# A continuum model of crystal melting

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Based on the Born hypothesis that the shear modulus reduces to zero at a critical point, we construct a continuum theory of melting. We show that the fundamental contribution to the variation of the shear modulus is given by dislocations, and obtain a dependence of the effective shear modulus on the temperature of the crystal that agrees well with the experimental data.

## INTRODUCTION

Among the multitude of papers on the theory of melting (based on the Lindemann criterion,[1] computer modeling methods,[2] use of an empirical equation of state[1,3]) the dislocation model of melting apparently reflects most adequately the underlying physical process.[4–7] This model starts with a quasimicroscopic picture of the phenomenon, in which the crystal is treated as an elastic medium with line defects, i.e., dislocations. It is assumed that melting of the material occurs at the instant when dislocations of infinite length can form in the materials,[8] leading to a loss of long-range crystal order.[7] The description of dislocations in these papers is carried out by using a three-component complex "disorder" field.[8] The appearance of a phase transition in the disorder field then corresponds to a phase transition in the dislocation system of the crystal with the formation of dislocations of infinite length.[7,8] Despite the fact that work in this direction has been carried extremely far, no one has calculated the temperature for melting of real materials within the framework of this approach.

On the other hand, there is a well-known macroscopic criterion for melting: the Born criterion.[1,8] The Born criterion assumes that the melting of a material takes place at that temperature for which the shear modulus vanishes. The Born hypothesis agrees with experiment; the empirical dependence of the shear modulus $\tilde{\mu}(T)$ on the temperature $T$ for metals has a simple and universal form:[1]

$$\tilde{\mu}/\mu=1-(T/T_M)^2, \qquad (1)$$

where $\mu$ is the shear modulus at $T=0$, and $T_M$ is the melting temperature of the metal.

The idea of Born is attractive by virtue of its generality; however, it says nothing about the physical model of the process, and does not answer the question of why the shear modulus behaves in this way. Attempts to calculate the change in the elastic moduli by taking into account phonon anharmonicity have not led to any desirable results.[1]

It is obvious that the Born criterion and the dislocation model are saying the same thing; reduction of the shear elastic modulus to zero corresponds to reduction to zero of the energy per unit length required to create a dislocation. Accordingly, both models lead to the appearance of a phase transition in the crystal's dislocation system.

The goal of this paper is to construct a model of melting that unites the Born criterion with ideas from the dislocation model of melting. It turns out that this unification allows us not only to explain the relation (1), but also to calculate melting temperatures for real metals that agree with the experimental temperatures. In order to describe melting as an essentially macroscopic phenomenon, we must first parametrize correctly all the possible microscopic configurations of the crystal that give or can give contributions to the physical process. In this paper we adopt the following parametrization: the vibration of atoms around their equilibrium position is described by phonon modes, which are treated within the framework of elasticity theory. As the temperature rises, effects due to anharmonicity become important: local modes appear that are connected with point defects of the crystal lattice, along with larger collective displacements of atoms from their equilibrium positions, i.e., dislocations. Within this parametrization, the real behavior of condensed matter is extrapolated by using functions that are correct in the limits of small and large displacements of atoms from their equilibrium positions.

A description of melting within the framework of this parametrization reduces to investigating static properties and calculating effective elastic moduli for a material system containing a phonon component (treated in this paper within elasticity theory), a component due to local modes (i.e., of point defects) and a component due to dislocations, and all possible interactions between these components.

The identification of the class of condensed matter states listed above is also a fundamental approximation of this paper.

The paper is set up as follows. In the first section we obtain general relations that allow us to calculate the effective elastic moduli of a material containing defects of various types. In the second section we construct a vacancy model of melting. As it turns out, this model does not agree with experiment, leading us to construct a dislocation model of melting based on the Born hypothesis. This is done in the third section of the paper.

## 1. VARIATION OF ELASTIC MODULI OF AN ISOTROPIC CRYSTAL IN THE PRESENCE OF DEFECTS

The Hamiltonian of an isotropic elastic material which contains defects (both point and line) can be written in the form

$$H=H_{\rm el}+H_{\rm disl}+H_{\rm pd}+H_{int}, \qquad (2)$$

where $H_{\rm el}$, $H_{\rm disl}$, $H_{\rm pd}$, and $H_{\rm int}$ are, respectively, the Hamiltonians of elastic deformation, dislocations, point defects, and the interactions between them. In this case

$$H_{\rm el}=\int\left\{\frac{Ku_{ll}^2}{2}+\mu\left(u_{ik}-\frac{1}{3}\delta_{ik}u_{ll}\right)^2\right\}d\mathbf{r}. \qquad (2')$$

Here $K$ and $\mu$ are the elastic moduli of a defectless crystal,

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and $u_{ik}$ is a deformation tensor. The Hamiltonians $H_{\rm disl}$, $H_{\rm pd}$, and $H_{\rm int}$ will be determined below.

The partition function $Z$ of the system is an integral of the probability density $W \sim e^{-H/T}$ of the various configurations of condensed matter with respect to all realizable configurations of defects and fields $u_{ik}$:

$$Z = \int D\{\Gamma\} Du_{ik} e^{-H/T}. \tag{3}$$

Here $D\{\Gamma\}$, $Du_{ik}$ are integration measures in the spaces of defect configurations and fields $u_{ik}$, respectively.

Introducing the effective Hamiltonian $H_{\rm eff}$,

$$H_{\rm eff}[u_{ik}] = -T \ln \int D\{\Gamma\} \exp\{-(H_{\rm disl} + H_{\rm pd} + H_{\rm int})/T\}, \tag{4}$$

we can cast the partition function (3) in the form

$$Z = \int Du_{ik} e^{-H_{\rm el}/T} e^{-H_{\rm eff}/T}. \tag{5}$$

By expanding $H_{\rm eff}[u_{ik}]$ in a series with respect to $u_{ik}$ and retaining terms up to quadratic in $u_{ik}$, we find that the presence of defects in the crystal structure leads to the following change in the elastic moduli of condensed matter:

$$\frac{\tilde{K}(\mathbf{r},\mathbf{r}')}{2} - \frac{\tilde{\mu}(\mathbf{r},\mathbf{r}')}{3} = \left(\frac{K}{2} - \frac{\mu}{3}\right)\delta(\mathbf{r}-\mathbf{r}') + \left.\frac{\delta^2 H_{\rm eff}}{\delta u_{ll}(\mathbf{r})\,\delta u_{ll}(\mathbf{r}')}\right|_{u_{ik}=0},$$

$$\tilde{\mu}(\mathbf{r},\mathbf{r}') = \mu\delta(\mathbf{r}-\mathbf{r}') + \left.\frac{\delta^2 H_{\rm eff}}{\delta u_{ik}(\mathbf{r})\,\delta u_{ik}(\mathbf{r}')}\right|_{u_{ik}=0}. \tag{6}$$

Here $\tilde{K}$, $\tilde{\mu}$ are the effective moduli of condensed matter with defects. For the case of homogeneous matter, Eq. (6) is conveniently written by passing to a Fourier representation with respect to the variable $|\mathbf{r} - \mathbf{r}'|$:

$$\frac{\tilde{K}(\mathbf{p})}{2} - \frac{\tilde{\mu}(\mathbf{p})}{3} = \left(\frac{K}{2} - \frac{\mu}{3}\right) + \left.\frac{\delta^2 H_{\rm eff}[u_{ik}(\mathbf{p})]}{\delta u_{ll}(\mathbf{p})\,\delta u_{ll}(-\mathbf{p})}\right|_{u_{ik}=0},$$

$$\tilde{\mu}(\mathbf{p}) = \mu + \left.\frac{\delta^2 H_{\rm eff}[u_{ik}(\mathbf{p})]}{\delta u_{ik}(\mathbf{p})\,\delta u_{ik}(-\mathbf{p})}\right|_{u_{ik}=0}. \tag{7}$$

From Eq. (7) it follows that in the general case the presence of defects leads to the appearance of dispersion in the elastic properties of the condensed matter.

## 2. A VACANCY MODEL OF CRYSTAL MELTING

Relation (7) allows us to construct a vacancy model of crystal melting. Let us construct this model in the following way: at nonzero temperature point defects, specifically vacancies, are present in the crystal, whose concentration increases with temperature. This increase in the vacancy concentration leads to a change in the elastic moduli of the material. According to the Born criterion, the temperature at which the modulus of uniform shear $\tilde{\mu}(\mathbf{p} = 0)$ reduces to zero will be the melting temperature $T_M$ of the crystal in this model. Other types of defects are not taken into account here.

Let us turn to calculating the change in the shear modulus $\mu$ due to the effect of point defects. The effective Hamiltonian (1) of an elastic medium in the presence of point defects can be written in the form

$$H_{\rm eff} = -T \ln \int \exp\left\{-\frac{H_{\rm int}[\rho, u_{ik}] + F[\rho, u_{ik}]}{T}\right\} D\{\rho\}, \tag{8}$$

where $F[\rho, u_{ik}]$ is the free energy of the system of point defects in the elastic deformed medium and $D\{\rho\}$ denotes integration over all configurations of the defect density $\rho(\mathbf{r})$. The interaction Hamiltonian $H^{\rm pd}_{\rm int}$ is expressed in terms of the stress tensor $\sigma^{\rm pd}_{ik}$ caused by a single point defect in the following way:

$$H^{\rm pd}_{\rm int} = \int u_{ik}(\mathbf{r})\sigma^{\rm pd}_{ik}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')\,d\mathbf{r}'\,d\mathbf{r}. \tag{9}$$

In the functional integral (8) the primary contribution comes from configurations for which

$$\delta H^{\rm pd}_{\rm int}/\delta\rho + \delta F/\delta\rho = 0. \tag{10}$$

For a system of point defects $\delta H^{\rm pd}_{\rm int}/\delta\rho$ has the sense of an external field

$$V_{ext} = \frac{\delta H^{\rm pd}_{\rm int}}{\delta\rho}, \quad H^{\rm pd}_{\rm int} = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r}. \tag{11}$$

In an undeformed medium the equilibrium density of point defects $\bar{\rho}$ is determined by the condition

$$\left.\frac{\delta F}{\delta\rho}\right|_{\rho=\bar{\rho}} = 0. \tag{12}$$

Assuming the deviation of the density $\delta\rho$ from $\bar{\rho}$ associated with the strain $u_{ik}$ in the medium is small, by combining Eqs. (11) and (12) it is not difficult to obtain

$$H_{\rm eff}[u_{ik}] = \int V_{ext}(\mathbf{r})\bar{\rho}(\mathbf{r})\,d\mathbf{r} + F[\bar{\rho}] + \frac{1}{2}\int V_{ext}(\mathbf{r})\beta(\mathbf{r},\mathbf{r}')V_{ext}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}', \tag{13}$$

where $\beta(\mathbf{r},\mathbf{r}')$ is the linear response function of the system of point defects to the external field:

$$\delta\rho(\mathbf{r}) = \int \beta(\mathbf{r},\mathbf{r}')V_{ext}(\mathbf{r}')\,d\mathbf{r}'. \tag{14}$$

The quantity $\sigma^{\rm pd}_{ik}$ can be calculated in the model by considering a point defect as a dilatation center:[9]

$$\sigma^{\rm pd}_{ik}(\mathbf{r}) = \left\{(K - {}^2/_3\mu)\delta_{ik}\delta(\mathbf{r}) - 2\mu\frac{\partial^2}{\partial x_i\,\partial x_k}\frac{1}{r}\right\}\Delta V, \tag{15}$$

where $\Delta V$ is the dilatation volume of the defect.

At low temperatures the dilatation volume for the vacancy comes to $\Delta V \approx (0.1\text{–}0.2)a^3$, where $a$ is the lattice constant.

Using Eq. (15) we obtain for the term in $H_{\rm eff}$ that is quadratic in $u_{ik}$

$$\frac{1}{2}\int V_{ext}\beta V_{ext}\,d\mathbf{r}\,d\mathbf{r}' = 2\mu^2\Delta V^2 \int u_{ik}T_{iklm}u_{lm}\,d\mathbf{r}\,d\mathbf{r}', \tag{16}$$

where

$$T_{iklm}(\mathbf{r},\mathbf{r}')=\int a_{ik}(\mathbf{r}-\boldsymbol{\xi})\,\beta(\boldsymbol{\xi}-\boldsymbol{\xi}')\,a_{lm}(\mathbf{r}'-\boldsymbol{\xi}')\,d\boldsymbol{\xi}\,d\boldsymbol{\xi}',$$
$$a_{ik}(r)=(\delta_{ik}r^2-3x_ix_k)/r^5. \qquad (17)$$

In the Fourier representation the integral (16) and the tensor $T_{iklm}(p)$ have the form

$$\frac{1}{2}\int V_{ext}\beta V_{ext}\,d\mathbf{r}\,d\mathbf{r}'$$
$$=2\mu^2\Delta V^2\int u_{ik}(\mathbf{p})\,T_{iklm}(\mathbf{p})\,u_{lm}(-\mathbf{p})\frac{d\mathbf{p}}{(2\pi)^3}, \qquad (18)$$

$$T_{iklm}(\mathbf{p})=\int e^{i\mathbf{p}\mathbf{r}}\,T_{iklm}(\mathbf{r})\,d\mathbf{r}. \qquad (19)$$

Averaging the tensor $T_{iklm}(\mathbf{p})$ over the directions of the vector $\mathbf{p}$ and combining Eqs. (16), (15), and (7), after some simple calculations we obtain an expression for the effective shear modulus $\mu(\mathbf{p}=0)$ in an elastic medium with vacancies:

$$\tilde{\mu}(\mathbf{p}=0)=\mu+\frac{4}{15}\pi^4(\mu\,\Delta V)^2\beta(\mathbf{p}=0). \qquad (20)$$

In deriving this relation we have used the elastic modulus of a defectless material in expression (15); however, the problem is formulated so that the tensor $\sigma_{ik}^{\text{pd}}$ describes stresses that arise from point defects in some "composite" material consisting of an elastic medium that is described by the moduli $\mu$ and $K$, and a system of point defects. In connection with this, in Eq. (15) it would be correct to use a renormalized shear modulus $\tilde{\mu}$. However, the dilatation volume $\Delta V$ also depends on $\mu$:$\Delta V\sim 1/\mu$ (see Ref. 10), while in the final analysis Eq. (20) includes the combination $\mu\Delta V$, which is invariant relative to changes in $\mu$.

In order to determine $T_M$ it remains to calculate the response function $\beta(\mathbf{p}=0)$. The response function is connected with the pair correlation function of the system of interacting vacancies $g_2(\mathbf{r},\mathbf{r}')$ by the following relations:

$$T\beta(\mathbf{r},\mathbf{r}')=g_2(\mathbf{r},\mathbf{r}')-\bar{\rho}(\mathbf{r})\bar{\rho}(\mathbf{r}')+{}^1/_2(\rho(\mathbf{r})+\rho(\mathbf{r}'))\,\delta(\mathbf{r}-\mathbf{r}'), \qquad (21)$$

$$F=F_0+\frac{1}{2}\int_0^1 g_2(\mathbf{r},\mathbf{r}',\alpha)\,U(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'\,d\alpha, \qquad (22)$$

where $F_0$ is the free energy of the noninteracting vacancies and $U$ is the potential of the vacancy interactions. Furthermore,

$$F_0=\int\varepsilon_v\bar{\rho}\,d\mathbf{r}+T\int[\bar{\rho}\ln\bar{\rho}/\rho_0-\bar{\rho}]\,d\mathbf{r}. \qquad (23)$$

Here $\varepsilon_v$ is the energy required to create a vacancy and $\rho_0$ is the number of atoms of the material per unit volume.

At small distances the potential $U$ has the form of a potential well, corresponding to the possibility of forming the experimentally observed coupled state of two vacancies (i.e., a divacancy) with a binding energy $\varepsilon_d$ (Ref. 11). At large distances the vacancies interact via the elastic field, which corresponds to

$$U(\mathbf{r})=S(\mathbf{n})/r^3,\qquad \int S(\mathbf{n})\,d\mathbf{n}=0,\qquad \mathbf{n}=\mathbf{r}/r. \qquad (24)$$

The equilibrium concentration of vacancies $\bar{\rho}$ is determined by Eq. (12) which, in view of Eq. (23), has the form

$$\varepsilon_v+T\ln\bar{\rho}/\rho_0+\frac{1}{2}\frac{\delta}{\delta\rho}\left\{\int_0^1 g_2(\lambda,\mathbf{r},\mathbf{r}')\,U(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'\,d\lambda\right\}=0. \qquad (25)$$

In what follows we will show that up to the melting temperature we have $\bar{\rho}/\rho_0\ll 1$.

The last term in Eq. (25) is of order $(\bar{\rho}/\rho_0)\varepsilon_d$. According to the experimental data we have $\varepsilon_v\sim 1$–$3$ eV, $\varepsilon_d\sim 0.1$–$0.5$ eV (Ref. 11). We can therefore neglect the vacancy-vacancy interactions in this case and assume that

$$\bar{\rho}/\rho_0=e^{-\varepsilon_v/T}. \qquad (26)$$

In order to obtain the response function $\beta(\mathbf{p}=0)$ of interest to us it is convenient to make use of the relation

$$\frac{\partial P}{\partial\bar{\rho}}=-\bar{\rho}\beta^{-1}(\mathbf{p}=0), \qquad (27)$$

which follows from Eq. (21) and the thermodynamic identity (see Ref. 12)

$$\frac{\partial P}{\partial\bar{\rho}}=\frac{T}{1+\bar{\rho}\nu(\mathbf{p}=0)}, \qquad (28)$$

where

$$\nu(\mathbf{r})=\frac{g_2(\mathbf{r})}{\bar{\rho}^2}-1.$$

Here $P=\partial F/\partial\Omega$, and $\Omega$ is the system volume.

In order to calculate the quantity $P$ in a system with a specified interaction potential $U$ we make use of the Van der Waals approximation;

$$P(\bar{\rho})=\frac{\bar{\rho}T}{1-\bar{\rho}/\rho_0}-\frac{7}{2}\frac{\varepsilon_d\bar{\rho}^2}{\rho_0}. \qquad (29)$$

Using Eqs. (27) and (28) we find the response function

$$\beta(\mathbf{p}=0)=-\frac{\bar{\rho}(1-\bar{\rho}/\rho_0)^2}{T-7\varepsilon_d\bar{\rho}/\rho_0(1-\bar{\rho}/\rho_0)^2}, \qquad (30)$$

after which we finally obtain from Eqs. (7) and (20) an expression for the shear modulus $\tilde{\mu}$ in an elastic medium with vacancies:

$$\tilde{\mu}=\mu-\frac{4}{15}\pi^4(\mu\,\Delta V)^2\frac{\bar{\rho}(1-\bar{\rho}/\rho_0)^2}{T-7\varepsilon_d\bar{\rho}/\rho_0(1-\bar{\rho}/\rho_0)^2}. \qquad (31)$$

Figure 1 shows curves plotted using the functions based on Eqs. (31) and (26) calculated for various metals. In this case we have assumed $\Delta V=0.2a^3$. The value of the parameters $\mu$, $a$, $\varepsilon_v$, $\varepsilon_d$ are given in the table. The values of $\mu$ and $a$ are taken from Ref. 13, $\varepsilon_v$ and $\varepsilon_d$, from Ref. 11. The choice of the quantity $\bar{\rho}/\rho_0$ in the table is based on the theoretically calculated transition temperature $T=T_{\text{M}}^{\text{theor}}$. Figure 1 reveals a significant disagreement between the shape of the curves that were obtained based on Eq. (31) ($\sim e^{-\varepsilon_v/T}$) and the experimental curves ($\sim T^2$). Furthermore, the quantity $T_{\text{M}}^{\text{theor}}$ at which $\tilde{\mu}$ reduces to zero in Eq. (31) differs by a

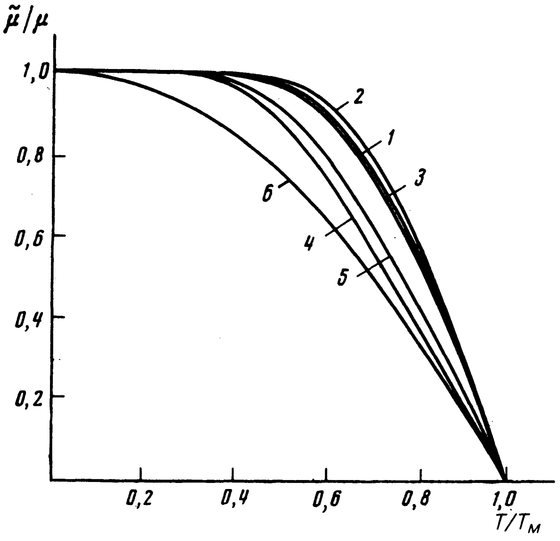

FIG. 1. Temperature dependence of the effective shear modulus in the vacancy melting model: 1—Al, 2—Cu, 3—Fe, 4—Na, 5—K, 6—experiment.[1]

factor of 1.5 to 2 from the experimental melting temperature $T_M$. Thus, despite the encouraging similarity of the curves $(\tilde{\mu}/\mu)$ $(T/T_M)$ for various metals, the vacancy model can not claim to be a quantitative and qualitative description of the process of crystal melting.

## 3. THE DISLOCATION MODEL OF CRYSTAL MELTING BASED ON THE BORN HYPOTHESIS

Let us calculate the contribution of dislocations to the change in the elastic modulus of a crystal. To do this we use the disorder field technique developed in Refs. 6 and 7, which allows us to calculate the partition function of a system of dislocations in an elastically deformed crystal.

In order to describe the system of dislocations we introduce three complex fields $\Psi_\nu(\mathbf{x})$, $\nu = 1,2,3$ (where $\mathbf{x}$ is the coordinate of a site of a cubic lattice). Let $\tilde{\varepsilon}$ be the energy per unit length of a dislocation. Then the partition function of a system of dislocations located in an external strain field $u_{ik}$ has the form[7]

$$Z_{\text{disl}} = e^{-H_{\text{eff}}/T} = \int e^{-H_{\text{disl}}/T} e^{-H_{int}/T} D\{\Gamma_D\}$$
$$= \int \prod_\nu d\Psi_\nu \, d\Psi_\nu^* \exp\{-\tilde{H}[\Psi, u_{ik}]/T\}, \tag{32}$$

$$\tilde{H} = \sum_{\nu=1}^{3} \Big\{ \int d\mathbf{r} [\,|\Psi_\nu|^2 + g|\Psi_\nu|^4]$$
$$- \int d\mathbf{r}\, d\mathbf{r}' \, \Lambda(\mathbf{r}-\mathbf{r}') \Psi_\nu(\mathbf{r}) \Psi_\nu^* G^{(\nu)}(\mathbf{r},\mathbf{r}'), \tag{33}$$

where

$$\Lambda = \sum_{\mathbf{a}} \delta(\mathbf{r}-\mathbf{r}'-\mathbf{a}),$$

($\mathbf{a}$ is the lattice parameter),

$$G^{(\nu)}(\mathbf{r},\mathbf{r}') = CJ(\mathbf{r},\mathbf{r}') \exp\Big\{ -\frac{1}{T} \int_{\mathbf{r}}^{\mathbf{r}'} \Phi_{ij}(\mathbf{R}) b_j^{(\nu)} \, dR_i \Big\},$$

$$J = \exp\Big\{ -\frac{\tilde{\varepsilon} l(\mathbf{r},\mathbf{r}')}{T} \Big\}; \tag{34}$$

$$C = \frac{\int_0^\infty \exp(-x - gx^2)\, dx}{\int_0^\infty x \exp(-x - gx^2)\, dx}. \tag{35}$$

The summation with respect to $a$ implies a summation over the nearest neighbors to the site of $\mathbf{r}'$; $l(\mathbf{r},\mathbf{r}')$ is the length of a dislocation line with a distance $|\mathbf{r} - \mathbf{r}'|$ between its ends, and $\mathbf{b}^{(\nu)}$ is the Burgers vector with orientation along the $\nu$th axis of the crystal. The tensor $\Phi_{ij}$ describes the interaction of the stress field caused by the dislocations with the elastic strain

$$H_{int} = \sum_D \int \Phi_{ij}(\mathbf{r}') b_j^{(\nu)} \, dx_i, \tag{36}$$

$$\Phi_{ij}(\mathbf{r}) = \int u_{kl}(\mathbf{r}') D_{ijkl}(\mathbf{r}-\mathbf{r}') \, d\mathbf{r}'. \tag{37}$$

Here $\Sigma_D$ denotes a summation over all the dislocations. The fourth-rank tensor $D_{ijkl}$ is evaluated by means of the well known expression for the stress field of a dislocation loop and has the form:[10]

$$D_{ijkl}(\mathbf{r}) = -\frac{\mu}{8\pi} \partial_m \Delta r \{\varepsilon_{mki}\delta_{jl} + \varepsilon_{mkj}\delta_{il}\}$$
$$- \frac{\mu}{4\pi(1-\sigma)} \varepsilon_{mkl} (\partial_m \partial_i \partial_j r - \delta_{ij} \partial_m \Delta r), \tag{38}$$

where

$$\sigma = \frac{1}{2} \frac{3K - 6\mu}{3K + 2\mu}$$

is the Poisson coefficient.

The constant $g$ in Eq. (33) corresponds to the energy of intersecting dislocations. For $u_{ik} = 0$ the partition function (33) describes a dislocation system in which a phase transition is possible; in Refs. 6 and 7 this transition was identified with melting.

In the Hamiltonian in Eq. (33) we have neglected the long-range part of the dislocation interaction. We can in-

TABLE I.

| | $\mu$, eV/Å$^3$ | $a$, Å | $\varepsilon_v$, eV | $\varepsilon_d$, eV | $T_M^{\text{theor}}$, K | $T_M$, K | $\bar{\rho}/\rho_0$ | $\Delta T_{max}$, K | $\xi$ |
|---|---|---|---|---|---|---|---|---|---|
| Al | 0,19 | 4,04 | 0,8 | 0,2 | 2200 | 933 | $5\cdot10^{-5}$ | 40 | 0,94 |
| Cu | 0,47 | 3,61 | 1,0 | 0,25 | 2480 | 1356 | $2\cdot10^{-4}$ | 52 | 0.86 |
| Fe | 0,73 | 2,87 | 1,2 | 0,3 | 3390 | 1808 | $5\cdot10^{-4}$ | 70 | 1,1 |
| Na | 0,03 | 4,3 | 0,5 | 0,12 | 1880 | 371 | $3\cdot10^{-4}$ | 25 | 1,2 |
| W | 0,72 | 3,2 | 2,0 | 0,5 | 4120 | 3683 | $2\cdot10^{-5}$ | 38 | 1,1 |

clude this interaction within the continuum approach by introducing three vector fields $B^{(\nu)}$ whose interaction with the disorder field is through the gauge-invariant combination $\partial_j^{(\nu)} \to \partial_j^{(\nu)} + iB_j^{(\nu)}$. In Ref. 6 it was shown that by taking into account the long-range part of the dislocation interaction we are led to the appearance in the Hamiltonian $\widetilde{H}[\Psi, u_{ik}]$ of a term proportional to $|\Psi_\nu|$.[3] This is equivalent to changing the order of the phase transition in the dislocation system. However, it turns out that the corresponding first-order phase transition is close to a second-order transition.[7]

The calculation of the effective Hamiltonian that corresponds to the dislocation contribution to the shear modulus (7) can be carried out by expanding $\widetilde{H}$ in powers of $u_{ik}$ and limiting ourselves to terms that are quadratic in $u_{ik}$. It turns out that the calculation of the partition function (32) is significantly different for crystals that are near the melting temperature and those far from it.

Near the melting temperature the primary contribution to $H_{\text{eff}}$ is given by dislocation configurations whose size is comparable to a characteristic interatomic spacing of the system.[6] In this case expanding $\widetilde{H}[u,\Psi]$ with respect to the field $u_{ik}$ we obtain

$$H_{\text{eff}} = -\frac{3}{2}\frac{1}{T}a^4\left(\int A_i^2 d\mathbf{r}\right)\left\{\frac{1}{18}\sum_{\mathbf{a}}\int G_0(\mathbf{p})e^{i\mathbf{p}\mathbf{a}}\frac{d\mathbf{p}}{(2\pi)^3} + \frac{1}{36}\sum_{\mathbf{a},\mathbf{a}'}\int |G_0(\mathbf{p})|^2 e^{i\mathbf{p}(\mathbf{a}+\mathbf{a}')}\frac{d\mathbf{p}}{(2\pi)^3}, \right. \qquad (39)$$

where

$$A_i = {}^1\!/_2 \partial_l \Phi_{k\nu}(\mathbf{r})\, b_k \varepsilon_{il\nu},$$

$$b_k = {}^1\!/_3 \sum_{\nu=1}^{3} b_k^{(\nu)}, \qquad (40)$$

$$G_0(\mathbf{x}-\mathbf{y}) = \langle \Psi_\nu(\mathbf{x})\Psi_\nu^*(\mathbf{y})\rangle. \qquad (41)$$

The brackets $\langle\ldots\rangle$ denote averages over all realizations of the Hamiltonian $H[u_{ik}=0, \Psi]$. For $g>0$ $G_0(\mathbf{p})$ is the Green's function of the $n$-component complex field.[14]

The energy of formation of a unit length of dislocation in the continuum model has the form[10]

$$\varepsilon = \frac{\tilde{\mu} b^2 \xi}{4\pi(1-\tilde{\sigma})}, \quad \xi = \ln\frac{L}{d}, \qquad (42)$$

where $L$ is the length of the dislocation and $d$ is the radius of its core. In Eq. (42) we have used the effective moduli $\tilde{\mu}$ and $\widetilde{K}$ because we are investigating the formation of dislocations in a "composite" medium made up of material consisting of an elastic medium with moduli $\mu$ and $K$ and the dislocation system. In fact the use of $\tilde{\mu}$ and $\widetilde{K}$ in Eq. (42) is also an operation that makes the problem of calculating the effective modulus self-consistent.

Near $T_M$ the fundamental contribution to $G_0(\mathbf{p})$ is given by small $\mathbf{p}$. Using the results of the fluctuation theory of phase transitions we find[14]

$$G(p=0) = \frac{2}{(J_0^{-1}-1)^\gamma}, \quad J_0 = e^{-\tilde{\varepsilon}a/T}, \qquad (43)$$

where $\gamma$ is the corresponding critical index. Within the framework of the $\varepsilon$-expansion, $\gamma$ has the form[14]

$$\gamma = 1 + {}^2\!/_7\varepsilon.$$

Substituting Eq. (43) into Eq. (39), we find the following effective Hamiltonian as $T \to T_M$:

$$H_{\text{eff}} = -\frac{4\pi}{T}a\left\{\frac{1}{3(J_0^{-1}-1)^\gamma} + \frac{2}{(J_0^{-1}-1)^{2\gamma}}\right\}\int A_i^2 d\mathbf{r}. \qquad (44)$$

Using the explicit form of the tensor $\Phi_{ij}(\mathbf{r})$ in Eq. (37) and Eqs. (38) and (39), after some uncomplicated but tedious calculations we obtain (see Appendix)

$$\widetilde{K} = K - \frac{8}{15}\theta(\tilde{\mu}, T),$$

$$\tilde{\mu} = \mu - \frac{5}{3}\theta(\tilde{\mu}, T), \qquad (45)$$

$$\theta(\tilde{\mu}, T) = \frac{T 8\pi^3}{3b^2 a \xi^2}\left\{1 - \frac{2}{7}\varepsilon \ln\frac{\tilde{\mu} b^2 a}{T 2\pi\xi}\right\}. \qquad (46)$$

Relation (45) allows us to determine the melting temperature of the crystal. Assuming that the parameter

$$\varkappa_0 = \frac{2}{7}\varepsilon \ln\frac{\tilde{\mu} b^2 a}{T 2\pi \xi}$$

is small compared to unity ($\varkappa_0 \ll 1$) and considering a dislocation with minimum Burgers vector $b = a$, we obtain from Eq. (45)

$$\tilde{\mu}(T_M) = 0, \quad T_M = \frac{9\mu a^3 \xi^2}{40\pi^3}. \qquad (47)$$

For the majority of metals the melting temperature calculated based on Eq. (47) coincides with the experimental values of $T_M$ if we take $\xi \approx 1$. In this case, when we pass from one metal to another, the parameter $\xi$ varies insignificantly. The value of $\xi$ that insures agreement between the theoretical and experimental values of $T_M$ is given in the table.

It should be noted that the contribution of vacancies to the renormalization of $\tilde{\mu}$ and $\widetilde{K}$ is insignificant at these temperatures and can be neglected.

The accuracy with which the melting temperature $T_M$ is determined based on Eq. (47) is limited by the smallness of the parameter $\varkappa_0$. Near $T_M$ we obtain the following expression for the shear modulus $\tilde{\mu}$ ($\Delta T = T_M - T$)

$$\tilde{\mu}(T_M - \Delta T) = \mu\frac{\Delta T}{T_M}\left\{1 - \frac{2}{7}\varepsilon \ln\frac{\mu a^3}{2\pi\xi T_M}\frac{\Delta T}{T}\right\}. \qquad (48)$$

The logarithmic terms in Eq. (48) can be neglected if

$$\frac{\Delta T_{min}}{T_M} > e^{-7/2\varepsilon}\frac{T_M 2\pi\xi}{\mu a^3}. \qquad (49)$$

For metals the value of the parameter $\mu a^3/2\pi\xi$, is of order 20 eV. Therefore, the inequality (49) is fulfilled everywhere except for a narrow region $\Delta T/T \sim 10^{-3}$ near the melting temperature.

In the low-temperature limit ($T < T_M$) the region of applicability of expression (48) is limited by the possibility of expanding the exponent in Eq. (43). In the table we present values of the parameter $\Delta T_{\max}$ that determine the conditions of applicability of Eq. (48):

$$T_M-\Delta T_{max}<T<T_M<T_M-\Delta T_{min}.$$

At low temperatures the primary contribution to the effective Hamiltonian comes from dislocation configurations that differ in size from the smallest possible. In order to take this into account, let us define a sublattice in the original crystal the distance between whose sites is $\mathbf{R} = m\mathbf{a}$, $m > 1$. A dislocation is represented for the original lattice by a broken line consisting of submonomers with size on the order of $R$. For such a line relation (33) is valid, with $a$ replaced by $R$. As for the energy for the formation of a submonomer the spacing between the ends of which equals $l$, this quantity is not a linear function of $R$ and is determined by the average length of a dislocation line that joins the ends of the submonomer.

Therefore, in place of Eq. (34) we must write

$$G^{(\nu)}=CJ\exp\left\{-\int_{\mathbf{r}}^{\mathbf{r}'}\Phi_{ij}(\rho)\,b_i^{(\nu)}\,d\rho_j\right\},$$

$$J\propto\exp\left\{-\frac{\mu b^2 l(\mathbf{r},\mathbf{r}')}{4\pi(1-\sigma)}\xi\right\}, \tag{50}$$

where $l$ is the length of a chain based on the original lattice the distance between whose ends equals $|\mathbf{r}-\mathbf{r}'|$. This quantity can be obtained for a submonomer by using the Fleury theory,[15] according to which

$$l(R)=a\left(\frac{6}{\omega}\right)^{1/3}\left(\frac{R}{a}\right)^{(\omega+2)/3}, \quad R=|\mathbf{r}-\mathbf{r}'|, \tag{51}$$

where $N(R)$ is the dimension of the space.

The number of submonomers $N(R)$ of size $R$ that belong to a single unit cell can be determined by averaging the square of the absolute value of the disorder field $\Psi_\nu$ over all realizations of the Hamiltonian $\widetilde{H}_R$ that are defined on the sublattice $R$ (Ref. 16). Using Eqs. (33), (41), and (50), we obtain

$$N(R)=\exp\left\{-\frac{\mu b^2\xi l(R)}{4\pi(1-\sigma)T}\right\}, \tag{52}$$

where $l(R)$ is determined from Eq. (51). In Eq. (52) we have used the renormalized value of the modulus $\mu$ because we are discussing the limit of low temperatures.

The effective Hamiltonian that takes into account dislocation configurations that differ from a loop of minimal size is obtained by averaging the effective Hamiltonian defined on the sublattice of size $R$ with the distribution function $N(R)$. From Eqs. (33), (50), and (52), we find

$$H_{\text{eff}}=-\frac{2\pi}{3T}\left\{\int A_i^2 d\mathbf{r}\right\}\frac{\langle S^2(R)\rangle}{a^3}. \tag{53}$$

Here the vector $A_i$ is determined by relation (40) while $\langle S^2\rangle$ is the average value of the squared area of a minimal loop defined on the size-$R$ sublattice. It is natural to assume that

$$S=tR^2, \tag{54}$$

where $t$ is a number that is in fact a fitting parameter of the theory. Then

$$\langle S^2\rangle=t^2\int_0^\infty R^2\exp\left\{-\frac{\mu b^2 l(R)\xi}{4\pi T(1-\sigma)}\right\}dR\Bigg/$$

$$\int_0^\infty\exp\left\{-\frac{\mu b^2 l(R)\xi}{4\pi T(1-\sigma)}\right\}dR. \tag{55}$$

Using Eqs. (53) and (55), after some uncomplicated but tedious calculations we obtain

$$\frac{\tilde{\mu}}{\mu}=1-\frac{400}{81}\pi^4\left(\frac{\omega}{6}\right)^{4\chi/3}\frac{t^2}{\xi^2}\frac{\Gamma(5\chi)}{\Gamma(\chi)}$$

$$\times\left(\frac{3(1-\sigma)\xi}{10\pi^2}\right)^{4\chi}\left(\frac{T}{T_M}\right)^{4\chi-1}\left(\frac{\tilde{\mu}}{\mu}\right)^{2-4\chi}, \tag{56}$$

$$\frac{\tilde{K}}{\mu}=\frac{K}{\mu}-\frac{124}{243}\pi^4\left(\frac{\omega}{6}\right)^{4\chi/3}_{.}\frac{t^2}{\xi^2}\frac{\Gamma(5\chi)}{\Gamma(\chi)}\left(\frac{3(1-\sigma)\xi}{10\pi^2}\right)^{4\chi}$$

$$\times\left(\frac{T}{T_M}\right)^{4\chi-1}\left(\frac{\tilde{\mu}}{\mu}\right)^{5-4\chi}, \quad \chi=\frac{\omega+2}{3}, \tag{57}$$

where $\Gamma(x)$ is the gamma function.

Relations (56) and (57) determine the law of variation of the elastic moduli near zero temperature. Equation (56) gives a power-law dependence for the temperature variation of the elastic modulus that is close to the experimental dependence. It is obvious that we can obtain more accurate agreement with experiment if we make use of more general relations between the area and the length of dislocations and, more specifically, take into account that $S\sim R^\lambda$. The choice of the parameter $t$ (and for that matter, the choice $t = 3.1$) can bring about satisfactory agreement between the theoretical dependences of $\tilde{\mu}$ and $\tilde{k}$ and the experimental function Eq. (1).

Figure 2 shows calculated curves for $\tilde{\mu}(T/T_M)$ for a number of metals. In the region $T_1<T<T_M$, where $T_1 = T_M - \Delta T_{\max}$, the curves are plotted by using a spline interpolation between the point $T_1/T_M = 0.3$ and $T/T_M = 1$. At the point $T = T_M$ the derivative $T_M d\tilde{\mu}/dT$ is chosen to equal 2 in order to agree with the law (1). In this choice there is no contradiction with Eq. (48), because the law (1) itself was obtained in the region $T\sim T_M$ by extrapolation.[1]

In calculating the effective Hamiltonian we have neglected the interaction of point defects with the dislocation configurations. We can take this interaction into account within the approach developed here in the following way. The contribution to the partition function from these interactions can be separated into two parts—a fluctuation part and a mean-field part. The mean-field contribution corresponds to including the interaction of dislocations with an "external" elastic field which is determined by the mean defect concentration. This contribution is small; its smallness is on the order of the ratio $\bar{\rho}/\rho_0$ (see Table I). The fluctuation part corresponds to taking into account the interaction of fluctuations in the defect density with dislocations. It follows from Eqs. (33) and (34) that the fluctuation contribu-

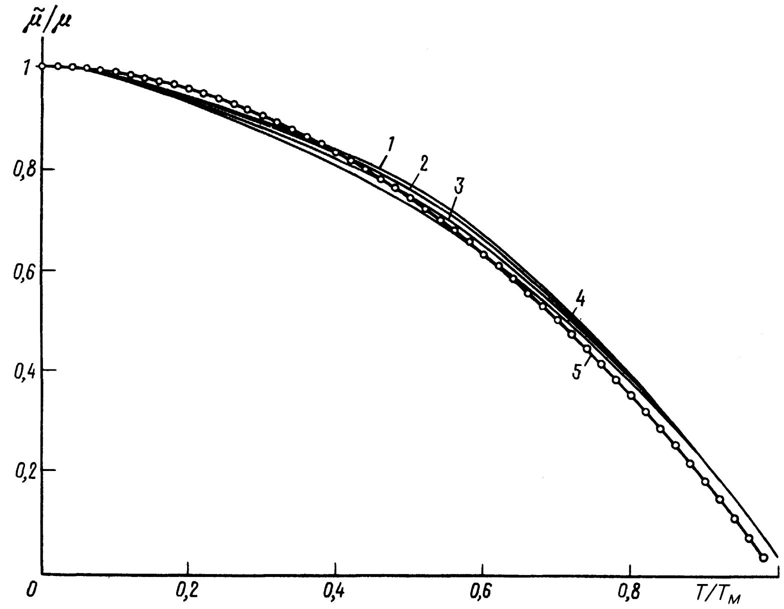

FIG. 2. Temperature dependence of the effective shear modulus for various metals obtained within the framework of the dislocation model of melting: 1—Al, 2—Cu, 3—Fe, 4—W, 5—experiment.[1]

tion leads to a term of the form $\beta(\mathbf{p})|\Psi|^4$. From this we see that if the constant $g$ that determines the energy of intersecting dislocations is sufficiently large, the fluctuation part can also be neglected.

## CONCLUSION

The satisfactory description of the melting of crystals within the framework of the model presented here is in our view related to our fortunate choice of the configurations of states of the solid. In addition to addressing the problem investigated here, our approach can also be applied to a description of surface melting. Furthermore, in constructing a quantitative theory of disruption of a crystal it is also necessary to take into account the mechanism by which the elastic moduli of the crystal are renormalized.

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## APPENDIX

In order to derive Eqs. (45)–(47) let us write the vector $A_i$ in explicit form using Eqs. (37), (38), and (40):

$$A_i=\frac{1}{2}\int u_{\alpha\beta}(\mathbf{r}')\,\partial_l D_{k\alpha\alpha\beta}(\mathbf{r}-\mathbf{r}')\,b_k\varepsilon_{ila}d\mathbf{r}'. \qquad \text{(A1)}$$

The calculation of the quantity $\int A_i^2 d\mathbf{r}$ is conveniently carried out if we pass to the Fourier transform:

$$\int A_i^2 d\mathbf{r}=\int d\mathbf{p}p_l D_{\alpha\beta\mu\nu}(\mathbf{p})\,\varepsilon_{il\beta}b_\alpha p_i D_{abmk}(\mathbf{p})\,\varepsilon_{ijb}b_a, \qquad \text{(A2)}$$

$$D_{\alpha\beta\mu\nu}(\mathbf{p})=\frac{1}{(2\pi)^3}\int D_{\alpha\beta\mu\nu}(\mathbf{r})\,e^{i\mathbf{pr}}d\mathbf{r}. \qquad \text{(A3)}$$

In order to calculate the Fourier components (A3) we make use of the obvious relations

$$\partial_i r=n_i,\quad \partial_i\partial_k r=\frac{\partial_{ik}-n_in_k}{r},\quad \Delta r=\frac{2}{r}, \qquad \text{(A4)}$$

whose Fourier transforms have the form

$$(\Delta r)_\mathbf{p}=\frac{8\pi}{p^2},\quad (\partial_i\Delta r)_\mathbf{p}=i\frac{8\pi}{p^2}p_i$$
$$(\partial_i\partial_k r)_\mathbf{p}=\frac{2\pi}{p^2}\left\{\frac{4+\pi}{3}\delta_{ik}-\pi\frac{p_ip_k}{p^2}\right\}. \qquad \text{(A5)}$$

Substituting (A5) into Eq. (38) which determines the tensor $D_{\alpha\beta mk}$, we obtain

$$D_{\alpha\beta mk}(\mathbf{p})=-\frac{i\mu}{8\pi}\left\{(\varepsilon_{im\alpha}\delta_{\beta k}+\varepsilon_{im\beta}\delta_{\alpha k})\frac{8\pi}{p}l_i\right\}$$
$$-\frac{i\mu}{4\pi(1-\sigma)}\left\{\varepsilon_{imk}\frac{2\pi}{p}l_i\left(\frac{4+\pi}{3}\delta_{\alpha\beta}-\pi l_\alpha l_\beta\right)-\frac{8\pi l_i}{p}\delta_{\alpha\beta}\varepsilon_{imk}\right\},$$
$$l_i=p_i/p. \qquad \text{(A6)}$$

Within the framework of the isotropic approximation used in this paper, in order to calculate the quantity (A2), we carry out an average over all directions of the vector $l_i$. By making use of the well known relations

$$\overline{l_il_j}={}^1/_3\delta_{ij},\quad \varepsilon_{i\mu\alpha}\varepsilon_{\sigma m\alpha}=\delta_{i\sigma}\delta_{\mu m}-\delta_{im}\delta_{\mu\sigma},$$
$$\overline{l_il_\beta l_jl_\sigma}={}^1/_{15}\{\delta_{i\beta}\delta_{j\sigma}+\delta_{ij}\delta_{\beta\sigma}+\delta_{i\sigma}\delta_{\beta j}\}, \qquad \text{(A7)}$$

we obtain for the effective Hamiltonian $H_{\text{eff}}$,

$$H_{\text{eff}}=-\frac{\pi}{3}\frac{\tilde{\mu}^2b^2}{T}a\left\{\frac{1}{3(J_0^{-1}-1)^\gamma}+\frac{2}{(J_0^{-1}-1)^{2\gamma}}\right\}$$
$$\times\left\{\frac{5}{3}\delta_{\mu m}\delta_{k\nu}-\frac{7}{15}\delta_{\mu\nu}\delta_{km}\right\}\int u_{\mu\nu}(\mathbf{p})\,u_{mk}(-\mathbf{p})\,d\mathbf{p}. \qquad \text{(A8)}$$

According to the Born hypothesis, as $T\to T_M$, the shear modulus $\tilde{\mu}\to 0$; therefore, Eq. (A8) should be expanded in a power series in $\tilde{\mu}$. By varying the effective Hamiltonian (A8) with respect to the strain tensor components $u_{\alpha\beta}$ we obtain from Eq. (7) the equations (45) and (46), from which there follows an equation which determines the melting temperature:

$$\tilde{\mu} - \frac{40\pi^3 T}{b^2 a \xi^2 9}\left\{1 - \frac{2}{7}\,\varepsilon \ln \frac{\mu b^2 a}{T 2\pi \xi}\right\} = 0. \tag{A9}$$

Considering the parameter

$$\varkappa_0 = \frac{2}{7}\,\varepsilon \ln \frac{\tilde{\mu}\, b^2 a}{T 2\pi \xi} \ll 1,$$

from (A9) we obtain Eq. (47) presented in the text for $T_M$. The accuracy with which this formula is obtained is discussed in detail in the text of the paper.

[1] J. H. Bilgram, Phys. Reports **153**, No. 1 (1987).

[2] G. Ziman, *Models of Disorder*, Cambridge Univ. Press, Cambridge (1979).

[3] Yu. Yu. Boguslavskii, Fiz. Tverd. Tela (Leningrad) **23**, 337 (1981) [Sov. Phys. Solid State **23**, 191 (1981)].

[4] B. I. Halperin, T. S. Lubensky, and S. K. Ma, Phys. Rev. Lett. **32**, 292 (1974).

[5] S. F. Edwards and M. Warner, Phil. Mag. **40**, 257 (1979).

[6] S. P. Obukhov, Zh. Eksp. Teor. Fiz. **83**, 1978 (1982) [Sov. Phys. JETP **56**, 1144 (1982)].

[7] A. Z. Patashinskii and B. I. Shumov, Zh. Eksp. Teor. Fiz. **89**, 315 (1985) [Sov. Phys. JETP **62**, 177 (1985)].

[8] M. Born, J. Chem. Phys. **7**, 591 (1939).

[9] D. Eshelby, *Continuum Theory of Dislocations*, Mir, Moscow, 1963.

[10] J. P. Hirth and J. Lothe, *Theory of Dislocations*, 2nd ed. Wiley, New York (1982).

[11] R. Thompson, *Defects and Radiation Damage in Solids*, Mir, Moscow, 1971.

[12] R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics*, Wiley-Interscience, New York (1975).

[13] C. Kittel, *Introduction to Solid-State Physics*; 5th ed., Wiley, New York (1976).

[14] S. Ma, *Modern Theory of Critical Phenomena*, Benjamin, Reading, MA (1976).

[15] P. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca, NY (1979).

[16] E. S. Nikomarev and S. P. Obukhov, Zh. Eksp. Teor. Fiz. **80**, 650 (1981) [Sov. Phys. JETP **53**, 328 (1981)].

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