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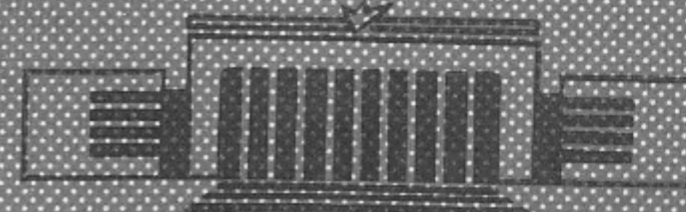
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СИБИРСКОЕ ОТДЕЛЕНИЕ АН СССР
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A.C.Mitus and A.Z.Patashinskii
THEORY OF CRYSTAL ORDER I. GENERAL
FORMULATION AND PRE-MELTING PHENOMENA

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THEORY OF CRYSTAL ORDER I. GENERAL FORMULATION
AND PRE-MELTING PHENOMENA

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A b s t r a c t

The crystallization is described as long-range ordering of a local tensor order parameter. A model hamiltonian of crystalline arrangement is proposed. Thermodynamics and elastic properties of the system are examined in the vicinity of the melting point T_c in mean-field approximation. The pre-melting anomalies are shown to exist and to be in a reasonable agreement with experimental data.

1. Crystal-order parameter

In this work the crystalline-ordering is described as due to long-range correlations of a local order parameter $\Lambda(\vec{x})$.

In traditional description, started by Landau, [1], the particle density $n(\vec{x})$ plays the central role. The symmetry change of the system from the rotation - translation group of 3-D space in liquid phase to the crystalline one is described by Landau theory: quadratic terms $\sim |n(\vec{x}) - \langle n \rangle|^2$ in thermodynamical potential $\Phi\{n(\vec{x})\}$ make the translational symmetry vanish and fix the modulus of a wave-vector k . The higher-order terms fix the star of k_i vectors, describing the crystalline symmetry. Such a treatment is possible if crystallization is nearly a second-order phase transition (e.g. He³ - see [2]). This hierarchy of effects is broken when the jump of order parameter at melting point T_c is not small. It is known from experiments that in case of crystallization of the dense liquid the difference in local ordering between the liquid and the crystal is small.

In this work it is presumed that the space anisotropy of atoms' positions, uniform in crystal, is the main difference between ordered and disordered state. This fact can be formulated in terms of the density-function $n(\vec{x})$, stating that atoms form periodic structure (crystal lattice).

Let's introduce the field-parameter $\Lambda(\vec{x})$, describing the anisotropy of atoms' positions and of physical characteristics at point \vec{x} . The last one corresponds to a small volume of the system, containing a few crystal cells.

These ideas were first introduced in theory of liquid crystals (see, e.g. [3]). The field parameter $Q_{\alpha\beta}(\vec{x})$, describing orientational-ordering is interpreted either as the field of quadrupole moments of the system or as irreducible part of susceptibility $\chi_{\alpha\beta} - \frac{1}{3}\chi_{\gamma\gamma}\delta_{\alpha\beta}$. It is supposed that the last one contains the part due to anisotropic character of atomic arrangement.

The characteristic feature of the crystal that distinguishes it from the liquid is, as a rule, the existence of an anisotropic part in elastic constant tensor $\lambda_{\alpha\beta\gamma\delta}$. The elastic and space anisotropy are closely related; the details are examined in next paragraphs.

The location of atoms in a given volume is fully described by means of multipole moments of the density function $n(\vec{x})$,

which form a set of tensors. The higher multipole moments characterize the details of the relative arrangement and keep changing due to thermal motion. Unlike the microscopic description, the averaged (on atomic scales) one is given in terms of the field parameter $\Lambda(\vec{x})$ formed by a finite set of multipole moments. The following arguments show that it is sufficient and necessary to use the fourth-rank tensors. The systems examined here are supposed to have the inversion center. As a result all odd-rank tensors vanish. The second order can't describe the existence of crystalline symmetry e.g. in case of cubic symmetry it becomes isotropic tensor $\delta_{\alpha\beta}$ (i.e. scalar). The anisotropy of elastic properties is closely related to the existence of the irreducible part $\lambda_{\alpha\beta\gamma\delta}$ in elastic constant tensor $\lambda_{\alpha\beta\gamma\delta}$. Hence, the existence of the average $\langle \lambda_{\alpha\beta\gamma\delta} \rangle \neq 0$ states the crystalline character of the system in opposite to liquid in which $\langle \lambda_{\alpha\beta\gamma\delta} \rangle = 0$. Nevertheless, the elastic anisotropy can disappear also in crystal-state (e.g. for NaCl at $T \approx 690^\circ\text{K}$, [4]). In such a case other characteristics are to be treated. The "true" parameter $\Lambda(\vec{x})$ describes the anisotropy of atoms' arrangement; in other words $\Lambda(\vec{x})$ describes the directions of local crystal-axes and characterizes the displacements of atoms from the ideal lattice.

We introduce the parameter $\Lambda(\vec{x})$ as a set of tensor fields $\Lambda^{(n)}(\vec{x})$ with rank $n \leq 4$. The irreducible tensors of fourth- and second-rank are responsible for crystalline - and liquid crystal type of order, respectively.

2. Effective hamiltonian of space arrangement

Statistical mechanics of crystalline-order is given by the probability density $W\{\Lambda(\vec{x})\}$ of a given crystal-order parameter $\Lambda(\vec{x})$ configuration,

$$dW\{\Lambda(\vec{x})\} \sim \exp\{-H\{\Lambda(\vec{x})\}/T\} D\Lambda(\vec{x}). \quad (1)$$

Here $D\Lambda(\vec{x})$ is the measure in the space of configurations $\{\Lambda(\vec{x})\}$ and $H\{\Lambda(\vec{x})\}$ is the effective hamiltonian (non-equilibrium thermodynamical potential). Parameter $\Lambda(\vec{x})$ is the macroscopic quantity and $H\{\Lambda\}$ depends on thermodynamical variables (temperature T , pressure p e.t.c.).

In case of liquid-crystal phase transition being nearly a continuous one (He^3 , 2-D systems), in the vicinity of the melting point T_c , $H\{\Lambda\}$ can be expanded in terms of small $\Lambda(x)$. Thus, Landau theory or fluctuation theory of phase transitions [5] can be applied. The correlation radius for such a system is much bigger than the lattice size. This problem will be examined in another work.

In this article, we deal with the case when the change of the average $\langle \lambda_{\alpha\beta\gamma\delta} \rangle$ at the melting point is not small and the correlation radius is of order of a few lattice sizes. In this case the only way to follow is to examine model hamiltonians $H\{\Lambda(x)\}$. We refer to the analogy with theory of magnetism, where model hamiltonians are introduced (Ising, Heisenberg e.t.c., see e.g. [5]).

Two conditions should be fulfilled by $H\{\Lambda(x)\}$; (I), the coordinate-system rotation invariance, and (II), the finiteness of local-order interaction radius. The second one follows from formula (1), obtained from Gibbs distribution by taking average over atom-scale degrees of freedom.

For systems with relatively high density the form-fluctuations of $\Lambda(\vec{x})$ are expected to be negligible. In case of fixed local order

$$\Lambda(\vec{x}) = \hat{g}(\vec{x}) \Lambda_0 \quad (2)$$

where $\hat{g}(\vec{x})$ - rotation of axes at point \vec{x} , Λ_0 - fixed set

of tensors. In this approximation $D\Lambda(\vec{x}) = D\hat{g}(\vec{x})$ and $H\{\Lambda(\vec{x})\} = H\{\hat{g}(\vec{x})\}$.

The general hamiltonian H with two-body interactions only has the form

$$H\{\Lambda(\vec{x})\} = \int d\vec{x} d\vec{y} f(\vec{x}-\vec{y}, \Lambda(\vec{x}), \Lambda(\vec{y})), \quad (3)$$

with f being a scalar. Its invariance under $\hat{g}^{-1}(\vec{x})$ gives in approximation (2):

$$f(\vec{x}-\vec{y}, \Lambda(\vec{x}), \Lambda(\vec{y})) = f(\vec{x}-\vec{y}, \Lambda^+(\vec{x}) \Lambda(\vec{y})), \quad (4)$$

with $\Lambda^+ = \Lambda_0 \hat{g}^{-1}$. The simplest model (generalized Heisenberg model) is given by hamiltonian

$$H\{\Lambda(\vec{x})\} = \int d\vec{x} d\vec{y} \text{Tr} \{ J(\vec{x}-\vec{y}) \Lambda^+(\vec{x}) \Lambda(\vec{y}) \}. \quad (5)$$

It will be referred to as the continuous - rotation model (C - model).

The alternative model, examined in this article, is the discrete - rotation (or D-model), in which a very strong dependence of energy f on relative rotations at points \vec{x} and \vec{y} exists. As a result, there's only a discrete set of relative local-order orientations with non-negligible probability. In such a case, integration over $D\hat{g}(\vec{x})$ is equivalent to summing up over discrete orientations $\hat{g}_\nu(\vec{x})$ at each point \vec{x} .

Let's briefly examine small fluctuations of the form of local order. They can be treated as local strains $u_{\alpha\beta}(\vec{x})$. In harmonic approximation the H_u part of H , due to form-fluctuations, is

$$H_u = \int d\vec{x} \lambda_{\alpha\beta\gamma\delta}(\vec{x}) u_{\alpha\beta}(\vec{x}) u_{\gamma\delta}(\vec{x}). \quad (6)$$

It extends the well-known formula of the theory of elasticity [6]. The relation between $\lambda_{\alpha\beta\gamma\delta}$ and geometrical parameter Λ will be discussed later.

The Gibbs thermodynamical potential Φ is as follows:

$$Z = \int \exp \left\{ \frac{1}{T} [H\{\hat{g}\} + H_u\{\hat{g}, u\} - \delta_{\alpha\beta} \int u_{\alpha\beta} dx] \right\} D\hat{g}(\vec{x}) D\vec{u}(\vec{x}), \quad (7)$$

where $\delta_{\alpha\beta}$ denotes the stress tensor.

3. The cubic-symmetry case

Number of tensor fields forming the crystal-order parameter depends on local parameter Λ_0 symmetry. The cubic case is the simplest one. Let's introduce 3 mutually perpendicular unit vectors (directors) $\vec{n}^{(i)}(\vec{x})$, which fix the axes of local cubic arrangement of atoms in point \vec{x} . The irreducible part $\tilde{T}_{\alpha\beta\gamma\delta}(\vec{x})$ of the tensor $T_{\alpha\beta\gamma\delta}$, defined by

$$T_{\alpha\beta\gamma\delta}(\vec{x}) = A \sum_{i=1}^3 n_\alpha^{(i)}(\vec{x}) n_\beta^{(i)}(\vec{x}) n_\gamma^{(i)}(\vec{x}) n_\delta^{(i)}(\vec{x}), \quad (8)$$

is the local order parameter of a cubic system. The interaction energy of local orders at \vec{x} and \vec{y} is

$$H(x, y) = f(\vec{x}-\vec{y}, \sum_{i,j} (n^{(i)}(\vec{x}) n^{(j)}(\vec{y}))^4). \quad (9)$$

There is no analytical solution of the statistical mechanic problems in 3-D yet. In this work a meanfield approximation will be applied to obtain, at least, qualitative description. As usually, the interaction of a given local arrangement of atoms with mean field $h_{\alpha\beta\gamma\delta}$ is considered instead of the exact manybody problem. The interaction with the mean field takes the form:

$$H = f(\text{Tr } hT). \quad (10)$$

The self-consistence condition for $\langle T_{\alpha\beta\gamma\delta} \rangle$, the average of $T_{\alpha\beta\gamma\delta}$ in mean-field approximation (m.f.a) is as follows:

$$h_{\alpha\beta\gamma\delta} = \nu \langle T_{\alpha\beta\gamma\delta} \rangle, \quad (11)$$

where ν is the "number of nearest-neighbours".

In case of cubic symmetry, $\tilde{h}_{\alpha\beta\gamma\delta}$ and $\langle \tilde{T}_{\alpha\beta\gamma\delta} \rangle$ are

irreducible tensors of cubic symmetry, uniquely described by one invariant amplitude.

Analytical treatment in MFA is straightforward, although tedious. The most characteristic features of the function $h_{\alpha\beta\gamma\delta}(T)$ seem to be model-independent.

In the following, the results for a D-model, described as follows, are reported. The four main diagonals of a cube are drawn. The system of directors, introduced at the beginning of this section, is turned round each of the main diagonals over the angle $\pi/3$, from the initial position in which it coincides with the coordinate axes. One has four inequivalent discrete positions. They generate a non-abelian subgroup of 3-D rotations (cubic symmetry group).

The model is described by the following system of equations for $h_{\alpha\beta\gamma\delta}$:

$$h_{\alpha\beta\gamma\delta} = \frac{6}{Z} \sum_{\{x\}} T_{\alpha\beta\gamma\delta} \exp\{-H/T\}, \quad (12)$$

where T is temperature, Z - partition function, hamiltonian H is given by (10) with $f(x) = x$, and the sum extends over discrete positions.

Equations (12) were solved analytically in the vicinity of $T = T_c^*$, the point of absolute instability of the high temperature phase, where $h_{\alpha\beta\gamma\delta}$ is nearly "isotropic". For other temperatures, numerical methods were applied (see Appendix 1).

The physical behaviour of the system is fully described by the function $a(T)$, Fig. 1a, b. The solution of Eq. (12) in terms of $a(T)$, is

$$\begin{aligned} \langle T_{\alpha\alpha\alpha\alpha} \rangle &= \frac{11}{27}; \quad \langle T_{\alpha\alpha\beta\beta} \rangle = \frac{8}{27}, (\alpha \neq \beta); \\ \langle T_{1233} \rangle &= \langle T_{1122} \rangle = -\langle T_{1221} \rangle = \frac{1}{6} a(T); \\ \langle T_{1112} \rangle &= \langle T_{2221} \rangle = \langle T_{2211} \rangle = \langle T_{3322} \rangle = -\langle T_{1113} \rangle = -\langle T_{3331} \rangle = -\frac{a(T)}{12}. \end{aligned} \quad (13)$$

Together with (13) there exist 3 physically equivalent soluti-

ons. It is the result of existence of four discrete orientations for crystal axes. They are equivalent and at $T < T_c$ this symmetry is spontaneously broken.

Other models, including C-models given by (5), give (in MFA) qualitatively the same results.

The behaviour of the mean-field amplitude $a(T)$ results from: (I), there are no either stable or metastable macroscopically ordered states of the system at elevated temperatures, and (II), mean ordering tends to saturation as $T \rightarrow 0$.

The first order character of crystallization is due to the structure of symmetry group, resulting in existence of cubic invariants, e.g. $I_3 = \overline{h} T^3$.

Function $a(T)$ exhibits some interesting model-independent "numerical" features that reflect properties of $\Lambda(x)$ itself. First, $a(T)$ practically coincides with $a(0)$ over the interval $0 \leq T < T_m - \Delta T$ with $\Delta T/T_m \leq 0.2+0.3$. Second, in the neighbourhood of T_m $a(T) \sim (T_m - T)^{1/2} a_0$ with $a_0 = a(T_m) \approx a(0)/2$. As a result, (I), the metastable crystal-state temperature interval is very small, and (II), the pre-melting phenomena take place close to T_c . They are examined in the next section.

4. Thermodynamics and elastic properties of cubic system. Pre-melting phenomena.

In this section the most important characteristics of the model, resulting from solution (13) of Eq. (12) are briefly reported.

The melting-point T_c is very close to T_m , where the crystal becomes absolutely unstable. The following relation holds

$$\frac{T_m - T_c}{T_m} \approx 0.02 \quad (14)$$

In the neighbourhood of T_m $a(T)$ takes the form

$$T_M - T \approx g_0 (a - a_M)^2 + \dots, \quad (15)$$

with $a_M \approx 0.45$ and $g_0 \approx 95$. (16)

The configurational part of thermodynamical potential $\Delta\Phi$ per one cell is (see Appendix 2)

$$\Delta\Phi(a(T), T) = a^2(T) - \frac{2}{7} T \ln \left\{ e^{\frac{56}{9} \frac{a(T)}{T}} + 3 e^{-\frac{56}{27} \frac{a(T)}{T}} \right\}. \quad (17)$$

The melting point T_c is the solution of equation $\Delta\Phi = \Delta\Phi_0$ where $\Delta\Phi_0(T) \equiv \Delta\Phi(0, T)$ (see Fig. 2).

In the vicinity of T_M the life time of metastable state is small. It can be easily understood; at $T = T_c$ there is relatively high ($\approx 1/4$) density of "wrong" cells (see (22)) (i.e. cells with orientations that do not coincide with the average one), which give rise to liquid phase nuclei with dimensions of a few cells (i.e. $\sim 10r_0$, where r_0 is the lattice size). The existence of such defects severely reduces (to ΔT_M) the temperature interval, where the metastable crystal can be observed: $\Delta T_M \sim 0,1(T_M - T_c) \sim 10^{-3} T_c$

Heat capacity is given, near T_c , by

$$\Delta C(T) = -T \frac{\partial^2 \Delta\Phi}{\partial T^2} \sim -\frac{da}{dT} \sim \left(\frac{T_M - T}{g_0 T_M} \right)^{-1/2}. \quad (18)$$

The constant at singular part $(T_M - T)^{-1/2}$ is small and at $T = T_c$ $\Delta C(T_c) \sim 1,7$. Quantity C is the heat capacity of one cell, which contains ~ 10 atoms. Hence, in our model the ratio $\Delta C(T_c)/C_{DP} \sim 0,1$ where C_{DP} is the heat capacity of solids according to Dulong-Petit Law. It is assumed that Debye temperature T_D is lower than T_c : $T_c \gg T_D$.

Other degrees of freedom, e.g. the fonon ones, change the melting temperature. In case of increasing T_c (with T_M constant) the heat capacity jump $\Delta C(T_c)$ also increases.

The model examined here is volume - and pressure-independent. In order to obtain such a dependence, one has to add to the hamiltonian terms, describing the interaction between

strain and local order (striction). In magnetism such a program was carried out by Larkin and Pikin [7]. We obtain the wanted formulas starting from physical arguments.

For a given configuration $\{\Lambda(x)\}$ each "wrong" lattice-cell becomes a source of strain and related displacements, δu .

$$\delta \vec{u}(\vec{r} - \vec{r}') \sim \frac{\vec{r} - \vec{r}'}{|\vec{r} - \vec{r}'|^3} \quad (19)$$

where \vec{r}, \vec{r}' denote radii vectors of defect and examined point, respectively. Formula (19) follows from theory of elasticity and describes the displacement due to the action of the force $\vec{F}(\vec{r})$ satisfying the condition $\int \vec{F}(\vec{r}) dV = 0$. After the average over random positions and orientations of defects is taken, the anisotropic part of strain vanishes. As the result, the volume change δV of a body with radius R is

$$\delta V \sim R^3 \int \delta \vec{u}(\vec{R} - \vec{r}) n_d(\vec{r}) dV \sim V \bar{n}_d \quad (20)$$

where $n_d(\vec{r})$ and \bar{n}_d are local - and averaged density of defects, respectively (see (22)). The above formula (20) is formally equivalent to the one obtained with help of (7) in the approximation that for a given configuration $\{\Lambda(x)\}$ the only contribution to the integral over $D\vec{u}(\vec{r})$ comes from $\{\vec{u}(\vec{x})\}$ configurations with the lowest energy.

In this approximation, the mean isotropic strain of each cell vanishes, for fixed pressure $p = -\frac{1}{3} \partial_{\alpha\alpha}$. In other words, in process of volume change due to disorder, the cells are not deformed (on average), for $p = \text{const}$. Hence, the "mean" local parameter Λ_0 remains the same. As a result, the configurational part of thermodynamical potential (17) coincides with $\Phi(p, T)$.

The next approximations should take into account: (I), the energy due to non-uniform and anisotropic part of deformations (its main part is local and is included into Λ - field hamiltonian $H\{\Lambda(x)\}$; (II), the interaction of defects and; (III), the elastic constant renormalization (as temperature changes). The last point will be briefly discussed in this

section.

From the above arguments it follows that $\Delta C(T)$, Eq. (18), is in the first approximation isomorphic to experimental constant-pressure heat capacity (see also [8]) C_p .

Fig. 3 presents experimental data (ΔC_p) for AgCl 10, (line 2), and theoretical results, Eq. (18), (line 1). The experimental data for ΔC_p were obtained from C_p by subtracting its non-anomalous part. The constant A in $\Delta C_p(T) \approx A(T_m - T)^{-1/2}$ is taken as to fulfill the condition $\Delta C(T_c) = \Delta C_p(T_c)$.

For the coefficient of thermal expansion, one gets from (20)

$$\Delta \alpha_T \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \tilde{B} \frac{d\bar{n}_d}{dT} = -B \frac{da(T)}{dT}; \quad (21)$$

In Fig. 4 the temperature dependence of $\Delta \alpha_T$ Eq. (21) and experimental data for $\Delta \alpha_T$, [9], are presented, by crosses and dots, respectively. Normalization, analogous to the C_p case, was applied.

In the vicinity of the melting point T_c , Grüneisen Law, (stating that the ratio of thermal expansion coefficient to the heat capacity of solids is temperature independent, see e.g. [11]) approximately holds for and both in theory and experiment 9, 10. It results from Eq. (18) and (21); both these quantities are proportional to temperature derivate of energy density

In the following, the elastic properties of the system near the crystallization point are briefly examined. The irreducible (anisotropic) part of cubic elastic-constant tensor is described by one invariant amplitude. From here and from geometrical arguments (both they describe the same anisotropy of atoms' locations) it follows that irreducible parts of $\lambda_{\alpha\beta\gamma\delta}$ and $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ are proportional. The fact that $\tilde{\lambda}_{\alpha\beta\gamma\delta} \sim \lambda_{\alpha\beta\gamma\delta}$ and not to $\tilde{\lambda}_{\alpha\beta\gamma\delta}^{-1}$ (the elastic-moduli tensor), results from physical arguments, e.g. from the comparison of the formula for striction term $Tr(T_{uu})$ with formula (6).

Elastic behaviour of the system near T_c reflects the imperfectness of the lattice due to defects (texture). Let's find their concentration. Consider $\nu = N_d + N_r$ cells, with N_d "wrong" and N_r "right" ones. Suppose (for definiteness) that "right" cells occupy state 1 (i.e. have discrete orientation No 1), while defects occupy states 2,3,4. As a result of the symmetry the defect-states are energetically equivalent. The sum of T_{1123} over states 1,2,3 and 4 vanishes, so it doesn't contribute to $\alpha(T)$. The "right" cells give the contribution equal to $\alpha(0)/\nu$. One can easily obtain the following formulas for the density \bar{n}_r, \bar{n}_d of "right" and "wrong" cells, respectively:

$$\begin{aligned} n_r &= 1 - n_d; \\ n_d &= \frac{3}{4} \left(1 - \frac{\alpha(T)}{\alpha(0)} \right). \end{aligned} \quad (22)$$

The temperature dependence of n_d is plotted in Fig. 5. We find that $n_d(T_c) \approx 1/4$.

Suppose the inhomogenities are small. In this case the corrections to mean elastic constants can be found. Following Lifshitz and Rozenzweig [12] (L.R.)

$$\tilde{\Lambda}_{\alpha\beta\gamma\delta} = \tilde{\lambda}_{\alpha\beta\gamma\delta} + \tilde{\Delta}_{\alpha\beta\gamma\delta}, \quad (23)$$

where $\Lambda_{\alpha\beta\gamma\delta}$ is the effective elastic-constant tensor and $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ is averaged over the texture. The corrections $\tilde{\Delta}_{\alpha\beta\gamma\delta}$ contribute both to irreducible ($\tilde{\Lambda}$) and isotropic part of $\Lambda_{\alpha\beta\gamma\delta}$. In the latter case they describe anharmonicity due to disorder.

Analytical treatment carried along (L.R.) lines shows that, (1), $\tilde{\lambda} \sim \alpha(T)$ and (11), $\tilde{\Delta}_{\alpha\beta\gamma\delta}$ are small and proportional to $\alpha(T) \left(1 - \frac{\alpha(T)}{\alpha(0)} \right)$. The necessary isotropic parts of $\lambda_{\alpha\beta\gamma\delta}$ were taken from experiments [4,9]. The temperature dependence of $\tilde{\Lambda}_{1111}$ (solid line) and $\tilde{\lambda}$ (dotted line) is given in Fig. 6. The strong dependence on $T - T_c$ of $\Lambda_{\alpha\beta\gamma\delta}$

may explain the experimental fact of the rapid decrease of elastic constants near T_c [4].

In Fig. 7 the Young modulus $E(\vec{q})$, $\vec{q} = (1, 0, 0)$, is plotted against the reduced temperature $\tau = T/T_c$ (solid line); the experimental data, [13], are given by dots. The isotropic part of elastic-constant tensor was taken from experiment (such a procedure is not unique), so that $E(\tau = 1)/E(\tau = 0.29)$ equaled to its experimental value.

In the next approximation one has to take into account the anharmonicity effects, leading to the change of the characteristics of an elementary cell, i.e. corrections to $\lambda_{\alpha\beta\gamma\delta}$ proportional to temperature.

5. Summary

In our cell-model the concentration of defects even at the melting point is relatively small, so it seems reasonable to describe defects as cells with "wrong" orientations of crystalline-axes.

For the disordered phase (liquid) $\alpha = 0$ and the number of cells with every kind of orientation is the same. For that case every cell has at its surrounding cells with all kinds of orientations. Such a chaotic surrounding leads, in general, to the change of the characteristics Λ_c of local ordering. The treatment of that effect (necessary for the liquid state theory) exceeds the frames of this paper.

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The figure captions

- Fig. 1a, b The plott of function $\alpha(\tau)$ the solution of Eq. (A.9), versus the reduced temperature $\tau = \frac{T}{T_c}$
- Fig. 2 The plott of thermodynamical potential $\Delta\Phi(\tau)$ Eq. (17), versus the reduced temperature τ .
- Fig. 3 The temperature dependence of the heat capacity $\Delta C(T)$ Eq. (18) (line 1), and $\Delta C_p(T)$ for AgCl [10], (line 2).
- Fig. 4 The temperature dependence of the coefficient of thermal expansion $\Delta\alpha_T$ Eq. (21) (solid line) and $\Delta\alpha_T$ for AgCl [9] (crosses).
- Fig. 5 The temperature dependence of the concentration n_c of defects, Eq. (22).
- Fig. 6 The temperature dependence of $\tilde{\lambda}_{1111}$ (solid line) and λ_{1111} (dotted line), Eq. (23).
- Fig. 7 The temperature dependence of the Young modulus $E(\vec{q})$, $\vec{q} = (1,0,0)$, in theory (solid line) and experiment ([13], for KCl), (dotted line).

Appendix 1

In this Appendix the way, in which the solutions (13) of Eqs. (12) were obtained, is presented.

In our discrete model, the following symmetries take place (in each discrete position):

$$T_{\alpha\alpha\alpha\alpha} = \frac{11}{27}, \quad T_{\alpha\alpha\beta\beta} = \frac{8}{27}, \quad (\alpha \neq \beta),$$

$$T_{1112} = T_{1212} = -\frac{1}{2} T_{1233},$$

$$T_{1113} = T_{1313} = -\frac{1}{2} T_{1223},$$

$$T_{2223} = T_{2323} = -\frac{1}{2} T_{1123}.$$

(A.1)

That is, only three of $T_{\alpha\beta\gamma\delta}$ are independent. Let's introduce the variables x , y and z :

$$x = \langle T_{1123} \rangle; \quad y = \langle T_{1223} \rangle; \quad z = \langle T_{1233} \rangle.$$

(A.2)

In these variables the MFA hamiltonian H (10) is

$$H = -\text{Tr}(hT) = -14 [x T_{1123} + y T_{1223} + z T_{1233}]$$

(A.3)

In the vicinity of T_c^* , at which

$$x(T_c^*) = y(T_c^*) = z(T_c^*) = 0,$$

(A.4)

x , y and z are small and the Gibbs factor in Eqs. (12) can be expanded to the second order with respect to x, y, z . This yields

$$x - y = \frac{T_c^*}{T} (x - y) \left(1 + \frac{8}{3} \frac{z}{T}\right),$$

$$x + y = \frac{T_c^*}{T} (x + y) \left(1 - \frac{8}{3} \frac{z}{T}\right),$$

(A.5)

$$x - z = \frac{T_c^*}{T} (x - z) \left(1 + \frac{8}{3} \frac{y}{T}\right).$$

where $T_c^* = \frac{448}{243}$.

Eqs. (A5) have 5 solutions:

$$\begin{aligned} x=0, y=0, z=0; \\ x=\epsilon, y=-\epsilon, z=\epsilon; \\ x=-\epsilon, y=-\epsilon, z=-\epsilon; \\ x=\epsilon, y=\epsilon, z=-\epsilon; \\ x=-\epsilon, y=\epsilon, z=\epsilon; \end{aligned} \quad (\text{A.6})$$

where $\epsilon = \frac{1}{16} \frac{T^2}{T_c^*} (1 - \frac{T_c^*}{T})$. Let's consider (for definiteness) the second solution. It implies

$$\begin{aligned} \langle T_{1123} \rangle &= \frac{a(T)}{6}, \\ \langle T_{1213} \rangle &= -\frac{a(T)}{6}, \\ \langle T_{3312} \rangle &= \frac{a(T)}{6}, \end{aligned} \quad (\text{A.7})$$

with $a(T)$ to be found. The hamiltonian (A.3) becomes

$$H = -14a(T) [T_{1123} - T_{1213} + T_{1233}]. \quad (\text{A.8})$$

One obtains 3 identical equations for $a(T)$, of the form

$$a(T) = \frac{6}{Z} \sum T_{1123} \exp\{-H/T\}. \quad (\text{A.9})$$

From here

$$\frac{9 \cdot 27}{8 \cdot 224} \beta(T) = \frac{1}{T} \frac{e^{\beta(T)} - 1}{e^{\beta(T)} + 3}, \quad (\text{A.10})$$

with $\beta(T) = \frac{224}{27} \frac{a(T)}{T}$. This equation was solved numerically (fig. 1)

Let's derive the formula (17) for $\Delta\Phi(a(T), T)$. From the definition, the equation

$$\frac{d\Delta\Phi(a)}{da} = 0 \quad (\text{A.11})$$

should be equivalent to Eqs. (12) or (A.9). From (A.8) one has

$$\frac{d}{da} \ln Z \equiv \frac{1}{Z} \sum \frac{14}{T} (T_{1123} - T_{1213} + T_{1233}) \quad (\text{A.12})$$

which, with help of (A.9) and remarks done there, gives

$$\frac{d}{da} (\Delta\Phi(a, T)) = 0, \quad \text{with } \Delta\Phi \text{ given by (17).}$$

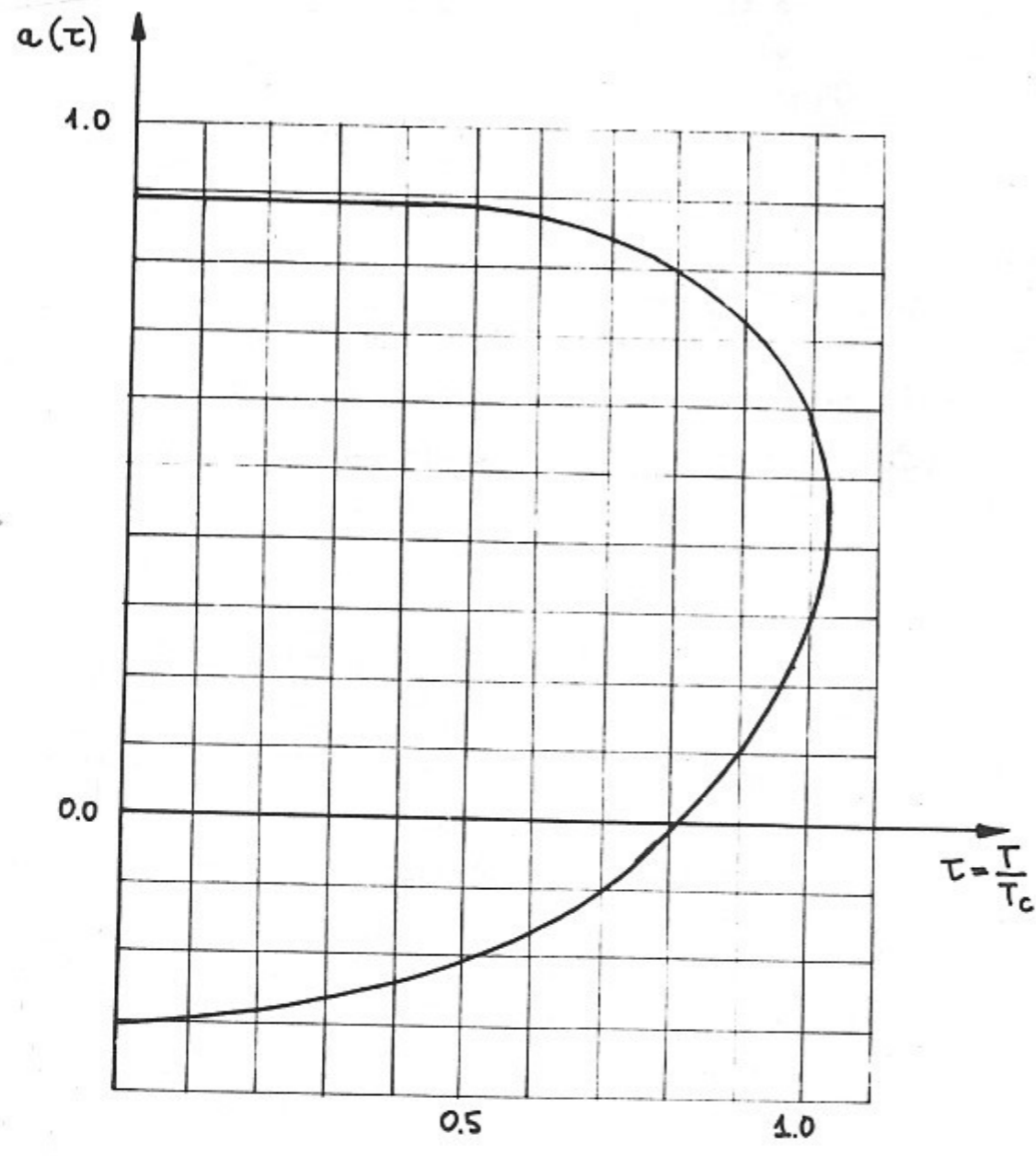


Fig. 1, a.

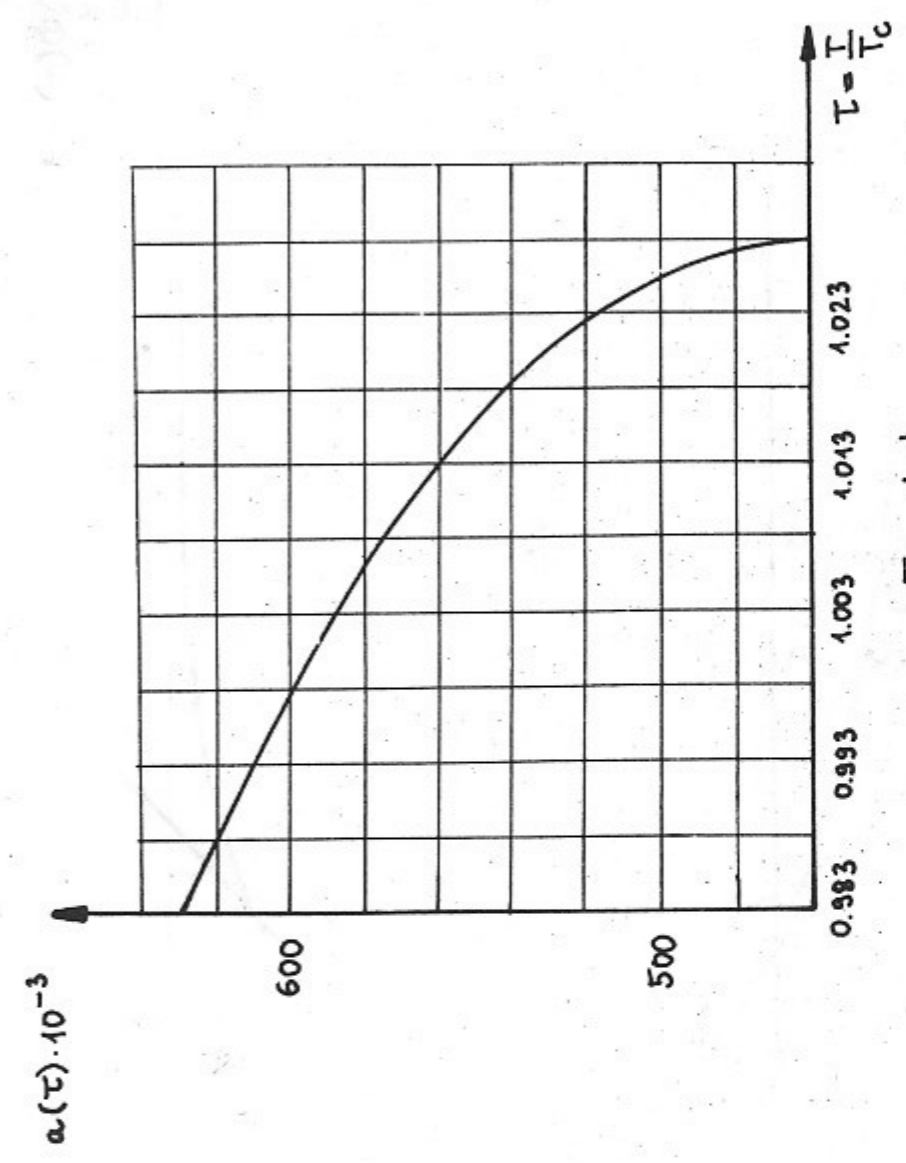
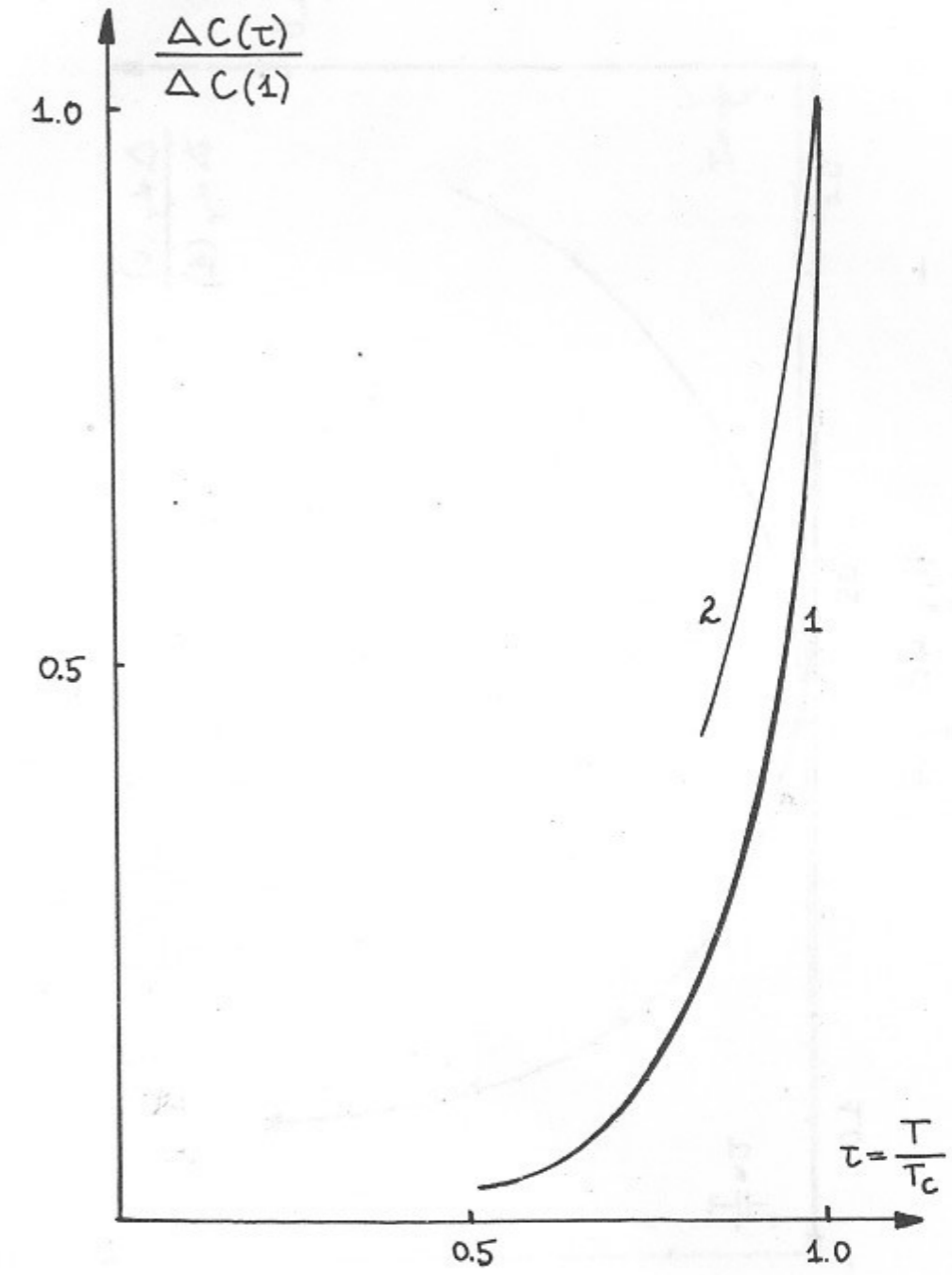
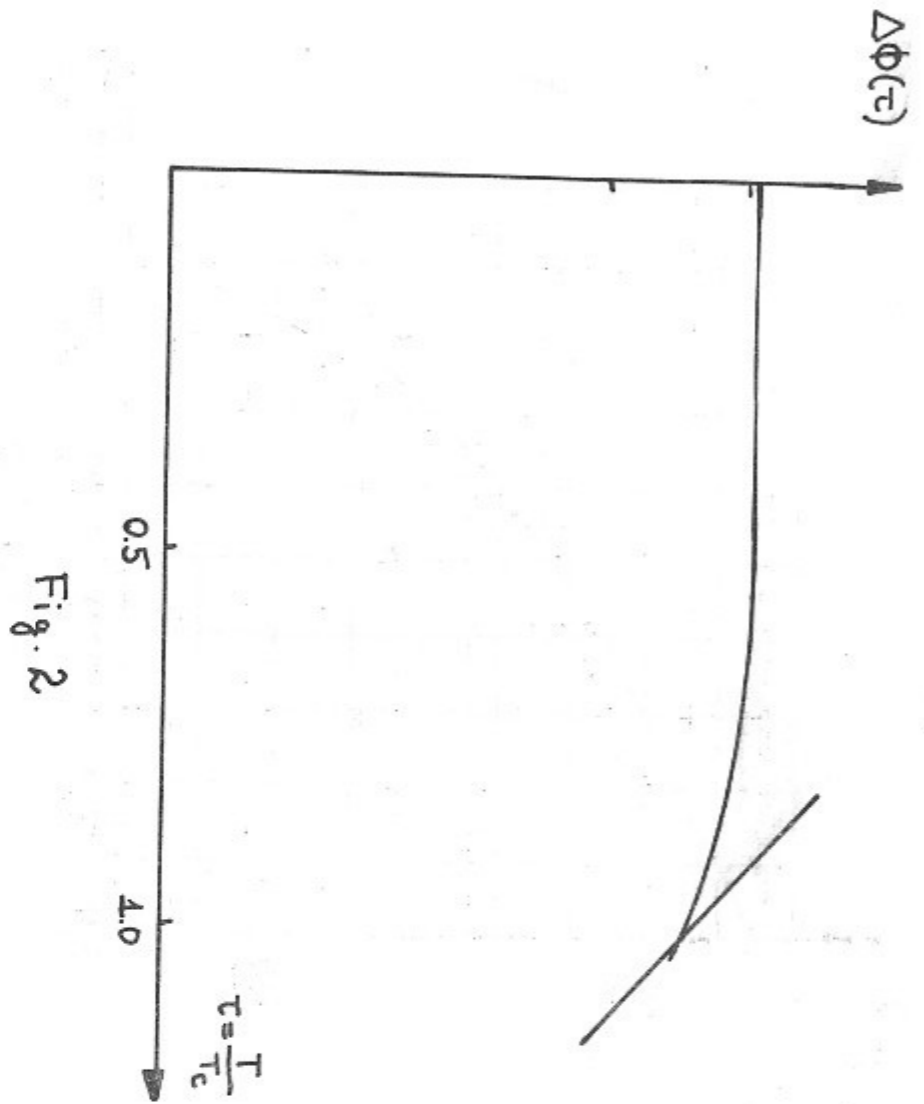


Fig. 1, b.



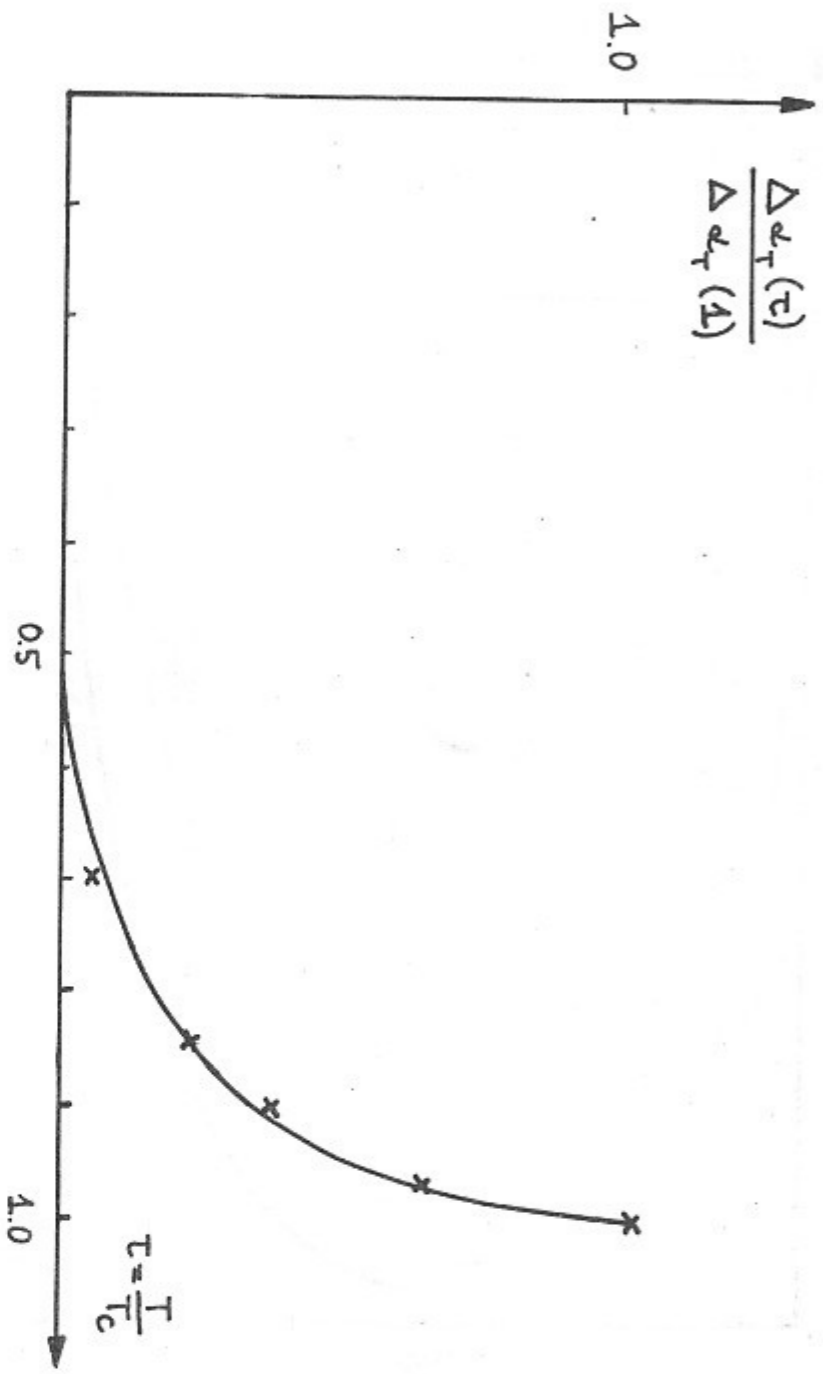


Fig. 4

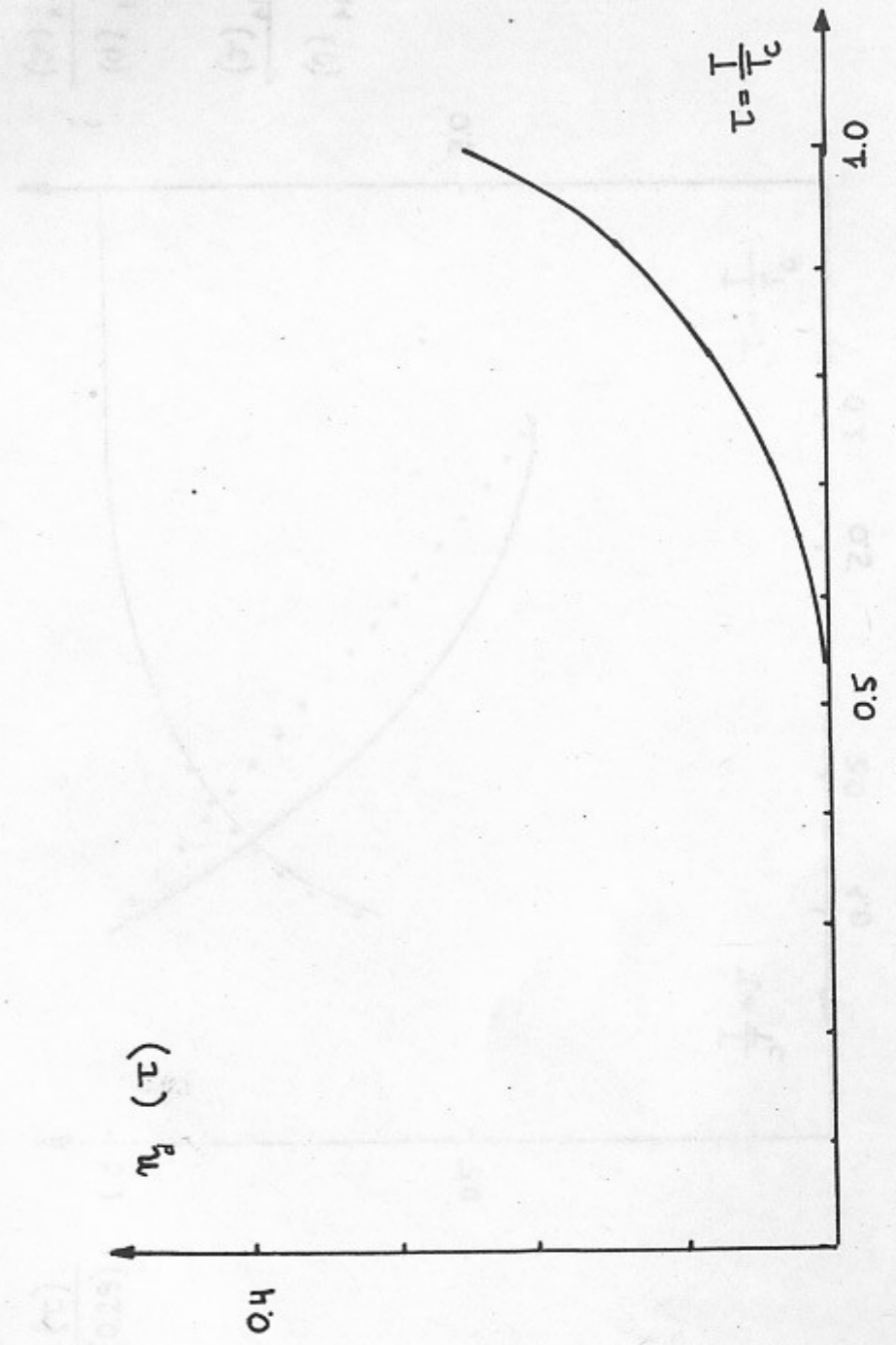


Fig. 5

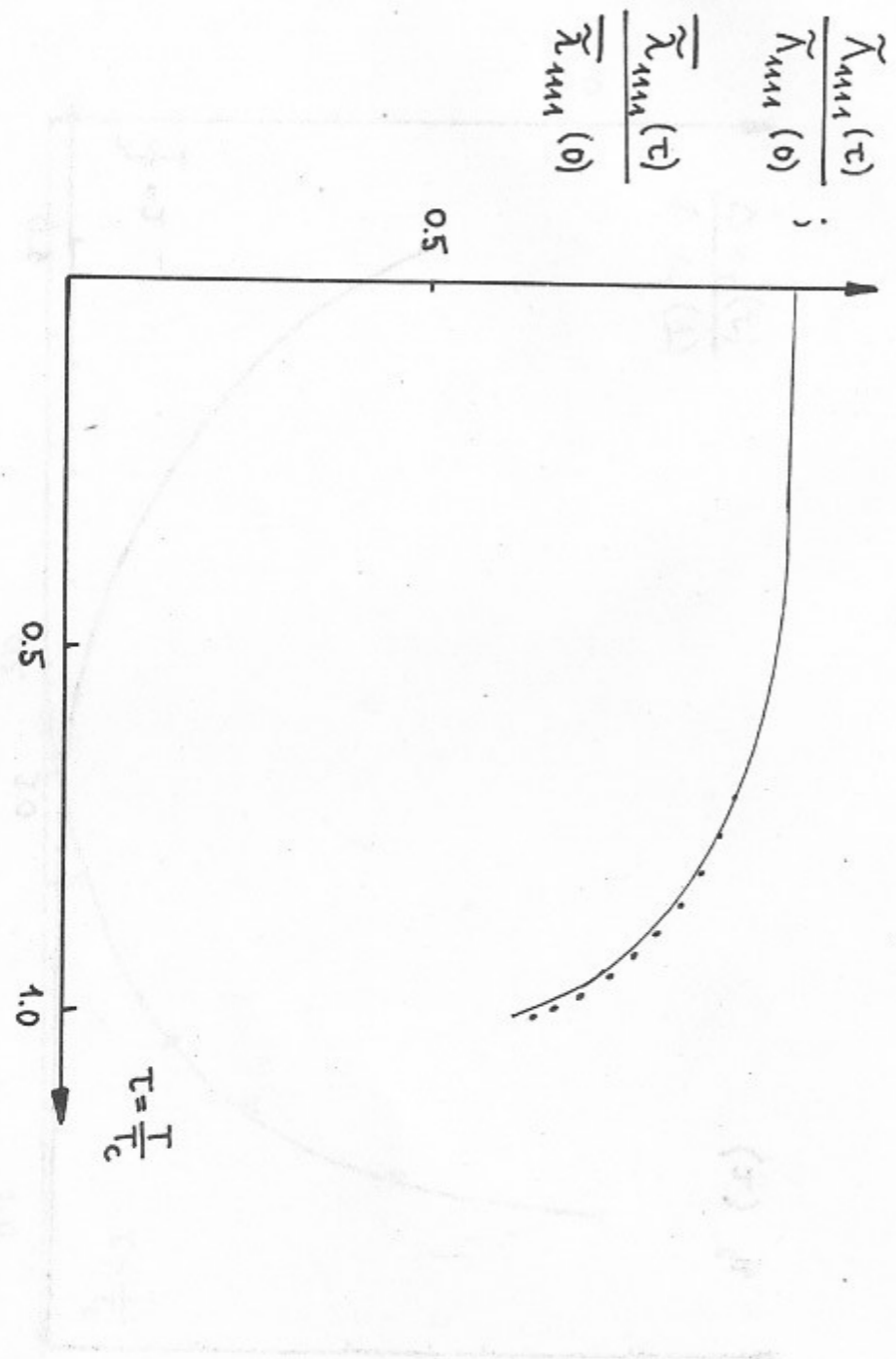


Fig. 6

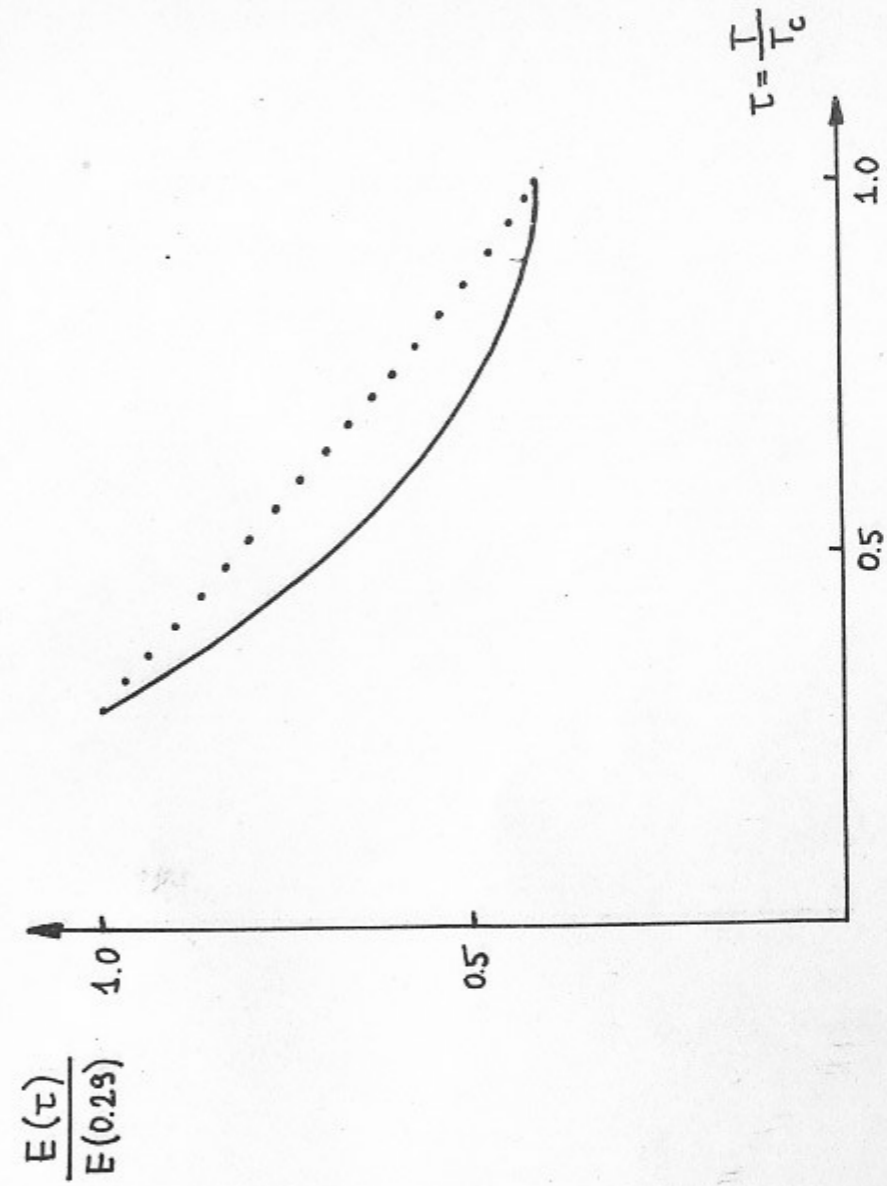


Fig. 7