$, 1.0

Fig. 5. The dependence of dielectric constant ε and specific heat C on τ_i ($= t - t_i$) at $\mu > 0$ and $a = 1.2$. Dashed lines C, continuous ε. The notations of the curves are the same as in Fig. 4

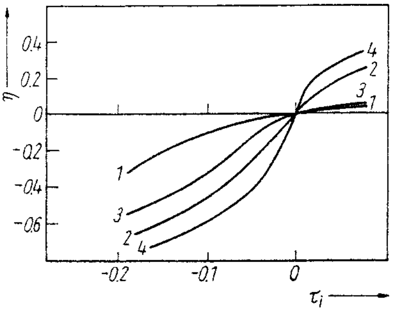

Fig. 6

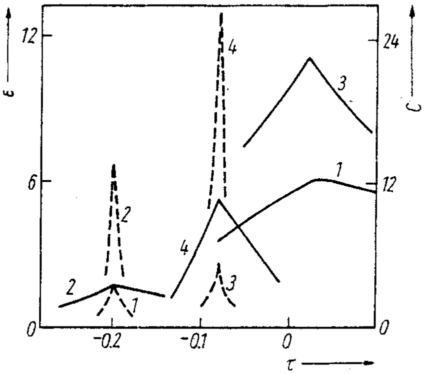

Fig. 7

Fig. 6. The dependence η on $\tau_i = t - t_i$ at $\mu < 0$ and $a = 1.2$. The notations of the curves are the same as in Fig. 4 having changed $\mu \to -\mu$

Fig. 7. The dependences of ε and C on τ_i at $\mu < 0$ and $a = 1.2$. The curve notations as in Fig. 6

When $\mu < 0$ the order parameter $\eta(\tau)$ (Fig. 6) smoothly passes through zero in the point $\tau_i = 0$. The maximum of ε (Fig. 7) can be reached not necessarily at $\tau_i = 0$, whereas $C = C_{\min}$ only in the point $\tau_i = 0$.

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