Heterogeneous states of degenerate semiconductors in the region of a first-order phase transition

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Some features of phase transitions in semiconducting systems with high dielectric constants and large interphase surface energies are considered under strong-doping conditions. At electron densities exceeding a certain critical value the phase transition in these systems occurs via an intermediate heterogeneous phase consisting of layers with the structure of phases I and II. Peculiarities of the phase diagrams and characteristics of the heterogeneous structures produced, due to long range Coulomb forces or to the electron-gas Fermi surface, are investigated for cases when the redistribution of the charge densities is relatively small. Heterogeneous states with strongly inhomogeneous ion distribution and almost homogeneous electron distribution are also considered.

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1. INTRODUCTION

Phase transitions in systems containing free charges (electrons and ions) can have characteristic distinguishing features, particularly some connected with long-range Coulomb forces. First-order phase transition are accompanied by a redistribution of impurities, say free charges, and to prevent buildup of a tremendous electrostatic energy the electrons and ions in the bulky sections of the phases must go over from one phase to the other in equal amounts. However, the energy gain following a transition to the second phase can differ greatly in magnitude for the electrons and ions, and can even be of opposite sign, so that in the presence of Coulomb forces it would be energywise more profitable to transfer charges predominantly of the same sign to this phase.

We consider semiconductor systems with large dielectric constants ϵ, in which the Coulomb forces are appreciably decreased. If sections of a second phase of small thickness $2R_2$ (not at equilibrium in the absence of free charges) are produced in such systems, then the resultant electrostatic energy is small and the energy gain in the case of a predominant transfer of charges of like sign to these sections can compensate both for the increase of the electrostatic energy and for the increase of the boundary and volume free energy of the medium (the latter is obviously small near the transition). In this case the heterogeneous state (HS) of the medium in which there coexist charged sections with the structures of the first and second phase having different electron and ion densities will be thermodynamically favored. Such an HS is obviously not a two-phase mixture (which can be separated into two phases) but a single one-phase system with a unique order.

The possible existence of such HS was demonstrated earlier in[1-3], and their features were investigated in the case when the energy U gained when the electron goes over to the section of the second phase is large enough in comparison with kT in nondegenerate semiconductors, or in comparison with the Fermi energy μ_0 prior to heterogenization in degenerate semiconductors, and the ion-energy change $-U'$ in this transition has a sign opposite to U and is also large. In this case, heterogenization results in a disperse system in which almost all the electrons go over into sections of the second phase (which forms particles of the metallic type), and the ions remain in the sections of the first phase (which has a low electronic conductivity).

In strongly doped semiconductors with appreciable carrier density n_0, however, the opposite condition, $\mu_0 \gg |U|$ can be satisfied. Then the heterogenization conditions are appreciably changed (for example, there is no need for stringent requirements on the sign and magnitude of U', structures can be produced with a period connected with the reciprocal diameter of the Fermi surface) and also in the singularities of the produced hS. In particular, unlike the case of large $|U|$ considered above, the relative changes of the density should obviously be small. We shall determine below the conditions for the formation of HS near first-order phase transitions at $|U| \ll \omega_0$, consider the resultant peculiar diagrams of state, and investigate the singularities of the phase transition in the HS, the characteristics of the HS, and the dependence of these characteristics on T and n_0. We shall discuss only the equilibrium properties, and not the kinetics of the heterogenization. The latter also has characteristic peculiarities due to the Coulomb forces, just as, for example, the kinetics of emulsion coalescence in electrolyte solutions[4].

We consider for the sake of argument degenerate semiconductors containing fully ionized impurity ions of only one type. The character of the screening and the peculiarities of the heterogenization depend essentially on whether the ions have sufficient mobility to become redistributed over distances on the order of the characteristic length of the inhomogeneity, leading to establishment of complete equilibrium (the rate of the phase transition is assumed in all cases to be fast enough for phase-composition equilibrium to be established). If the ion mobility is negligible, then the heterogenization is due only to the redistribution of the electrons with the ions "frozen." i.e., it takes place under conditions of incomplete equilibrium. Heterogenization of this type will be considered in Secs. 2 and 3. On the other hand if the ion mobility is noticeable, then a redistribution of both the electrons and the ions takes place, and complete equilibrium is established. The heterogenization in this case is considered in Secs. 4 and 5. The redistribution of the density is easier to effect in a nondegenerate gas of ions than in a degenerate electron gas. Therefore at sufficiently large $|U'|$ the main cause of the heterogenization may be the gain in the energy of the ions and not of the electrons. This can create HS with a strongly inhomogeneous distribution of the ions and an almost homogeneous distribution of the electrons. This is considered in Sec. 5.

In the case of large $|U| \gg \mu_0$[1,2] the dimensions of the particles of the second phase are determined by the ratio of the surface energy σ of the interphase boundary to the electrostatic energy. In the considered case $|U| \ll \mu_0$, the particle dimension is also determined by σ, if its value is large enough. However, if this dimension becomes comparable with the reciprocal diameter $(2k_0)^{-1}$ of the Fermi surface of the electrons, then a different type of structure of periodically alternating phase platelets is produced, with a period $2R \approx \pi/k_0$ that is connected with the characteristic fall-off of the dielectric constant $\epsilon(\mathbf{k})$ in the region $k \approx 2k_0$ (see Sec. 3).

Such HS can arise in various systems with large ϵ and not very large σ near first-order phase-transition points. In particular, they can take place in the region of polymorphic transformations, in crystallization, and in magnetic semiconductors with magnetic phase transitions of first order. In the latter case we shall consider systems in which the jumplike change of the magnetization in the transition greatly exceeds the change due to variation of the charge density inside the sections of the phases. The case when the change of the medium parameter in semiconductor solutions and ferromagnetic semiconductors is due to variation of the charge density is considered for $|U| \lesssim \mu_0$ in[5].

2. HETEROGENEOUS STATES IN SYSTEMS WITH IMMOBILE IONS

Assume that the equilibrium phase at the considered temperature in the absence of free charges is phase I. If heterogenization takes place in a semiconductor with free charges, then sections with the structure of phase II are produced. We assume, as in[1,2], that the heterogeneous system consists of periodically arranged identical "Wigner-Seitz cells" (violation of the periodicity can lead to more subtle effects, which will not be discussed).

In the macroscopic approximation, the order and the thermodynamic characteristics in the sections of the phases will be assumed to be the same as in the bulk phases. Then the change $\delta\Phi$ of the thermodynamic potential per unit volume of the system following heterogenization and the onset of the inhomogeneous charge distribution can be expressed in the form

$$\delta\Phi = p\varphi + \sigma S - U\delta N_2 - U'\delta N_2' + \int n' \ln\frac{n'}{n_0}\,d\mathbf{r} + \frac{1}{2}\int (n-n')\,y\,d\mathbf{r} + \delta E_\text{к}. \quad (1)$$

Here φ is the difference between the specific thermodynamic potentials of phases II and I at a homogeneous "average" density n_0 of the electrons and ions, p is the volume fraction of the sections with phase-II structure, S is the area of the boundaries per unit volume. δN_2 and $\delta N_2'$ are the changes in the numbers of the electrons and ions in the sections of phases II upon heterogenization, $n(\mathbf{r})$ and $n'(\mathbf{r})$ are their densities, $y(\mathbf{r})$ is the electrostatic energy of the electron, and δE_k is the change of the kinetic, exchange, and correlation energy of the electrons upon heterogenization; all the energies are measured in units of kT.

In accord with the statements made in the Introduction, we must have expressions for $n(\mathbf{r})$ and δE_k at relatively large dimensions $2R_1$ and $2R_2$ of the sections of the phases ($R_1, R_2 \gg \pi/2k_0$) and at $2(R_1 + R_2)k_0 \approx \pi$. The second case is considered in Sec. 3. In the first case, the quasiclassical approximation can be used. We assume first that the correlation and exchange energies are negligibly small (the corresponding criterion is given below). Recognizing also that at $|U| \ll \mu_0$ we need retain only the first terms of the expansion in powers of U and y, we find that $\delta n(\mathbf{r}) = n(\mathbf{r}) - n_0$; δE_k and $y(\mathbf{r})$ are given by

$$\delta n(\mathbf{r}) = \frac{n_0}{\mu_1}[U(\theta(\mathbf{r})-p) - y(\mathbf{r}) + \langle y\rangle], \quad \delta E_\text{к} = \frac{\mu_1}{2n_0}\int [\delta n(\mathbf{r})]^2\,d\mathbf{r},$$

$$\mu_1 \equiv n_0\frac{\partial\mu_0}{\partial n_0} = \frac{2}{3}\mu_0 \gg 1, \quad \Delta y = \frac{1}{2r_0^2 n_0}(\delta n' - \delta n), \quad r_0^2 = \frac{\varepsilon kT}{8\pi e^2 n_0}. \quad (2)$$

Here $\theta(\mathbf{r}) = 1$ in the second phase and $\theta(\mathbf{r}) = 0$ in the first, and it is assumed that the Fermi surface is spherical and the effective electron masses m and ϵ are the same in both phases.

In the case of frozen ions we have $n'(\mathbf{r}) = n_0$ and $\delta N' = 0$. For a concrete cell geometry it is easy to determine $y(\mathbf{r})$ and $n(\mathbf{r})$ from formulas (2) and obtain, by substituting them in (1), the values of $\delta\Phi$ accurate to terms $\sim U^2$ inclusive. The values of $\delta\Phi$ for spherical and cylindrical cell geometry turn out to be larger than for planar geometry, i.e., the layers should be made plane. For planar geometry we have

$$\delta\Phi = \varphi\frac{R_2}{R} + \frac{\sigma}{R} - \frac{U^2 n_0}{2\mu_1}\frac{\operatorname{sh}\varkappa R_1 \operatorname{sh}\varkappa R_2}{\varkappa R \operatorname{sh}\varkappa R}, \quad \mu_1 = \pi\left(\frac{\pi}{3}\right)^{1/3} E_0 (a^3 n_0)^{2/3},$$

$$E_0 = \frac{me^4}{\hbar^2\varepsilon^2 kT}, \quad a = \frac{\hbar^2\varepsilon}{me^2}, \quad \varkappa^{-1} = \sqrt{2\mu_1}\,r_0 = \frac{1}{2}\left(\frac{\pi}{3}\right)^{1/6}\frac{a}{(a^3 n_0)^{1/6}}. \quad (3)$$

Here a is the Bohr radius, $R = R_1 + R_2$, and $2R_1$ and $2R_2$ are the thicknesses of the layers of the first and second phases.

At low charge densities we have $\delta\Phi > 0$ and a homogeneous state is realized. The transition between two homogeneous phases occurs at a temperature T^0 for which $\varphi(T^0) = 0$. If, however, σ is not very large and n_0 exceeds a critical value n_c determined from the condition

$$g = g(n_0) \equiv \frac{4\sigma\mu_1\varkappa}{n_0 U^2} = 1 \quad \text{at} \quad n_0 = n_c \quad \text{or} \quad n_c = \frac{\pi}{3}\left(\frac{8\pi\sigma a^2 E_0}{U^2}\right)^6 a^{-3},$$

then $\delta\Phi < 0$ in the region $T \approx T^0$ and the HS are thermodynamically favored in a certain temperature interval $T_1^0 > T > T_2^0$. The upper temperature T_1^0 of the transition to the HS is determined from the condition $\delta\Phi(T_1^0) = 0$ and lies above T^0, while the lower T_2^0 is determined from the condition $\delta\Phi(T_2^0) = \varphi(T_2^0)$ and lies below T^0 (in the course of heterogenization, sections with the structure of phase I, which is not at equilibrium in the absence of charges, are produced in this case in phase II). The phase diagram in the coordinates T and n_0 takes the form shown in Fig. 1. We note that if n_c is smaller than the degeneracy density n_{c1} of the electron gas then the HS is produced at all $n_0 > n_{c1}$.

The equilibrium thicknesses $2R_1 = 2x_1\kappa^{-1}$ and $2R_2 = 2x_2\kappa^{-1}$ are connected with the screening length κ^{-1} and are obtained from the condition that $\delta\Phi$ be minimal with respect to R_1 and R_2. In the middle of the heterogeneous region, on the phase diagram at $T = T^0$, the thicknesses $2R_1 = 2R_2 = 2x\kappa^{-1}$ are equal and are determined by the quantity $g(n_0)$ with the aid of the equation $\tanh x - x \cosh^{-2} x = g$. As $n_0 \to n_c$, the value of x increases logarithmically and at $n_0 \gg n_c$, if $g \sim n_0^{-1/6}$ is not much smaller than unity, x lies in the interval from 1 to 2.5, i.e., $2R$ is in the interval $(4-10)\kappa^{-1}$ (see Fig. 2). When T rises above T^0 the value of R_2 decreases while R_1 increases (and vice versa below T^0). As $T \to T_1^0$, in the model considered here, $R_1 = x_1/\kappa$ increases in proportion to $\ln(T_1^0 - T)$, while R_2 tends to a finite limit $R_2 = x_2^0/\kappa$.

It follows from (3) that T_1^0 and the limiting values x_1 and x_2 are given by

$$\frac{T_1^0-T^0}{T^0}=\frac{T^0-T_2^0}{T^0}=\frac{U^2n_0}{2\mu_1 q}\exp(-2x_2^0), \qquad (1+2x_2^0)\exp(-2x_2^0)=1-g,$$

$$(x_1+x_2^0-{}^1/_2)\exp(-2x_1)=\frac{x_2^0}{4\,\mathrm{sh}^2\,x_2^0}\frac{T_1^0-T}{T_1^0-T^0} \quad (T\to T_1^0-0), \tag{4}$$

where $q = T^0 \partial\varphi/\partial T$. Plots of x_2^0 and $T_1^0 - T^0$ as functions of g are shown in Fig. 2.

The specific entropy of the heterogeneous phase near T_1^0 contains an additional term $\delta s = -qR_2(T^0R)^{-1}$ with a logarithmic singularity. In the considered model, δs varies continuously, just as the fraction $p = R_2/R$ of the second phase, near the transition point. This continuity is physically due to the repulsion of the charged particles of the plates in the screening medium. However, since the logarithm in the formulas for R_2/R and δs is not very large already at $T_1^0 - T \sim (10^{-3}$ to $10^{-4})T_1^0$ and varies slowly, these quantities increase to finite noticeable values in a very narrow temperature region, i.e., in the experiment the transition will be similar to a first-order phase transition even though, strictly speaking, in this model it is of second order (with an unusual singularity).

Actually, however when the model is made more precise, say by taking into account elastic stresses, the non-Coulomb interaction between layers, the fluctuations of the layer shapes and dimensions, or deviations from the quasiclassical approximation (see Sec. 3), the character of the singularities of R_2/R and δs may change. For example, if the Van der Waals attraction energy between the remote layers KSR_2^2/R^4 is taken into account in (3), then layers with structure of phase II are produced at the transition point not at maximally large distances, but at finite distances $2R_1 = 2x_1^0\kappa^{-1}$, so that their fraction p^0 and the heat of the transition $Q \approx kp^0$ are finite. If $K_1 = 2K\mu_1\kappa^3/U^2n_0 \ll 1$, then $x_2^0 \sim 1$ is determined as before by formula (4), and $x_1^0 \sim 1$ (meaning also p^0 and Q) and the transition-point shift δT_W due to the Van der Waals forces are given by the formulas

$$(x_1^0)^5\exp(-2x_1^0)=4K_1(x_2^0)^2[1-\exp(-2x_2^0)]^{-2},$$

$$\delta T_W=K_1x_2^0\exp(2x_2^0)(x_1^0)^{-4}(T_1^0-T^0).$$

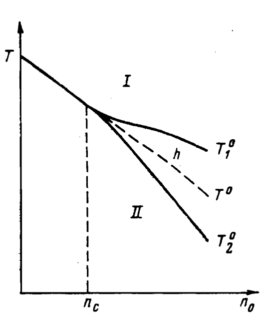

FIG. 1

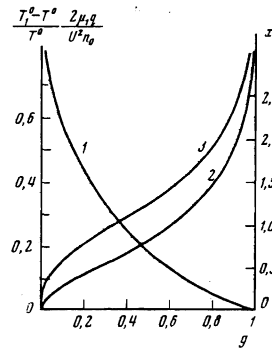

FIG. 2

FIG. 1. Phase diagram in the case of immobile ions (at $U + U' < 0$, $q > 0$). The dashed line is determined by the equation $\varphi(T^0) = 0$ and is a continuation of the equilibrium line between the homogeneous phases I and II. The region of heterogeneous states at $n_0 > n_c$ is marked by the letter h.

FIG. 2. Dependence of the transition temperature T_1^0 (curve 1) and of the layer thicknesses $2R_2 = 2x_2^0\kappa^{-1}$ and $qR_1 = 2R_2 = 2x\kappa^{-1}$ respectively at the point of transition and in the middle of the heterogeneous region at $T = T^0$ (curves 2 and 3) on the parameter $g \sim n_0^{-1/6}$.

Allowance for the anisotropy leads to definite orientations of the layers. They should actually form colonies oriented in various crystallographic directions. In crystals, strictly speaking, it would also be necessary to take account of the fact that $2R_1$ and $2R_2$ should be commensurate with the lattice parameter at each temperature. At large $2R$, however, the corresponding singularities are weakly pronounced on the temperature curves (see[6]).

We now discuss the conditions for the applicability of the assumed approximations. The assumption that it is possible to neglect the exchange energy and the correlations of the conduction electrons is valid at large electron n_0, when the known parameter r_s is small. In strongly-doped semiconductors $r_s < 1$ because $\epsilon m_0/m$ is large (m_0 is the mass of the free electron). Moreover, the formulas given above make it possible in essence to take into account also the corrections that arise at not very small r_s. In fact, using the formalism of density functionals[7,8] and recognizing that $\delta n(r)$ is small, it is easy to verify that these formulas remain in force also when correlation and exchange are taken into account, provided that μ_1 is taken to mean the actual value of $n_0\partial\mu_0/\partial n_0$ for the interacting electrons rather than $2\mu_0/3$. In particular, at not very large r_s,

$$\mu_1\simeq E_0(1.23r_s^{-2}-0.204r_s^{-1}-0.010), \qquad r_s=({}^4/_3\pi a^3n_0)^{-1/3}$$

(see, e.g.,[8]). We note that in particles of metallic type produced after dispersion at large $|U| \gg \mu_0$,[1,2] at typical values of the parameters ($\epsilon m_0/m > 20$), we obtain $r_s < 1/2$, i.e., the neglect of the exchange and correlation energies is justified.

A more stringent restriction on n_0a^3 is imposed by the requirement that the fluctuations δy of the potential energy be small in comparison with $|U|$. In strongly-doped semiconductors with randomly distributed donors, at small $|\delta y|$, the fluctuations have a Gaussian distribution

$$\exp[-(\delta y)^2/\gamma^2], \qquad \gamma^2=4\pi e^4\varepsilon^{-2}n_0\varkappa^{-1}(kT)^{-2}$$

(see, e.g.,[9]). To be able to neglect these fluctuations, the following condition must be satisfied

$$\gamma/|U|=0.53(a^3n_0)^{-1/4}\mu_0/|U|\ll 1, \tag{5}$$

i.e., a^3n_0 must be large enough. If the donor distribution is not random but corresponds to the equilibrium that is established at $T_1 > T$, then $\gamma/|U|$ changes by a factor $(T_1T)^{1/2}\mu_0^{-1/4}$.

Even if condition (5) is satisfied, large fluctuations of the potential and of the charge density, corresponding to the tail of the distribution function, should lead to the appearance, above T_1^0, of heterophase fluctuations, which are peculiar to strongly-doped semiconductors, of sections of the phase II (these differ in their character from the known Frenkel heterophase fluctuations).

In this case, however, they have a small total volume. On the other hand if $\gamma \gg |U|$, then at small σ in a temperature interval of width

$$\sim\gamma|U|n_0(\mu_1 q)^{-1}T^0 \gg |T_1^0-T^0|$$

a complicated distribution of sections of the two phases ($p \sim 1$) is produced around T^0 and is due to fluctuations of the potential and of the electron density. In particular, it can form interpenetrating phase skeletons. The structure of this distribution and the character of the phase transition at $\gamma > |U|$ will not be considered here.

The influence of the deviations from the quasiclassical approximation can be estimated by considering the term $(72n_0)^{-1}|\nabla n(\mathbf{r})|^2 E_0 a^2$ in the electron-energy density.[10,8] Its contribution to $\delta\Phi$ can be represented approximately in the form of a sum of two terms due to the smooth variation of $n(r)$ inside each of the phases, with an abrupt change of $n(r)$ (over a distance shorter than κ^{-1}) at the interphase boundary. The ratio of the first of these terms to the last term of formula (3) for $\delta\Phi$ is smaller than $0.017(a^3n_0)^{-1/3}$ and can be neglected. The second term leads to an electron contribution to the interphase-boundary energy

$$\sigma' \sim 0.1U^2n_0(a^3n_0)^{1/6}/\mu_1\varkappa,$$

which can be regarded as already included in σ.

We note that the entire last term of (3) can be regarded at large R_1 and R_2 as a negative electronic contribution to the interphase surface energy, due to the redistribution of the electrons over distances $\sim\kappa^{-1}$. In this formulation, the HS are produced when the summary surface energy becomes negative at $n_0 > n_c$. From this point of view, a qualitative remark that heterogenization is possible was apparently first made in a paper by Larkin and Khmel'nitskiĭ[11] (devoted to another type of nonequilibrium HS in ferroelectrics).

It follows from the presented results that to satisfy the criteria of the theory and to obtain HS with relatively large layer thicknesses, systems with large ϵ and n_0 and with small m and σ are favorable. For example at $\epsilon m_0/m = 30$, $T = 300$ K, $\sigma kT = 30$ erg/cm^3, $U = 0.8\mu_0 = 20$ ($UkT = 0.5$ eV), $n_c = 1.5 \times 10^{21}$ cm^{-3} and for $n_0 = 2.3 \times 10^{21}$ cm^{-3} we get $T_1^0 - T^0 = 2$ K ($q = 3 \cdot 10^{22}$ cm^{-3}). At the transition point we have $2R_2(T_1^0) = 25$ Å, and at $T = T^0$ we have $2R_1 = 2R_2 = 29$ Å.

3. PERIODIC HETEROGENEOUS STRUCTURE

At small σ, the parameter g is not large, R is small, and the quasiclassical approximation ceases to hold (we can no longer confine ourselves to the first terms in the gradient expansion of the electron density). To determine the electronic energy it is convenient in this case to expand the "external" potential energy $U(\mathbf{r}) = U\theta(\mathbf{r})$ in a Fourier series

$$\sum_{\mathbf{k}} U_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}.$$

In the considered second-order perturbation theory approximation, the contributions of the various Fourier components are additive, while the contribution of each individual component to the electronic energy is expressed in terms of the dielectric constant $\epsilon(\mathbf{k})$ of the electron gas (see, e.g.,[2]). As a result $\delta\Phi$ takes the form

$$\delta\Phi = p\varphi + \frac{\sigma}{R} - \frac{n_0}{2\mu_1}\sum_{\mathbf{k}}|U_{\mathbf{k}}|^2\frac{k^2}{\varkappa^2}\left(1-\frac{\varepsilon}{\varepsilon(\mathbf{k})}\right). \qquad (6)$$

$\delta\Phi$ is a minimum for a one-dimensional distribution of the phase sections with a period $2R$ when $k_x = \pi m/R$ ($m = \pm1, \pm2, \ldots$) in (6).

Using the random-phase approximation for $\epsilon(\mathbf{k})$, which is sufficiently accurate if $r_s < 1$, we rewrite (6) in the form

$$\delta\Phi = \varphi p + \frac{\sigma\varkappa}{\pi\sqrt{B}}z - \frac{U^2n_0}{\pi^2\mu_1}\sum_{m=1}^{\infty}\frac{\sin^2(\pi pm)}{m^2}f(zm,B),$$

$$B = \frac{\varkappa^2}{4k_0^2} = \frac{1}{3^{1/3}\pi^{5/3}(a^3n_0)^{1/3}}, \quad z = \frac{\pi}{2k_0R} = \frac{\pi\sqrt{B}}{\varkappa R},$$

$$f(x,B) = \frac{x^2\chi(x)}{x^2+B\chi(x)}, \quad \chi(x) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\frac{1+x}{|1-x|}. \qquad (7)$$

At small x we have $f \approx x^2(x^2+B)^{-1}$, and then this function reaches at $x \sim 1$ a maximum whose position x_0 depends slowly on B, ranging from 0.40 to 0.73 when B changes from 0.01 to 0.2. Therefore if the minimum of $\delta\Phi$ is realized at large R and small z ($g \sim 1$, $\sqrt{B} \ll 1$ or $0 < 1 - g \ll 1$), then all the terms must be included in the sum over m in (7). The summation over m then leads to the previous result (3). If, however, $g \ll 1$ is small and the minimum of $\delta\Phi$ corresponds to $z \sim 1$, then the principal role in the sum over m in (7) is played by the first term, and the higher terms can be neglected (the correction connected with these terms is easily calculated: at $g < \sqrt{B}$ it is less than 5%, if $B = 0.1$, and $\lesssim 10\%$ if $B = 0.01$).

The equilibrium period of the structure $2R = \pi/zk_0$, and the fraction p of the sections of phase II are then determined by the equations that follow from the condition that $\delta\Phi$ be minimal with respect to z and p:

$$\sin^2\pi p\frac{\partial f(z,B)}{\partial z} = \frac{\pi g}{4\sqrt{B}},$$
$$f(z,B)\sin 2\pi p = \frac{\pi\mu_1}{U^2n_0}\frac{q}{T^0}(T-T^0). \qquad (8)$$

Formulas (8) make it possible to determine $z(T)$ and $p(T)$ numerically for concrete values of the parameters B and g, in particular, at $T = T^0$ we have $p = 1/2$.

At the point of transition to the HS ($\delta\Phi = 0$), as follows from (7) and (8), p and z take on nonzero values p^0 and z^0, i.e., a first-order phase transition takes place.[1)] The temperature and heat of transition are given by

$$\frac{T_1^0-T^0}{T^0} = \frac{U^2n_0}{\pi^2\mu_1 qp^0}\left[\sin^2\pi p^0 f(z^0,B) - \frac{\pi}{4}\frac{g}{\sqrt{B}}z^0\right],$$
$$Q = q\frac{T_1^0}{T^0}p^0.$$

In the case of extremely small surface energies, when $g < \sqrt{B}$, the value of p^0 is determined by the equation $\tan\pi p^0 = 2\pi p^0$ ($p^0 < 0.5$), i.e.,

$$p^0 = 0.37, \quad \frac{T_1^0-T^0}{T^0} = 0.23\frac{n_0U^2}{\mu_1 q}f(z^0,B), \quad Q = 0.37q\frac{T_1^0}{T^0}$$

in the zeroth approximation in $g/\sqrt{B}$. With decreasing temperature, p increases in accord with (8) in the interval $0.37 < p < 0.63$. The structure period $2R = \pi/k_0z$ is independent of T in the zeroth approximation and is given by the equation $\partial f/\partial z = 0$, $z \approx (3B)^{1/4}$ at $\sqrt{B} \ll 1$, while the T-dependent correction to z is proportional to $g/\sqrt{B}$.

Unlike the case considered in Sec. 2, in the periodic structures considered here the screening of the potential does not play an important role. The period of the structure is connected here not so much with the values of the surface and electrostatic energies as with the value of the Fermi diameter $2k_0$. The onset of such a structure is due to the abrupt change of $\epsilon(k)$ in the region $2k_0$, which leads to a maximum of $f(z, B)$.

It should be noted that if the reciprocal-lattice vector of the periodic structure is almost equal to $2k_0$ and $|U|/\mu_0$ is not very small ($|z - 1| < |U|/2\pi\mu_0$), then it is necessary to take into account the restructuring of the electronic spectrum, and the second-order perturbation-theory approximation employed here no longer is valid.[12,13]. The characteristics of the periodic structure can be determined in this case by using the results of Dzyaloshinskiĭ, who determined the singular part of the function f was with allowance for the indicated restructuring of the spectrum.

4. SYSTEMS WITH MOBILE IONS

If the ions have sufficient mobility, the heterogenization is connected with the redistribution of both the electrons and the ions, and in the calculation of $\delta\Phi$ we must take into account also the terms connected with the change of the ion density $\delta n'(\mathbf{r})$. If $|U'| \ll 1$, then

$$\delta n'(\mathbf{r}) \approx n_0[U'(\theta(\mathbf{r}) - p) + y(\mathbf{r}) - \langle y\rangle]$$

is not large, the equation for the potential remains linear, and in the calculation of $\delta\Phi$ we can confine ourselves to terms quadratic in δn and $\delta n'$. Calculating, as before, the different terms in $\delta\Phi$ for large $2R$, when the quasiclassical approximation can be used, we find that for planar geometry (which is thermodynamically favored) we have

$$\delta\Phi = \varphi\frac{R_2}{R} - \frac{n_0(U+U')^2}{2(1+\mu_1)}\frac{R_1R_2}{R^2} + \frac{\sigma}{R} - \frac{n_0\mu_1}{2(\mu_1+1)}\left(U' - \frac{U}{\mu_1}\right)^2\frac{\operatorname{sh}\varkappa'R_1\operatorname{sh}\varkappa'R_2}{\varkappa'R\operatorname{sh}\varkappa'R},$$

$$\frac{1}{\varkappa'^2} = \frac{2\mu_1}{1+\mu_1}r_0{}^2 \approx 2r_0{}^2. \tag{9}$$

In the case of bulky phases, the change of the thermodynamic potential following formation of the second phase, accompanied by a redistribution of a certain number of electron and ion pairs, is determined by the first two terms of (9), while the last two terms are added in the HS. So long as the charge density $n_0 < n_c$ is small, the HS is not favored thermodynamically and the system remains in the homogeneous state, or else, at $T_2' < T < T_1'$, in the form of a two-phase mixture of bulky homogeneous phases. But if $n_0 > n_c$, then the sum of the last two terms in (9) becomes negative and a heterogeneous phase is produced below the second temperature $T_1^0 > T_1'$ (and above the temperature $T_2^0 < T_2'$). It follows from (9) that, just as in the case of immobile ions, in this model the transition to the HS occurs continuously (R_2/R increases from zero). The expressions for T_1', T_1^0, and n_c then become

$$\frac{T_1' - T^0}{T^0} = \frac{T^0 - T_2'}{T^0} = \frac{(U+U')^2 n_0}{2(\mu_1+1)q},$$

$$\frac{T_1{}^0 - T_1'}{T^0} = \frac{\mu_1(U' - U/\mu_1)n_0}{2(\mu_1+1)q}\exp(-2x_2{}^0),$$

$$(1+2x_2{}^0)\exp(-2x_2{}^0) = 1 - g', \qquad g' = g'(n_0) = \frac{2^{3/2}(\mu_1+1)^{3/2}\sigma}{\mu_1^{3/2}r_0n_0(U' - U/\mu_1)^2},$$

$$g'(n_c) = 1. \tag{10}$$

The form of the phase diagram and the parameters of the heterogeneous phase depend significantly on the ratio of $|U|$ and $|U'|$. If $\sqrt{\mu_1}\,|U'| \gg |U|$, then the second term of (9) is much smaller than the last and $T_1^0 - T^0 \gg T_1' - T^0$, while the formulas for the layer thicknesses and T_1^0 turn out to be the same as in the case of immobile ions (Sec. 2), provided U^2 and κ are replaced in them by $U'^2\mu_1$ and κ'. This replacement is necessitated by the fact that now the main physical cause of the heterogenization is the redistribution not of electrons but of ions, while the ions cause screening of the charges over a length $1/\kappa' \approx \sqrt{2}r_0$ (the redistribution of the electrons is made difficult by their Fermi degeneracy). Similar results are obtained in the special case $U \approx -U'$, when $(U + U')^2 \ll U'^2\mu_1$. Just as in the case of immobile ions, a refinement of the model, say allowance for the Van der Waals forces, leads to a transformation of the continuous transition into a first-order transition with a jump $p = p^0$. Accordingly, the electron-ion pairs are redistributed between the heterogeneous phase and phase I (or II), and the two-phase regions indicated in Fig. 3 appear between these phases on the phase diagram. If, however, the factors that refine the model are small, then p^0 is small, the two-phase regions are narrow, and the characteristics of the HS are not greatly changed. An approximate form of the resultant phase diagram is shown in Fig. 3 for the case $\sqrt{\mu_1}|U'| \gg |U|$.

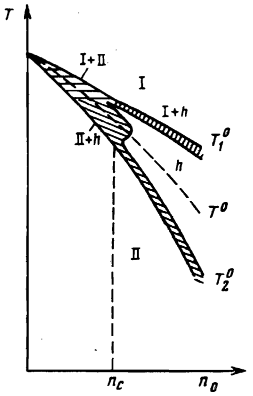

FIG. 3. Phase diagram in the case of mobile ions, showing the curves corresponding to equilibrium between phases I and II and the heterogeneous phase h, and also the two-phase regions.

At sufficiently small $\sqrt{\mu_1}|U'| \ll |U|$, the second term of (9) is significant and $|T_1^0 - T_1'| \ll T_1' - T^0$. The expression for $T_1^0 - T_1'$ now differs from the expression for $T_1^0 - T^0$ in the case of immobile ions in that U^2 is replaced by $(U - \mu_1 U')^2(\mu_1 + 1)^{-1}$ (and g is replaced by g'). If the stronger condition $|U'| \ll |U|/\mu_1$ is satisfied, then $g'(n_0)$ is a decreasing function of n_0. In this case the region of existence of the heterogeneous phase on the (T, n_0) diagram is not to the right of the critical density n_c (as shown in Fig. 3), but to the left. With decreasing n_0 at $\mu_0 \sim U$ the heterogeneous states goes over into the sharply inhomogeneous dispersed state considered in[1,2], and then the region of its existence terminates at the left-hand critical density.

In the case of mobile ions, a HS can arise only at noticeably smaller σ than in the case of immobile ions, and the layers turn out to be much thinner. For example at $U/\mu_1 = -U'/2 = 1/2$, $T = 1500$ K, $\epsilon = 30$, $\sigma kT = 5$ erg/cm^3 and $q = 10^{22}$ cm^{-3} we get $n_c = 8.6 \times 10^{20}$ cm^{-3}, and at $n_0 = 10^{21}$ cm^{-3} we have $T_1^0 - T^0 = 2$ K and $2R_2(T_1^0) = 20$ Å.

Since the screening is produced mainly by the ions, the criterion that the fluctuations of the potential energy be small now takes in place of (5) the form

$$\gamma \sim e^2(n_0r_0{}^3)^{1/2}/\varepsilon kTr_0 \ll |U'|,\ |U|,\ 1 \tag{11a}$$

or

$$E_0^{3/4}(a^3n_0)^{1/4}\ll|U'|,\ |U|,\ 1. \tag{11b}$$

When condition (11) is satisfied, the ratio

$$\frac{\pi}{2k_0R}\approx 1.8\left(\ln\frac{10}{1-g'}\right)^{-1}E_0^{1/2}(a^3n_0)^{1/6}$$

can be small (especially as $g'\to 1$), and then the quasiclassical approximation can be used to describe the electrons. If, however, the criterion (11) is satisfied "at the limit," and $g'\sim 1$, then $\pi/2k_0R\sim 1$ and to describe the electrons it would be necessary to go outside the framework of the quasiclassical approximation (see Sec. 3). Nonetheless, at amall $|U|\ll|U'|\sqrt{\mu_1}$ this circumstance is immaterial, and the results presented are valid because in this case the electron contribution to $\delta\Phi$ can be generally neglected.

5. HETEROGENIZATION WITH A STRONG REDISTRIBUTION OF THE IONS

In the considered case of small $|U'|\ll 1$ (and $|U|\ll\mu_0$) the ion-density change $|\delta n'|\sim n_0|U'|$ is small, and the phase diagram is symmetrical about the $T^0(n_0)$ lines. These results change at $|U'|\gtrsim 1$, when the ion distribution becomes essentially inhomogeneous and the ions can go over almost completely to sections with the structure of one of the phases. At $|U'|\gtrsim 1$ it is necessary to use the complete expression $n'(\mathbf{r})=D\exp[U'\theta(\mathbf{r})+y(\mathbf{r})]$ (D is a normalization constant determined from the condition $\int\delta n'(\mathbf{r})d\mathbf{r}=0$), without expanding it in powers of U' and y. Confining ourselves to the case when only the ions are noticeably redistributed, and not the electrons, we shall assume that $|U|\ll|U'|\sqrt{\mu_0}$ and $|U'|\ll\mu_0$ (but admit the case $\exp|U'|\gg 1$). We can then neglect the electron contribution to $\delta\Phi$ and to the equation for $y(\mathbf{r})$, and take into account only the ion contribution. Solving the Poisson distribution with the indicated distribution $n'(\mathbf{r})$ for plane layers and calculating the different contributions to $\delta\Phi$, we find that

$$\delta\Phi=(\varphi+n_0U')\frac{R_2}{R}+\frac{\sigma}{R}+n_0\ln D_1$$

$$+\frac{r_0n_0}{R}\left[\int\limits_0^{Y_1}\frac{2t+D_1-1}{[D_1(e^t-1)-t]^{1/2}}dt+\int\limits_0^{Y_2}\frac{Y_1+Y_2-2t+D_2-1}{[t-D_2(1-e^{-t})]^{1/2}}dt\right],$$

$$R_1=r_0\int\limits_0^{Y_1}[D_1(e^t-1)-t]^{-1/2}dt,\quad R_2=r_0\int\limits_0^{Y_2}[t-D_2(1-e^{-t})]^{-1/2}dt, \tag{12}$$
$$R=R_1+R_2,$$

where

$$D_1=D\exp[y(R)],\quad D_2=D_1\exp[U'+Y_1+Y_2],\quad Y_1=y(R_2)-y(R),$$
$$Y_2=y(0)-y(R_2),\quad D_1(e^{Y_1}-1)-Y_1=Y_2-D_2(1-e^{-Y_2}).$$

The condition relating the potential drops Y_1 and Y_2 across the sections of phases I and II is the condition that the induction be continuous.

The variables with respect to which $\delta\Phi$ is minimized are best chosen to be not the layer thicknesses $2R_1$ and $2R_2$, but the quantities D_1 and Y_1. Carrying out this minimization numerically, we can easily obtain the functions $R_1(T)$ and $R_2(T)$ and determine the transition temperature T_1^0 for different values of the parameter σ/n_0r_0. By way of illustration, Fig. 4 shows $R_1(T)$ curves in a certain temperature interval $T<T_0$ (which does not reach T_2^0) for $\sigma/n_0r_0=1$ and 3. ($R_2(T)$ is almost constant in this interval.)

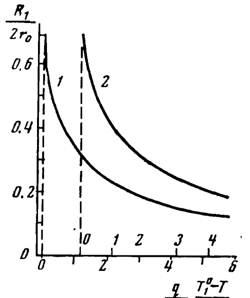

FIG. 4. Temperature dependences of the layer thicknesses $2R_1$ for $\sigma/n_0r_0=1$ (curve 1) and $\sigma/n_0r_0=3$ (curve 2). The lower and upper scales on the abscissa axis pertain to curves 1 and 2, respectively.

In the analytic investigation of the resultant structure we confine ourselves to the most interesting case $\mu_0\gg|U'|\gg 1$, U^2/μ_0 and put for the sake of argument $U'<0$ (to which the case $U'>0$ reduces when the phases are renumbered). At not very small R_1/R practically all the ions go over in this case to the layers of phase I. On the other hand in the layers of phase II ($-R_2<x<R_2$) we shall have $n'(r)\ll n_0$ and these layers turn out to be uniformly charged (since the redistribution of the electrons over a length $\sim(\kappa')^{-1}\ll\kappa^{-1}$ is small at $|U|\ll|U'|\sqrt{\mu_0}$). We can therefore assume that $D_2=0$ and $R_2=2r_0\sqrt{Y_2}$. Near the upper temperature of the transition T_1^0, depending on the model, R_2/R tends to zero or is small, i.e., $n'(r)\approx n_0$ and $D_1\approx 1$. Substituting formulas (12) with $D_1\approx 1$ and $D_2=0$ in the conditions $\partial\delta\Phi/\partial Y_1=0$ and $\delta\Phi(T_1^0)=0$, we readily obtain analytic expressions for T_1^0 and also for R_2, Y_1, and Y_2 at the transition point

$$\frac{q}{n_0}\frac{T_1^0-T^0}{T^0}=|U'|-1-2^{3/4}s^{1/2},\quad 2R_2=4\cdot 2^{1/4}s^{1/2}r_0$$
$$\text{if}\ \ s=\frac{\sigma}{2r_0n_0}\ll 1; \tag{13}$$
$$\frac{q}{n_0}\frac{T_1^0-T^0}{T^0}=|U'|-\left(\frac{3}{2}s\right)^{2/3}-\frac{2}{3}\ln\left(\frac{3}{2}s\right),\quad 2R_2=4r_0\left(\frac{3}{2}s\right)^{1/3}$$
$$\text{if}\ \ s\gg 1.$$

It is seen from (13) and (10) that at small s the temperature T_1^0 of the transition to the HS is much higher than the temperature T_1' of the transition with separation of a bulky phase II ($|U'|\gg U^2/\mu_1$), and that T_1^0 almost corresponds to a transition into a system without ions. With increasing s, the contribution of the surface energy increases, T_1^0 decreases and coincides with T_1' at $s\approx(2.3)|U'|^{3/2}$. At larger s, i.e., at large σ or small n_0, no HS is produced.

With decreasing temperature, R_1 decreases rapidly (see Fig. 4), so that at

$$qn_0^{-1}(T_1^0-T)/T^0\gg s^{2/3},\ 1$$

we have $R_1\ll R_2$, and the charge density in the thin layers with the structure of phase I is almost constant, and the potential drop $Y_1\ll 1$ is small. Minimizing expression (12) for $\delta\Phi$ with respect to the variables D_1 and Y_1 we find that in this temperature region

$$2R_2=\frac{q}{n_0}\frac{T_1^0-T}{T^0}2R_1=4\left(\frac{3}{2}s\right)^{1/3}r_0,\quad Y_2=\frac{q}{n_0}\frac{T_1^0-T}{T^0}Y_1=\left(\frac{3s}{2}\right)^{2/3},$$
$$n'(R)=\frac{q}{n_0}\frac{T_1^0-T}{T^0}n_0,\quad n'(0)\ll n_0. \tag{14}$$

The indicated region is bounded from below by the requirement

$$n'(0)=n'(R)\exp[-|U'|+Y_1+Y_2]\ll n_0,$$

i.e.,

$$q(T_1{}^0-T)/T^0 \ll n_0 \exp\left[|U'|-(3s/2)^{2/3}\right].$$

With further decrease of temperature, the layers I become so thin that they cannot contain the majority of the ions (in spite of their high concentration), and the ions go over into layers II, the thickness of which begins to increase, Near the lower temperature T_2^0 we have $R_1/R_2 \rightarrow 0$, $n'(0) \rightarrow n_0$, and $D_2 \approx 1$. At not too large s, owing to the small thickness of layers I, we have $Y_1 \ll 1$ and in accord with (12), at $s \ll 1$,

$$\frac{q}{n_0}\frac{T_1{}^0-T_2{}^0}{T^0}=\exp(|U'|), \quad 2R_1=2^{9/4}s^{1/2}\exp(-|U'|)r_0, \tag{15a}$$
$$Y_1=2^{3/2}s\exp(-|U'|), \quad Y_2=2^{3/4}s^{1/2},$$

and at $s \gg 1$,

$$\frac{q}{n_0}\frac{T_1{}^0-T_2{}^0}{T_0}=\exp(|U'|-Y_2), \quad 2R_1=4\left(\frac{3s}{2}\right)^{1/3}\exp(-|U'|+Y_2)r_0,$$
$$Y_1=\exp(-|U'|+Y_2)Y_2, \quad Y_2=\left(\frac{3s}{2}\right)^{2/3}+1. \tag{15b}$$

It is seen from (14) and (15) that in the region of the temperatures T_2^0 the thicknesses $2R_1$ usually become very small (except for systems with very large ϵ and r_0 or the case $n_0 \approx n_c$), and the employed macroscopic approximation becomes strictly speaking inapplicable. These results lead nonetheless to qualitative conclusions, that the layers of phase I become abruptly thin with decreasing temperature and that the width of the heterogeneous phase is considerably larger at $T < T^0$ than at $T > T^0$ if $U' < 0$. For the case $U' > 0$, to the contrary, the heterogeneous phase region is much wider at $T > T^0$. Appreciable deviations from macroscopicity, and also the already mentioned factors, make the transition at T_2^0 ($U' < 0$) a well pronounced first-order phase transition and a relatively broad two-phase region (much broader than near T_1^0) appears in this case on the phase diagram.

In the same way, the region of the heterogeneous phase is essentially asymmetrical with respect to $T^0(n_0)$ line in the case of spontaneous dispersion due to electrons (at $|U| \gg \mu_0$). At $U > 0$ this region subtends a certain temperature interval above T^0, given according to (18) of[2] by

$$T_1{}^0-T^0=\frac{0.43}{\alpha_4^{5/2}}\frac{T^0}{qv}\left(\frac{WkT^0}{\Delta E}\right)^{3/2}W$$

(v is the volume of the unit cell, ΔE is of the order of the width of the conduction band, while $W \sim U$ and $\alpha_4 \sim 1$ are defined in[2]), while below T^0 there may be no HS at all. Just as in the case considered here, in the model that takes into account only the Coulomb interaction between the particles, the transition to the HS is continuous, and the first to be produced are only the extremely remote particles containing only a small fraction of the electrons, but following a slight decrease in the temperature, amounting to $\delta T \sim (T_1^0 - T^0)/U \ll T_1^0 - T^0$, practically all the electrons go over to the particles. On the other hand, allowance for, say, the Van der Waals forces makes this a first-order transition and leads in the case of mobile ions to the appearance of a small two-phase region. Since these effects of transition smearing (which are only mentioned in[1,2]) occur in a temperature interval ΔT that is narrow and difficult to investigate in practice, they can be neglected.

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1) Even at very small equilibrium values of z, the terms with $m \gg 1$ in the sum of (7), calculated with the exact function f(zm, B) (and not with its approximate expression $z^2m^2[z^2m^2 + B]^{-1} \approx 1$), are negligibly small. This leads to certain deviations from (3) and transforms the continuous phase transition into a first-order transition with a finite (albeit small) p^0 and a finite (albeit large) R.

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