Theory of crystal ordering

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The degree of ordering in small regions of a dense system is described with the aid of a macroscopic short-range order-parameter field $\Lambda(x)$. This parameter turns out to be a fourth-rank tensor. Crystallization is described in terms of the appearance of long-range order in the $\Lambda(x)$ field. The simplest model Hamiltonian is considered, and the properties of the system are computed in the mean-field approximation. It is shown that the relative width τ of the metastability region of the crystal is small: $\tau = 0.02$. The thermodynamic properties in the vicinity of the melting point (the premelting anomalies) are found. The results are in qualitative agreement with experiment.

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§1. MACROSCOPIC CRYSTAL-ORDER PARAMETER

During the phase transition from the liquid into the crystalline state the symmetry of the system decreases from the Galilean to crystal-lattice symmetry. To describe the system, we consider, following Landau,[1] the particle number density field $n(\mathbf{x})$. At the crystallization point T_c there arises abruptly in the space of the wave vectors $\mathbf{k}$ at points $\mathbf{k}_i$ a "condensate" corresponding to the periodic—on the average—disposition of the atoms in a lattice. For a dense medium such a description is in fact microscopic: it is necessary to describe the interaction over atomic distances $a \sim 1/k_i$, and the density field $n(\mathbf{x})$ to within the localization of the atoms in the unit cells of the lattice. In other words, it is necessary to take into consideration right from the start all the system's degrees of freedom that correspond to the atomic scales. At the same time, the experimental data on the crystallization of dense liquids indicate that the volume of the system changes during crystallization by an amount $\delta V/V \sim 10^{-1}$–10^{-2} and that in order of magnitude the melting heat per atom constitutes the same fraction of the characteristic energy $E_a \sim kT_c$, which indicates relatively slight changes in the correlations in small volumes of the system. The x-ray scattering data indicate that in dense liquids the order over short distances reflects the order in the crystal. The concept of a locally-crystalline structure of a liquid can be traced back to Frenkel'.[2]

For all the differences among the properties of materials, common properties are present for the transition into the crystalline state. Among them are, besides the above-indicated smallness of the changes that occur in the local characteristics during crystallization, the smallness of the existence domain for the metastable crystal and the characteristic anomalies occurring in the thermal and elastic properties in the vicinity of the melting point. The purpose of our paper is to describe the general properties of crystals in the vicinity of the melting point within the framework of a model that takes account of only the important change that occurs during crystallization in the character of the correlations in the system. A fundamental feature of the description is the introduction of a macroscopic field $\Lambda(x)$ describing the local ordering of the particle disposition in the system.

We assume that at the densities and temperatures in question the atoms in small volumes of the system are ordered in a way characteristic of a crystal. The disposition of the atoms in a finite volume can be characterized by a set of density multipole moments, to which correspond tensors of appropriate ranks (a scalar corresponds to the density; a vector, to the displacement of the center of gravity; etc.). Treating a small volume as a "physical point," we obtain for the characterization of the disposition of the parts of the system a set of macroscopic field tensors $\Lambda^{(n)}(\mathbf{x})$. The x-ray structural analysis and other data allow us to hope that the size of the physical point, i.e., the distance over which the $\Lambda(\mathbf{x})$ fields are smoothed out, covers several interatomic distances, and that $n_a \sim 10^1$–10^3 atoms. The high multipole moments describe the rapidly varying details of the disposition of the atoms during the thermal motion. To describe the crystal ordering it is sufficient to restrict ourselves to the fourth- and lower-rank tensors. Tensors of rank lower than the fourth describe not the crystal ordering proper, but only the liquid-crystal type of ordering. It is sufficient to note that for a lattice of cubic symmetry the irreducible tensors of rank $n < 4$ are isotropic, and do not describe the anisotropy in the properties of the crystal. At the same time the appearance of a nonvanishing irreducible tensor of the fourth rank indicates the appearance in the properties of an anisotropy typical of a crystal.

In the theory of liquid crystals, the local order is specified by a second-rank field tensor $Q_{\alpha\beta}(\mathbf{x})$ (Ref. 3). The quantity $Q_{\alpha\beta}(\mathbf{x})$ is interpreted either as the quadrupole moment of the physical point $\mathbf{x}$ (the geometrical interpretation), or as the irreducible part of the susceptibility (the material interpretation). It is assumed that the susceptibility manifests a contribution reflecting the anisotropy in the disposition of the particles. For a crystal the role of the material characteristic distinguishing it from a liquid is played by the elasticity tensor $\lambda_{\alpha\beta\gamma\delta}$. The irreducible part $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ of this tensor can, if it does not vanish, serve as the crystal-order parameter. Through some accidental causes $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ can vanish at some temperature T_e (for example, at $T = T_e \approx 690$ K in NaCl; see Ref. 4). Therefore, we shall consider below the parameter $\Lambda(\mathbf{x})$ to be the geometric characteristic of the direction of the axes and the degree of

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perfection of the local "lattice." In the general case the character of the ordering in the system is described by the set of irreducible $\Lambda^{(n)}(\mathbf{x})$ field tensors of rank $n \leqslant 4$. The irreducible fourth-rank $\Lambda(\mathbf{x})$ tensors describe the crystal order proper, while the tensors of rank $n < 4$ describe the magnetic, electric, and liquid-crystal ordering.

§2. THE EFFECTIVE HAMILTONIAN OF THE SPATIAL ORDERING

The statistical mechanics of crystal ordering is determined by the expression for the probability $dW\{\Lambda(x)\}$ of a given configuration of the crystal-order parameter field $\Lambda(\mathbf{x})$:

$$dW\{\Lambda(\mathbf{x})\} \propto \exp\{-H\{\Lambda(\mathbf{x})\}/T\} D\Lambda(\mathbf{x}). \tag{2.1}$$

Here $D\Lambda(\mathbf{x})$ is an element in the configuration space $\{\Lambda\}$, and $H\{\Lambda(\mathbf{x})\}$ is the effective Hamiltonian (the nonequilibrium thermodynamic potential). The parameter $\Lambda(\mathbf{x})$ has a macroscopic character, and $H\{\Lambda\}$ depends on the thermodynamic variables (temperature T, pressure p, etc.) as parameters.

For the case in which the liquid-to-crystal phase transition is nearly of second order (He^3, two-dimensional systems), we can expand $H\{\Lambda\}$ in the vicinity of the transition point T_c in powers of the small $\Lambda(\mathbf{x})$, and construct a theory in the spirit of the Landau theory or the fluctuation theory of phase transitions.[5] The condition for the applicability of such an approach is that the correlation length be long compared to the lattice constant.

Reversing this case for another paper, we shall consider here the situation in which the jump occurring in the mean value $\langle\Lambda\rangle$ during crystallization is not small, and the correlation length has the order of magnitude of several lattice constants. For such a system we can investigate only model Hamiltonians $H\{\Lambda\}$. Let us point out the analogy with the theory of magnetism, in which as models we use, for example, the Ising, Heisenberg, etc., models.

The general restrictions imposed on $H\{\Lambda(\mathbf{x})\}$ amount to the requirement that it be invariant under a general rotation of the reference system and that the radius of the interaction between the local orders be finite. The latter condition arises from physical considerations: in deriving (2.1) from the exact Gibbs distribution, we should average the degrees of freedom of the atomic scales.

For sufficiently dense systems, it can be expected that the fluctuations in the form of $\Lambda(\mathbf{x})$ will be relatively small. In other words, we assume that the local $\Lambda(\mathbf{x})$ order in sufficiently small parts of the system is due to interactions whose energy is high compared to the energy ($\sim T_c$) of the thermal motion. Let us recall that we are dealing with that moment of the local density of the material which corresponds to the $\Lambda^{(n)}(\mathbf{x})$ tensors of ranks $n \leq 4$, and not with the rigid fixing of all the interatomic distances. Let us, to begin with, neglect the fluctuations in the form, and consider only the fluctuations in the direction of the axes of the local order:

$$\Lambda(\mathbf{x}) = g(\mathbf{x})\Lambda_0, \tag{2.2}$$

where $\hat{g}(\mathbf{x})$ denotes the rotation of the axes at the point $\mathbf{x}$ and Λ_0 is a fixed set of tensors. In this approximation $D\Lambda(\mathbf{x}) = D\hat{g}(\mathbf{x})$.

The general form of $H\{\Lambda(\mathbf{x})\}$ with allowance for only the pair interaction of the local ordering is as follows:

$$H\{\Lambda(\mathbf{x})\} = \int d\mathbf{x}d\mathbf{y} f(\mathbf{x}-\mathbf{y}; \Lambda(\mathbf{x}), \Lambda(\mathbf{y})), \tag{2.3}$$

where f is a scalar. Let us take into account the invariance of H under the rotation $\hat{g}^{-1}(\mathbf{x})$ in the approximation (2.2):

$$f(\mathbf{x}-\mathbf{y}; \Lambda(\mathbf{x}), \Lambda(\mathbf{y})) = f(\mathbf{x}-\mathbf{y}; \Lambda_0, g^{-1}(\mathbf{x})g(\mathbf{y})\Lambda_0) = f(\mathbf{x}-\mathbf{y}; \Lambda^+(\mathbf{x})\Lambda(\mathbf{y})), \tag{2.4}$$

where $\Lambda^+(\mathbf{x}) = \Lambda_0\hat{g}^{-1}(\mathbf{x})$. The simplest model, which generalizes the Heisenberg model, is given by the Hamiltonian

$$H\{\Lambda(\mathbf{x})\} = \int d\mathbf{x}d\mathbf{y} J(\mathbf{x}-\mathbf{y}) \operatorname{Sp}[\Lambda^+(\mathbf{x})\Lambda(\mathbf{y})]. \tag{2.5}$$

We shall call this the model of continuous rotations, or the C-model.

Another model that we shall consider below is the model of discrete rotations (the D model). In this model we assume that there is a very strong dependence of the energy on the relative rotation at the points $\mathbf{x}$ and $\mathbf{y}$, so that only the local orders' preferred relative orientations, which form a discrete set, have appreciable probabilities. In this case the integration over $D\hat{g}(\mathbf{x})$ is equivalent to summation over these discrete orientations, $g_k(\mathbf{x})$, at each point $\mathbf{x}$.

Let us now turn to the consideration of the fluctuations in the form of the local order. These (small) fluctuations can be described with the aid of the local-strain tensor $u_{\alpha\beta}(\mathbf{x})$. Allowing for the local-strain energy only in the harmonic approximation, we write for the contribution H_{el} of the form fluctuations the effective Hamiltonian

$$H_{el} = \int d\mathbf{x} \lambda_{\alpha\beta\gamma\delta}(\mathbf{x}) u_{\alpha\beta}(\mathbf{x}) u_{\gamma\delta}(\mathbf{x}), \tag{2.6}$$

which generalizes a well-known formula of the theory of elasticity.[6] The expression for $\lambda_{\alpha\beta\gamma\delta}$ in terms of the "geometric" parameter $\Lambda(\mathbf{x})$ will be given below.

The Gibbs thermodynamic potential Φ for our model is given by the well-known formula

$$\Phi = -T \ln Z, \quad Z = \int Dg(\mathbf{x}) D\mathrm{u}(\mathbf{y}) \exp\left\{ -\frac{1}{T}\left[H\{g(\mathbf{x})\} + H_{el}\{\hat{g}, u_{\alpha\beta}\} - \sigma_{\alpha\beta} \int u_{\alpha\beta}(\mathbf{z})\, dz \right] \right\} \tag{2.7}$$

where $\sigma_{\alpha\beta}$ is the stress tensor. The really analytical calculations with the formula (2.7) meet with as yet unsurmounted difficulties. As in the case of other three-dimensional problems, we can hope for a numerical investigation of the problem with the use of a computer. Here it is sufficient to consider a lattice model consisting of quite a small number of cells, since the correlation length at the transition point T_c is of the order of unity. The qualitative characteristics of the system can be obtained by studying the problem in the self-consistent field approximation. We shall consider the system for which the local parameter Λ_0 is an irreducible tensor with cubic symmetry. Thus, we restrict ourselves in this paper to the study of crystallization proper, leaving out the electric, magnetic, and liquid-crystal components of the crystal order.

§3. THE CUBIC SYSTEM IN THE SELF-CONSISTENT FIELD APPROXIMATION

The order parameter for a system with cubic symmetry in the approximation (2.2) of unchanged local structure can be constructed in the following manner. Let us consider the three mutually orthogonal unit vectors (directors) $\mathbf{n}^{(i)}(\mathbf{x})$ $(i=1,2,3)$ specifying the directions of the axes of the local cubic order at the point $\mathbf{x}$. Let us construct the reducible tensor

$$T_{\alpha\beta\gamma\delta}(\mathbf{x})=A\sum_{i=1}^{3}n_\alpha^{(i)}(\mathbf{x})n_\beta^{(i)}(\mathbf{x})n_\gamma^{(i)}(\mathbf{x})n_\delta^{(i)}(\mathbf{x}). \tag{3.1}$$

The tensor $T_{\alpha\beta\gamma\delta}(\mathbf{x})$ (more exactly, its irreducible part) is the order parameter for a system with cubic symmetry. The interaction energy (2.4) can be written with the aid of (3.1) in the form

$$H=\int d\mathbf{x}d\mathbf{y}f(\mathbf{x}-\mathbf{y};\sum_{i\neq j}(\mathbf{n}^{(i)}(\mathbf{x})\mathbf{n}^{(j)}(\mathbf{y}))^4). \tag{3.2}$$

To carry out a qualitative investigation of the system, we use the self-consistent field approximation. A general feature of this approximation is the replacement of the effect of all the parts of the system on the ordering at a given point by a mean field $h_{\alpha\beta\gamma\delta}$. The interaction with the mean field has the form

$$H=f(\mathrm{Sp}\,\hat{h}\hat{T}). \tag{3.3}$$

The mean value found with the aid of (3.3) satisfies the self-consistency condition

$$h_{\alpha\beta\gamma\delta}=\nu\langle T_{\alpha\beta\gamma\delta}\rangle, \tag{3.4}$$

where ν is the effective number of neighbors. In the $f(x)=x$ model considered below, the quantity ν determines only the numerical quantity T_c, and, on going over to the temperature $\tau=T/T_c$, the dependence on ν disappears to within the normalization. For definiteness, we set $\nu=6$ (the number of nearest neighbors in a three-dimensional cubic lattice). In the case of cubic symmetry the quantities $\hat{h}_{\alpha\beta\gamma\delta}$ and $\hat{T}_{\alpha\beta\gamma\delta}$ are irreducible tensors with a single independent invariant amplitude.

The computations turn out to be tedious even in the self-consistent field approximation. The self-consistent field vs temperature curves for the various interaction models turn out to be close. We shall give the results of the computation for the model with discrete rotations. The model is specified as follows. From the center of the cube we draw lines to its vertices, producing the four principal diagonals. Let us rotate the system of three mutually orthogonal directors describing the local cubic structure from the initial state, in which it coincides with the axes of the coordinate system, through an angle of $\pi/3$ about each of the principal diagonals. We obtain four inequivalent discrete positions that transform into each other under the symmetry operations of the cube. The rotations connected with them form a non-Abelian subgroup of the group of three-dimensional rotations.

Let us write down the system of equations for the quantities $h_{\alpha\beta\gamma\delta}$:

$$Zh_{\alpha\beta\gamma\delta}=\nu\sum T_{\alpha\beta\gamma\delta}e^{-H/T};\ Z=\sum e^{-H/T}, \tag{3.5}$$

where T is the temperature, Z is the partition function, H is given by the expression (3.3) for $f(\mathbf{x})=\mathbf{x}$, and the summation is performed over the above-described four inequivalent positions.

The system of equations (3.5) was solved analytically in the vicinity of the point, T, of absolute instability of the high-temperature phase, where $\hat{T}$ and $\hat{h}$ differ little from their isotropic values. In the remaining part of the temperature region we used numerical methods.

The behavior of the system is fully described by the function $a(T)$ (Fig. 1); the solution to the system (3.5) can be expressed in terms of $a(T)$ as follows:

$$\begin{gathered}\langle T_{\alpha\alpha\alpha\alpha}\rangle=\frac{11}{27};\ \langle T_{\alpha\alpha\beta\beta}\rangle=\frac{8}{27},\ \alpha\neq\beta;\\ \langle T_{1123}\rangle=\langle T_{3312}\rangle=-\langle T_{2213}\rangle={}^1/_6a(T);\\ \langle T_{1112}\rangle=\langle T_{2221}\rangle=\langle T_{2223}\rangle=\langle T_{3332}\rangle=-\langle T_{1113}\rangle=-\langle T_{3331}\rangle=-{}^1/_{12}a(T).\end{gathered} \tag{3.6}$$

There exist three more physically-equivalent solutions besides the solution (3.6). The existence of four solutions is due to the presence of four possible orientations for the crystal axes in our model. These orientations are equivalent: a spontaneous breaking of this symmetry occurs at $T<T_c$.

The results for the other models [including the continuous-rotation model (2.5)] in the self-consistent field approximation qualitatively coincide with the results (3.6) above. The behavior of the mean-field amplitude $a(T)$ is determined by the fact that at a sufficiently high temperature the system possesses neither stable nor metastable states with a nonzero mean crystal order, while the mean order approaches saturation as $T\to 0$. The symmetry-group structure that admits of, for example, the cubic invariant $I_3=\mathrm{Sp}\,\hat{T}^3$ is responsible for the discontinuous character of the phase transition.

Let us note at once some "numerical" characteristics of the curve $a(T)$ that do not depend on the specific choice of the Hamiltonian, and are therefore a consequence of the properties of the parameter $\Lambda(\mathbf{x})$ itself.

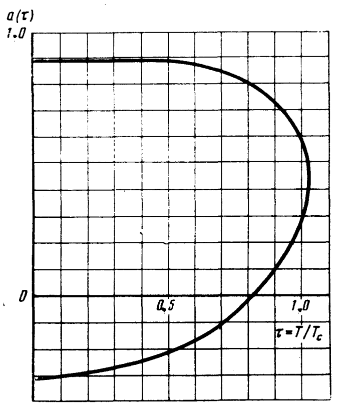

FIG. 1.

The $a(T)$ curve practically coincides with $a(0)$ in the range $0 \leqslant T < T_t - \Delta T$, where $\Delta T/T_t \sim 0.2-0.3$ (see Fig. 1). In the vicinity of the cuspidal point T_t, rapid variation of $a(T) \propto |T_t - T|^{1/2}$ takes place. The value $a(T_t) \approx a(0)/2$. This behavior of $a(T)$ leads to a small existence domain of the metastable crystal and to the appearance near the melting point T_c of anomalies, described in the following section, in the system's properties.

§4. THERMODYNAMIC PROPERTIES OF THE CUBIC SYSTEM

Let us briefly describe the main properties of the solution (3.5), (3.6). The function $a(T)$ in the vicinity of the cuspidal point T_t can be represented in the form

$$T_t - T = d(a - a_t)^2 + \dots \qquad (4.1)$$

For the model (3.5)

$$a_t \approx 0{,}45; \quad d \approx 2.6. \qquad (4.2)$$

The equilibrium-crystallization point T_c turns out to be numerically close to the point T_t at which the crystalline state becomes absolutely unstable:

$$(T_t - T_c)/T_t \approx 0{,}02. \qquad (4.3)$$

The configuration part, corresponding to the formula (3.5), of the thermodynamic potential of one unit cell is

$$\Delta\Phi = \frac{7}{2} a^2(T) - T \ln\left\{\exp\left(\frac{56}{9}\frac{a(T)}{T}\right) + 3\exp\left(-\frac{56}{27}\frac{a(T)}{T}\right)\right\}. \qquad (4.4)$$

The crystallization point T_c is determined by the condition $\Delta\Phi(T_c) = \Delta\Phi_0(T_c)$, where $\Delta\Phi_0(T)$ describes the high-temperature phase, and is equal to the expression (4.4) with $a \equiv 0$: $\Delta\Phi_0 = -2T \ln 2$.

The lifetime of the metastable state in the vicinity of T_t is short: at high ($\sim\frac{1}{3}$) concentrations of the "defective" regions the system contains many liquid-state nucleating centers with dimensions of the order of those of several unit cells (i.e., $\sim 10 r_0$, where r_0 is the interatomic distance). Estimates of the region ΔT_m in which the lifetime of the metastable crystal is not too short yield a value significantly smaller than $\Delta T = 0.02\ T_t$.

The contribution of the crystal order to the specific heat C of the system behaves in the vicinity of T_t like

$$\Delta C = -T\frac{\partial^2\Delta\Phi}{\partial T^2} \sim -T\frac{da}{dT} \approx d^{-1/2}\left(1 - \frac{T}{T_t}\right)^{-1/2}. \qquad (4.5)$$

The coefficient of the singular part of ΔC is numerically small. At the point T_c we have $\Delta C(T_c) \approx 5.3$. The quantity ΔC is the heat capacity per unit cell, taken as a physical point and containing n_0 atoms. From this we find that the ratio $\Delta C/C$ of the jump (4.5) to the total heat capacity C is $\Delta C/C \sim n_0^{-1}$ when the melting point T_c is lower than, or of the order of, the Debye temperature. For $n_0 \sim 10 - 10^2$ we have $\Delta C/C \sim 10^{-1} - 10^{-2}$.

The transition point T_c will be shifted if we take into account the nonuniversal contribution to the thermodynamic potential from the phonon and other degrees of freedom, a contribution which has different values in the ordered and disordered states. The contribution to the heat-capacity jump (4.5) is higher in the case in which the shift is toward T_t.

Our model does not explicitly take account of the dependence of the quantities of the theory on the volume V of the system or the external pressure p. To take the dependence on these parameters into account consistently, we must include in the Hamiltonian the terms describing the interaction between the order-parameter field $\Lambda(\mathbf{x})$ and the local-strain field $u_{\alpha\beta}(\mathbf{x})$ (i.e., the striction effects). Such an allowance has been made in the case of magnetic ordering by Larkin and Pikin.[7] We shall derive the corresponding relations with the aid of physical arguments.

In a given $\{\Lambda(\mathbf{x})\}$ configuration each defective region of the lattice is a source of elastic strains and corresponding displacements, which decrease with increasing distance $|\mathbf{r} - \mathbf{r}'|$ from the defect according to the law

$$\delta u_i(\mathbf{r} - \mathbf{r}') \propto \frac{r_i - r_i'}{|\mathbf{r} - \mathbf{r}'|^3}, \qquad (4.6)$$

where r′ is the position of the defect.

The formula (4.6) is easily derived by considering a body force, $\mathbf{F}(\mathbf{r})$, acting on an elastically isotropic body, and satisfying the condition $\int \mathbf{F}(\mathbf{r})d\mathbf{r} = 0$. The anisotropic part of the strains vanishes when averaged over the randomly arranged and randomly oriented defects. For the resulting mean displacement for a body of dimension R we obtain the volume change

$$\delta V = \int \left\{\nabla_\alpha \int \delta u_\alpha(\mathbf{r} - \mathbf{r}') n_d(\mathbf{r}') d\mathbf{r}'\right\} d\mathbf{r} \propto V\bar{n}_d, \qquad (4.7)$$

where $n_d(\mathbf{r})$ and $\bar{n}_d$ are the local the mean defect concentrations. The formula (4.7) formally corresponds to the evaluation of the integral for the thermodynamic potential $\Phi\{\sigma_{\alpha\beta}\}$ defined by the expression (2.7), in an approximation in which for each $\{\boldsymbol{\Delta}(\mathbf{x})\}$ configuration we take into account only the contribution to the integral over the displacements $u_\alpha(\mathbf{x})$ from the $\{u_\alpha(\mathbf{x})\}$ configuration that yields the minimum energy.

In our approximation the mean isotropic deformation of each element of the system under constant external pressure is equal to zero. In other words, in considering the body-dilatation effect associated with the variation of the degree of crystal order, we do not deform the unit cells on the average, i.e., we do not vary the "mean" local parameter Λ_0. In this approximation the configuration part of the thermodynamic potential Φ [see (4.4)] coincides with the potential $\Phi(T, p)$. In the next approximation it is necessary to allow for the energy associated with the inhomogeneous part of the defect-induced deformation. The major portion of this energy is localized. This portion is included in the $\Lambda(\mathbf{x})$-field Hamiltonian. We neglect the resulting weak interaction between widely separated defects. The change occurring in the elastic moduli when the temperature is changed at constant pressure, which is computed below, also makes some contribution to C_p. It follows from the above arguments that the configurational part of the heat capacity in our model is close to the experimental value of C_p (see also Ref. 8).

In Fig. 2 we present the experimental data on the specific heat ΔC_p for AgCl (the curve 2)[9] and the theoretical curve (the curve 1). The experimental ΔC_p values were obtained by subtracting from C_p the

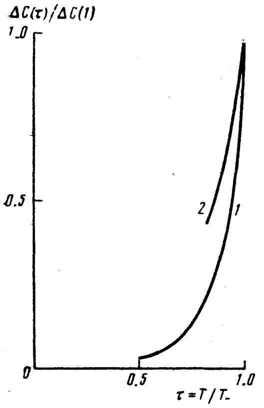

FIG. 2.

anomaly-free regular part, and the coefficient γ in the theoretical dependence $\Delta C_p = \gamma(T_t - T)^{-1/2}$ was obtained by fitting the curves at the point $T = T_c$.

For the volume expansion coefficient α we find from (4.7) that

$$\Delta\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \text{const}\frac{d\bar{n}_d}{dT} = -B\frac{da(T)}{dT}. \tag{4.8}$$

Figure 3 shows the plot of $\Delta\alpha_T$ as a function of the temperature $\tau = T/T_c$ (the continuous curve) and the experimental data for AgCl (points),[10] normalized to the $\Delta\alpha_T(1)$ value obtained from the theory at $T = T_c$.

Let us discuss the elastic properties of the model. The irreducible anisotropic part of the elasticity tensor $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ for the case of cubic symmetry is described by one coefficient. From this and geometric considerations we conclude that, without allowance for the Λ_0 fluctuations, the irreducible part of $\lambda_{\alpha\beta\gamma\delta}(\mathbf{x})$ is proportional to the irreducible part of $T_{\alpha\beta\gamma\delta}(\mathbf{x})$.

The elastic properties of the model in the vicinity of the melting point are determined by the fact that the crystal lattice contains an appreciable number of defects, i.e., of incorrectly oriented unit cells (texture). Let us find the defect concentration. Let us consider a system of ν cells, N_R of which have correctly, and N_d incorrectly, oriented axes. We shall, for definiteness, assume that the correct orientation corresponds to the discrete state 1, while the incorrect orientation corresponds to the states 2, 3, and 4. It follows from symmetry arguments that the states 2, 3, and 4 are energetically equivalent. In our model (3.5), the quantity T_{1123} arithmetically averaged over all the possible states is equal to zero, i.e., makes no contribution to $a(T)$. The cells in the state 1 make to $a(T)$ a contribution equal to $a(0)$. From this we easily find for the correct-cell and incorrect-cell (defect) concentrations, $\bar{n}_R$ and $\bar{n}_d$ respectively, the expressions

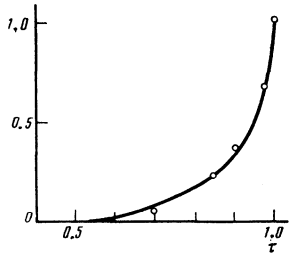

FIG. 3.

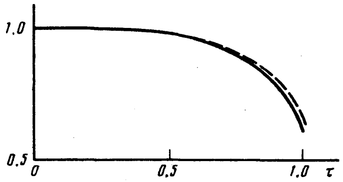

FIG. 4.

$$\bar{n}_d = \frac{3}{4}\left(1 - \frac{a(T)}{a(0)}\right);\quad \bar{n}_R = 1 - \bar{n}_d. \tag{4.9}$$

At the point $T = T_c$ we have $\bar{n}_d \approx 0.25$.

Let us assume that the anisotropic part of $\lambda_{\alpha\beta\gamma\delta}(\mathbf{x})$ is small compared to the isotropic part, and find the corrections to the mean elastic constants. Let us, following Lifshitz and Rozentsveĭg,[11] set

$$\tilde{\Lambda}_{\alpha\beta\gamma\delta} = \bar{\tilde{\lambda}}_{\alpha\beta\gamma\delta} + \Delta_{\alpha\beta\gamma\delta}. \tag{4.10}$$

Here $\Lambda_{\alpha\beta\gamma\delta}$ is the effective elasticity tensor and $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ is the texture-averaged constant. The corrections $\Delta_{\alpha\beta\gamma\delta}$ contain, besides the contribution to the irreducible part $\tilde{\Lambda}$ of the effective elasticity tensor, a contribution to the isotropic part $\Lambda - \tilde{\Lambda}$ of the tensor.

Our estimates (the values for the isotropic parts of the elastic coefficients were taken from the experimental data given in Refs. 4 and 12) show that in the model (3.5) $\tilde{\lambda} \sim a(T)$ and the corrections $\Delta_{\alpha\beta\gamma\delta}$ to the isotropic part are small on account of the smallness of $\tilde{\lambda}_{\alpha\beta\gamma\delta}$ in comparison with the isotropic part of $\lambda_{\alpha\beta\gamma\delta}$. Figure 4 shows the plots of $\tilde{\Lambda}_{1111}(\tau)/\tilde{\Lambda}_{1111}(0)$ (the continuous curve) and $\tilde{\lambda}_{1111}/\tilde{\lambda}_{1111}(0)$ (the dashed line) as functions of $\tau = T/T_c$. The strong dependence on $T - T_c$ of both $\tilde{\Lambda}$ and the corrections Δ to the isotropic part may be the cause of the experimentally observed rapid decrease of the values of the elastic constants in the immediate neighborhood of the melting point.[4]

The dependence of Young's modulus $E(\mathbf{q})$, $\mathbf{q} = (1, 0, 0)$, on the reduced temperature $\tau = T/T_c$ is shown in Fig. 5 (the continuous curve), where we also show the experimental data for KCl (the dashed line).[12] The necessary isotropic parts of the elastic moduli were taken from experiment, and the ratio $E_{\tau=1}/E_{\tau=0.29}$ was required to have the experimental value.

To carry out a comparison with experiment in a broader temperature region, and not only in the vicinity of T_c, we should take into account the variation, due to the anharmonicities, of the local moduli Λ_0 with temperature, which in the lowest approximation yields corrections to Λ_0 that are linear in the temperature.

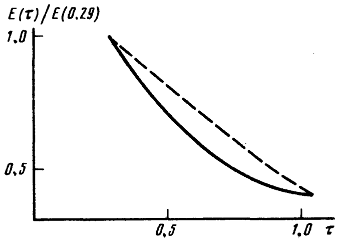

FIG. 5.

Thus, the above-described cellular model treats the texture as an ensemble of a relatively small number of incorrectly oriented regions in a regular-crystal matrix. Such a model is justified for the crystalline state.

In the disordered phase $a=0$, and the concentrations of cells of all orientations are the same. In this case each cell is, on the average, surrounded by cells of different orientations. The influence of such an environment leads, generally speaking, to a change in the character of the local order, i.e., of the quantity Λ_0. The consideration of these effects, which is necessary for the construction of a theory of the liquid state, falls, as does the calculation of the effects of the deviation from cubic symmetry, outside the limits of the present paper.

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