Theory of inhomogeneous crystal ordering

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Inhomogeneous crystal ordering is investigated within the framework of a theory in which a tensorial local-order parameter (a cubic nonor) is used. The correlation length in the vicinity of the point of absolute instability is found in the approximation of small fluctuations about the mean field: $r_c \sim r_0(\tau^*)^{-1/4}$, $r_c(T_m) \sim 2.4\, r_0$. The order near a plane surface of a crystal is found. The corrections due to the inhomogeneity of the surface layer are phenomenologically taken into account. The theory predicts that the temperature derivatives of the surface characteristics of the crystal can behave anomalously.

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1. INTRODUCTION

In the crystal-ordering theory developed by us earlier[1-3] the state of a crystal is described in terms of a local-crystal-order field $\Lambda(\mathbf{r})$. The quantity $\Lambda(\mathbf{r})$ for all crystals except those having hexagonal symmetry is a fourth-rank irreducible tensor representing the hexadecapole moment of the density distribution for the material in a small volume enclosing several coordination spheres. Various experiments indicate that this volume element contains about 10^2 atoms. Calculations with various model effective Hamiltonians[1-3] have shown that these models yield similar properties in the vicinity of the melting point T_m, and that these properties can be found to within 10% in the mean-field approximation.

In the cited papers we considered the case of homogeneous ordering in an infinite crystal. The purpose of the present paper is to consider inhomogeneous crystal ordering within the framework of the same models. In particular, an important source of inhomogeneity is the surface of a spatially bounded body. Outside the immediate neighborhood ($\Delta T \sim 0.1 T_m$) of the melting point, the crystal structure turns out to be rigid, and the correlation length, which coincides with the range of the influence of a point inhomogeneity on the order in the system, is small. As T_m is approached, this range increases, becoming infinite at the point of instability of the crystal.

2. EQUATIONS DESCRIBING THE INHOMOGENEOUS ORDER IN THE MEAN-FIELD APPROXIMATION

We limit ourselves to the case in which the Hamiltonian of the order has the form[1]

$$H\{\hat\Lambda\} = -\int [J(|\mathbf{r}-\mathbf{r}'|)\,\mathrm{Tr}\,\hat\Lambda(\mathbf{r})\hat\Lambda(\mathbf{r}') + \mathrm{Tr}\,\hat h_e(\mathbf{r})\hat\Lambda(\mathbf{r}')]\,dV\,dV', \qquad (1)$$

where $\hat h_e$ is the external field. In the mean-field approximation $\hat\Lambda(\mathbf{r})$ is replaced by its mean value $\langle\hat\Lambda(\mathbf{r})\rangle = \hat T$ at all points except the one in question, and for the point in question the probability distribution for $\hat\Lambda$ is equal to

$$dW\{\hat\Lambda\} = Z^{-1}\exp\{-H\{\hat\Lambda\}/T\}, \quad Z = \int d\hat\Lambda \exp\{-H\{\hat\Lambda\}/T\}. \qquad (2)$$

The Hamiltonian of the self-consistent field $H\{\hat\Lambda\}$ is

$$H\{\hat\Lambda\} = -\mathrm{Tr}\,\hat h\hat\Lambda, \quad \hat h(\mathbf{r}) = \hat h_e(\mathbf{r}) + \hat h_s(\mathbf{r}), \quad \hat h_s(\mathbf{r}) = \int J(|\mathbf{r}-\mathbf{r}'|)\,\hat T(\mathbf{r}')\,dV'. \qquad (3)$$

The mean value $\hat T$ of the parameter $\hat\Lambda$ is found from (2):

$$\hat T \equiv \langle\hat\Lambda\rangle = Z^{-1}\int \hat\Lambda \exp\left\{-\frac{H\{\hat\Lambda\}}{T}\right\} d\hat\Lambda. \qquad (4)$$

In Refs. 1–3 Eqs. (3) and (4) are solved for the case in which the integration over all the $\hat\Lambda$ configurations reduces to integration over all the rotations $\hat q$ of the three-dimensional rotation group $SO(3)$ ($\hat\Lambda = \hat q\hat\Lambda_0$; the continuous model[2]), or over the rotations forming a discrete subgroup of $SO(3)$ in the case of homogeneous ordering in zero external field (i.e., at $\hat h_e = 0$). Near the melting point the quantity $\hat T(\hat h)$ depends little on the model.

Let us consider a system in which the local order possesses cubic symmetry. In this case all the irreducible tensors $\hat T$, $\hat h$, $\hat h_e$, and $\hat\Lambda$ are proportional to the standard tensor $\bar\pi_{\alpha\beta\gamma\delta}$ (the cubic nonor), which is the irreducible part of the tensor

$$\pi_{\alpha\beta\gamma\delta} = \sum_{i=1}^{3} n_\alpha^{(i)} n_\beta^{(i)} n_\gamma^{(i)} n_\delta^{(i)}, \qquad (5)$$

where $\mathbf{n}^{(1)}$, $\mathbf{n}^{(2)}$, and $\mathbf{n}^{(3)}$ are the set of three mutually orthogonal unit vectors. Introducing the invariant amplitudes

$$\hat T(\mathbf{r}) = a(\mathbf{r})\bar\pi, \quad \hat h_s(\mathbf{r}) = h_s(\mathbf{r})\bar\pi, \quad \hat h_e(\mathbf{r}) = h_e(\mathbf{r})\bar\pi, \qquad (6)$$

we write Eqs. (3) and (4) in the form

$$a(\mathbf{r}) = a[h(\mathbf{r}), T];$$
$$h(\mathbf{r}) = h_e(\mathbf{r}) + \int J(|\mathbf{r}-\mathbf{r}'|)\,a(\mathbf{r}')\,dV'. \qquad (7)$$

In the discrete four-state model[1] with the temperature measured in units of the quantity

$$T_0 = \int J(|\mathbf{r}|)\,dV$$

the function $a(h)$ has the form[1]

$$a(h) = \frac{8}{9}\,\frac{\exp(224h/27T) - 1}{\exp(224h/27T) + 3}. \qquad (8)$$

Equation (7) with suitable boundary conditions describes the inhomogeneous ordering. Let us consider the solution to this nonlinear equation when the deviations from the homogeneous order in an infinite system with $h_e = 0$ are small:

$$h(\mathbf{r}) = h_0 + \delta h(\mathbf{r}),$$

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$$a(\mathbf{r})=a_0+\delta a(\mathbf{r})=a_0+\alpha\delta h(\mathbf{r}),\quad \alpha=\left(\frac{da}{dh}\right)_{h=h_0}, \tag{9}$$

$$\delta h(\mathbf{r})=h_e(\mathbf{r})+\alpha\int J(|\mathbf{r}-\mathbf{r}'|)\delta h(\mathbf{r}')dV'. \tag{10}$$

For the purpose of solving the linear equation (10), we go over to the Fourier transforms

$$\delta h(\mathbf{r})=\sum_k \delta h_k e^{i\mathbf{kr}},\quad h_e(\mathbf{r})=\sum_k h_{ek}e^{i\mathbf{kr}},$$

$$J(\mathbf{r})=\sum_k J_k e^{i\mathbf{kr}}.$$

We find from (10) that

$$\delta h_k=\frac{h_{ek}}{1-\alpha J_k}. \tag{11}$$

The solution for the change that occurs in the order when a delta-function perturbation $h_e(\mathbf{r})\sim\delta(\mathbf{r})$ is switched on at the coordinate origin is the Green function for Eq. (10), and coincides up to a constant factor with the correlation function in the approximation of small fluctuations about the mean field. Then h_{ek} = const, and it is necessary to consider the zeros of the denominator in (11), i.e., the roots of the equation

$$1-\alpha(T)J_k=0. \tag{12}$$

The line $h=J_0a$ touches the curve $a=a(h/T)$ at the point T^* of absolute instability of the crystal; therefore,

$$\alpha(T^*)=\frac{da}{dh}\bigg|_{h_0,T^*}=J_0^{-1}$$

and Eq. (12) has the root $\mathbf{k}_c=0$. For small $\tau^*=(T^*-T)/T^*$, the small $\mathbf{k}$ region where

$$J_k\approx J_0(1-k^2/k_0^2) \tag{13}$$

is important; the quantity $r_0\sim k_0^{-1}$ is the range of the interaction of the order parameter. The point of contact $a=a_0$ at $T=T^*$ is a regular point on the $a(h)$ curve, and near this point

$$\alpha(a)\approx\alpha(a_0)[1-\gamma(a-a_0)]. \tag{14}$$

Recognizing that $\alpha(a_0)=J_0^{-1}$ and that near T^* (see Ref. 1)

$$a(T)-a_0=(\tau^*/d)^{1/2}, \tag{15}$$

we find for the quantity k_c in the vicinity of T^* the expression

$$k_c^2=-k_0^2\gamma(\tau^*/\alpha)^{1/2}, \tag{16}$$

and for the Green function $G(r)$ the relation

$$G(r)\sim\frac{1}{r}\exp\left(-\frac{r}{r_c}\right),\quad r_c=\frac{1}{|k_c|}=r_0\left(\frac{d}{\gamma^2\tau^*}\right)^{1/4}. \tag{17}$$

The quantity r_c is the correlation length. Substituting the specific values for the constants of the four-state model (8) at the melting point T_m, we find that

$$r_c(T_m)\sim 2.4r_0. \tag{18}$$

The formulas (14) and (15) are valid in the immediate neighborhood ($\tau^*\sim 10^{-2}$) of T^*. Outside this neighborhood $r_c\approx r_0$.

We can expect that the quantity r_0 will be of the order of the cluster dimension, and that the interaction of the crystal order will primarily have the character of a nearest-neighbor interaction. In this case, as follows from experiment, r_0 is equal to four–seven interatomic distances. Far from the melting point the lattice defects having these characteristic dimension are localized, while in a narrow neighborhood of T_m the changes in the structure are smeared over an appreciably large region.

3. ONE-DIMENSIONAL INHOMOGENEITY. PLANE CRYSTAL BOUNDARY

Let us consider the case in which the order depends on only one coordinate x. We write Eq. (7) in the form

$$h(x)=h_e(x)+\int \tilde{J}(|x-x'|)a(x')dx', \tag{19}$$

where

$$\tilde{J}(|x|)=\int J(|\mathbf{r}|)dy\,dz. \tag{20}$$

We can expect the properties of the solutions to Eq. (19) for the function $\tilde{J}(|x|)$, which decreases fairly rapidly with increasing $x>x_0$ and varies little in the region $x<x_0$, to depend weakly on the specific form of $\tilde{J}(|x|)$. It is convenient to take $\tilde{J}$ in the form

$$\tilde{J}(|x|)={}^1/_2e^{-|x|}. \tag{21}$$

Here we have used the system of units in which $T_0=x_0=1$.

Differentiating (19) twice, we obtain a differential equation that takes at $h_e=0$ the form

$$d^2h/dx^2=h(x)-a[h(x)]. \tag{22}$$

Equation (22) coincides in form with the equation of the one-dimensional motion of a material particle with unit mass and with a coordinate h that depends on the time x. The role of the potential energy is played by the quantity

$$U(h)=-\int_0^h[y-a(y)]dy. \tag{23}$$

The solution to (22) is

$$x-x_0=\int_{h(x_0)}^{h(x)}\frac{dy}{[2(E-U(y))]^{1/2}}, \tag{24}$$

where E is a constant. The quantity $U(h)$ is directly related with the thermodynamic potential $\Phi(h)$. Thus, in the four-state model[1]

$$U(h)=-{}^1/_7\Phi(h)-{}^1/_7T\ln 4. \tag{25}$$

Figure 1 shows the plots of $U(h)$ for $T=T_m$ and $T_L<T<T_m$, where T_L is the absolute-instability temperature for the high-temperature phase (liquid).

The system exhibits behaves differently at different energies E, under different boundary conditions, and at different temperatures. The simplest solutions describe: the transition region between the liquid and crystal phases at $T=T_m$, the periodic oscillations of the order parameter about some mean value, plane nucleation centers of the corresponding phases, and the

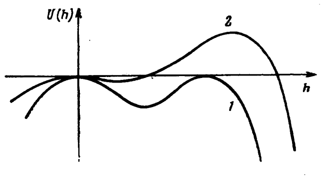

FIG. 1. Plot of $U(h)$ for $T = T_m$ (curve 1) and $T_L < T < T_m$ (curve 2).

small inhomogeneities due to the small deviation of the order from its homogeneous value.

We limit ourselves to the "domain wall" between the liquid and crystal phases at $T = T_m$. The boundary conditions $h \to h_B$ ($x \to +\infty$), $h \to 0$ ($x \to -\infty$), where h_B is the homogeneous-order parameter, are fulfilled for $E = 0$. The solution (24) describes three regions. For $|x - x_0| > L$ there occur two different phases whose order parameters approach the boundary values exponentially. The region $|x - x_0| < L$ is a domain wall with thickness $L \sim 1$. The plot of $h(x)$ is shown in Fig. 2.

Let us now consider the solution for the case in which the crystal occupies the half-space $x > 0$ and the crystal boundary lies in the plane $x = 0$, i.e., the case in which

$$a=0 \quad \text{for} \quad x<0. \tag{26}$$

The properties of the material at the surface are physically different from its properties in the interior. Thus, for example, the density of the surface layer is, generally speaking, not equal to the volume density. Equation (19) is therefore inapplicable in a small neighborhood of the point $x = 0$. We assume first that the change in the form of the equation is slight, and neglect this change. Differentiating Eq. (19) once at $x = 0$, we obtain in this approximation the boundary condition for the field $h(0)$ at the surface:

$$h'(0)=h(0). \tag{27}$$

The first integral of Eq. (22)

$$\tfrac{1}{2}(dh/dx)^2+U(h)=E \tag{28}$$

at the point $x = 0$ yields together with (27) the relation

$$E-\tfrac{1}{2}h^2(0)=U(h(0)). \tag{29}$$

The relation (29) determines the quantity $h(0)$. Figure 3 shows a plot of Eq. (29).

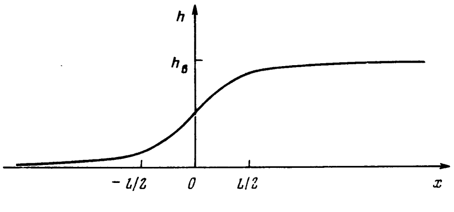

FIG. 2. Plane boundary between liquid and crystal at $T = T_m$.

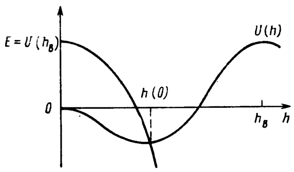

FIG. 3. Graphical solution of Eq. (29) for $h(0)$.

We expand $E = U(h_B, T)$ in powers of $\tau = (T - T_m)/T_m$ for $T < T_m$ near T_m. For sufficiently small h and $|\tau|$ we have $U(h, \tau) \approx U(h, 0)$. For $h(0)$ we get as a result

$$h(0) \sim (Q\tau)^{1/2}, \tag{30}$$

where Q is proportional to the heat of fusion. The solution (24) for $|\tau| \ll 1$ and with allowance for the condition (30) describes a crystal for which a layer of thickness λ at the surface is practically melted; for $\tau \to 0$ and $h \ll 1$ we have near the surface

$$h(x)=h(0)\exp(2.38x), \tag{31}$$

so that

$$\lambda(\tau)=|\ln h(0)| \sim |\ln|\tau||. \tag{32}$$

For sufficiently large $|\tau|$ outside a narrow range of temperatures near T_m, $h(0)$ and $a(0)$ are close to their values in the interior, the influence of the surface and the range of this influence are small, and a small change in the conditions at the surface has little effect on the solution. As $\tau \to 0$, small changes in the conditions in the surface layer greatly change the properties of the solution. We shall take account of the singular properties of the surface layer phenomenologically, introducing an additional field δh that acts on the surface and is responsible for the total effect of the surface-related distortions of the homogeneity of the material on the cubic component of the order parameter. Accordingly, in place of the condition (27), we write

$$h'(0)=h(0)+C. \tag{33}$$

As $\tau \to 0$ and at $h \ll 1$, the order parameter $h(x)$ near the surface is given by the formula (31), where

$$h(0)=1.2\,C+0.36(2.04\,C^2-\tau)^{1/2}. \tag{34}$$

It follows from (34) that, in the immediate neighborhood of the phase transition (i.e., for $|\tau| \ll C^2$), $\lambda(\tau)$ is a constant proportional to $-\ln C$, while $\lambda(\tau) \sim -\ln|\tau|$ for $C^2 \ll |\tau| \ll 1$.

An important characteristic is the derivative of $\lambda(\tau)$:

$$\frac{\partial\lambda}{\partial|\tau|}=-\frac{1.19}{(2.04C^2-\tau)^{1/2}[3.4C+(2.04C^2-\tau)^{1/2}]}. \tag{35}$$

Figure 4 shows the behavior of $\partial\lambda/\partial|\tau|$ for $C = 0.1$ and $C = 0.01$; from this it follows that for $C \leqslant 0.01$ at $T \approx T_m$ ($|\tau| \leqslant 10^{-3}$) the change in the character of the ordering in the boundary layer occurs rapidly as the temperature is varied.

In the region of metastable existence of the crystal (see Ref. 1), at $\tau_b = 2.04C^2$, radicand of (34) and (35)

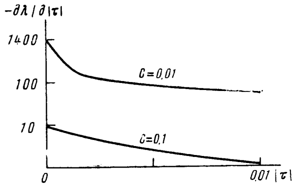

FIG. 4. Plot of $\partial\lambda/\partial|\tau|$ for $C = 0.1$ and $C = 0.01$.

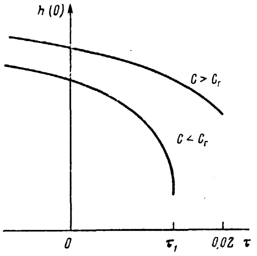

FIG. 5. The τ dependence of $h(0)$ as given by Eq. (34).

vanishes if C is sufficiently small. When $\tau > \tau_b$, the crystal disintegrates because of the instability of the surface. Using $(T^* - T_m)/T^* = 0.02$ as the width of the metastable region, we find for the constant C the boundary value $C_b = 0.1$. For $C > C_b$ the surface does not disintegrate spontaneously in the region of metastability of the crystal: the transition into the liquid state is due to volume effects. For $C < C_b$ there exists a region $\tau_1 < 0.02$ in which the surface is unstable; the destruction of the crystal structure is connected in this case with the surface or with defects. The dependence of $h(0)$ on τ is shown qualitatively for different values of C in Fig. 5.

The analytic formulas (34) and (35) are valid for $C \leqslant C_{\text{met}} \sim 0.1$ ($C_{\text{met}} \sim \frac{1}{6} h_B$). It is possible that the behavior of the surface characteristics of some crystals in the neighborhood of the melting point is connected with the small value of C (see below).

In the general case the extent to which the field δh affects the properties of the crystal near the surface and the value of C depends on the mutual orientation of the crystallographic axes and the surface. When this orientation is changed, the energy $U(h)$, i.e., Φ [see (25)], changes. In other words, the constant C is related to the surface tension of the crystal.

4. SURFACE EFFECTS

The difference between the physical properties of a crystal at its surface and in its interior is expressed by a number of surface characteristics: the blackness factor, the surface microhardness and conductivity, the work function, etc. Each of these characteristics contains integrated information about the character of the crystal ordering in a layer of thickness R near the surface. At low temperatures the entire crystal is almost homogeneous, and no strong surface anomalies occur. In the vicinity of the melting point the system behaves differently, depending on the ratio $\lambda(\tau)/R$. The quantities for which $\lambda(0)/R \ll 1$ have strong anomalies near the surface. In the $\lambda(0)/R \gg 1$ case the order in the entire crystal region that determines a given surface characteristic W differs greatly from the order in the interior of the crystal.

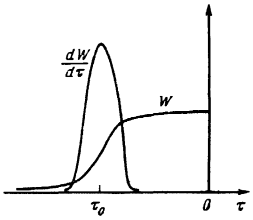

FIG. 6. Qualitative behavior of a surface characteristic W and of $dW/d\tau$ as functions of τ.

Let difference between the value of $W(\tau)$ and $W(\tau, h = h_B)$ be designated $\Delta W(\tau)$. For τ such that $\lambda(\tau)/R \ll 1$, we have

$$\Delta W(\tau) \sim \delta W(\tau) \lambda(\tau),$$

where $\delta W(\tau)$ is the change in the density $W(\tau)$. In the region $\lambda(\tau)/R \gg 1$

$$\Delta W(\tau) \sim \delta W(\tau) R.$$

If C is sufficiently small, then

$$\frac{\partial \lambda}{\partial \tau} \gg \frac{\partial \delta W}{\partial \tau} \sim -\frac{da}{d\tau}$$

(for small $|\tau|$). From this it follows that the derivative $dW/d\tau$ has a maximum at $\tau \sim \tau_0$ ($\lambda(\tau_0) \sim R$), and that the smaller C the greater this maximum. The behavior of W and $dW/d\tau$ as functions of the temperature is qualitatively depicted in Fig. 6.

It is possible that the experimentally observed[4,5] anomalies attest the smallness of the quantity C in the investigated materials, and that they are a manifestation of the effects described above [see (34) and (35)].

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