# Equilibrium heterogeneous states in metallic systems

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Thermodynamic-equilibrium heterogeneous states are considered in metallic solutions in which the superstructure reciprocal-lattice vectors $\mathbf{G}'$, which manifest themselves upon ordering, are close to the diameters $2\mathbf{k}_F$ of the flattened parts of the Fermi surface. If the ordering proceeds as a first-order phase transition, the produced heterogeneous state is strongly modulated in the amplitude of the order parameter and consists of alternating ordered and disordered sections. The physical factors that lead to stability of such a heterogeneous state are the large gain of the singular part of the electron energy at $\mathbf{G}' \approx 2\mathbf{k}_F$ for small ordered regions in the disordered matrix compared with the homogeneous ordering accompanied by restructuring of the spectrum, as well as the gain energy when the sites $\mathbf{G}'$ become split and shifted for the ordered or the deformed ordered regions. The characteristics of the heterogeneous states (sizes, shapes and fraction of the disordered region, relations between the phases of the neighboring disordered regions, the temperature interval in which the heterogeneous states exist), produced in systems with phase transition of the substitution and displacement type are considered. They correspond to the homogeneous-state singularities observed in diffraction and electron-microscopy investigations of a number of metallic solutions.

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## INTRODUCTIONS

The correlation in the arrangement of atoms in systems with short-range forces attenuates rapidly far from the phase-transition point (over distances of the order of the interatomic distance $r_0$), and such systems are quite homogeneous. In a number of metallic systems, however, states are observed with relatively large-scale inhomogeneities having characteristic lengths of the order of (5–10) $r_0$ and spanning over hundreds of atoms. Thus, an analysis of data on diffuse scattering of x rays and electron-microscopy investigations have shown that in many disordered metal solutions, at hundreds of degrees above the point of first-order phase transition into the disordered state, there exists, under equilibrium conditions, an appreciable fraction of ordered regions of the indicated size (see, e.g., Refs. 1 and 2), contained in a disordered matrix. In some transition-metal solutions with bcc lattice, in which a displacive phase transition into a trigonal $\omega$ phase can take place, extended quasilinear sections of the $\omega$ phase in a bcc were also observed in a wide temperature interval (see, e.g., Refs. 3–6). Regions with strongly differing local order exist also in certain other metallic systems.

In a system with short-range forces, the density of the thermodynamic potential $\varphi(\mathbf{r})$ depends locally on the order parameter $\eta(\mathbf{r})$ and the density of the thermodynamic potential of a heterogeneous system consisting of extended sections of two phases

$$\varphi=p\varphi_1+(1-p)\varphi_2+\gamma S$$

($\gamma$ is the surface energy and $S$ is the area of the interphase boundaries per unit volume) is a minimum when the fraction $p$ of one of the phases is equal to zero or unity, i.e., an equilibrium heterogeneous state is possible. Far from the phase-transition point it is practically impossible also for sections of a second phase to appear as a result of heterophase fluctuations.[7]

The situation changes qualitatively if the long-range forces are substantial. In metallic systems they can be due to indirect interaction due to the conduction electrons. It is known that such an interaction leads to the onset of ordered structures with large periods[8,9] and of charge-density waves.[10,11] In these cases, long-range order arises in the entire crystal, and its large-scale inhomogeneity reduces to modulation of the phase[12] and of the sign of $\eta(\mathbf{r})$ (and only within definite limits of the amplitude). As will be shown below, in systems where first-order phase transitions are possible, another strongly amplitude-modulated substantially inhomogeneous distribution of the order and of the composition can set in, wherein regions with high local alternate with disordered (or weakly ordered) regions.

The advantage of this heterogeneous state over the homogeneous ordered phase or over an ordered phase broken up into antiphase domains can be understood when account is taken of nonlocal effects in the dependence of $\varphi(\mathbf{r})$ on $\eta(\mathbf{r}')$ at $\mathbf{r}'\neq\mathbf{r}$, which lead to a nonlinear dependence of $\varphi$ on the fraction $p$ of the ordered regions and limiting the growth of $p$. These effects are of quantum origin and are due to the known peculiarity of the variation of the electron energy $E_e(\mathbf{k})$ under the action of the $\mathbf{k}$th perturbation wave in the region of values of $\mathbf{k}$ close to the diameter $2\mathbf{k}_F$ that joins flattened or cylindrical sections of the Fermi surface. In the course of ordering there appear potential-energy waves corresponding to superstructure vectors of the reciprocal lattice $\mathbf{G}'$ and leading to the lowering of the electron energy. It is important that at $\mathbf{G}'\approx 2\mathbf{k}_F$ the energy decrease per atom can be considerably larger when several disordered regions are produced in the disordered matrix than in the case of a homogeneously ordered crystal.

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This difference is due, first, to the fact that owing to the restructuring of the electron spectrum in the homogeneous ordering, the usual perturbation theory no longer holds and in the "special" region $\mathbf{k} \approx 2\mathbf{k}_F$ the energy $E_e(\mathbf{k})$ does not have a quadratic dependence on the perturbation amplitude.[13] On the other hand, the action of a small ordered region in the disordered crystal on the electrons is described in second-order perturbation-theory approximation, and the corresponding decrease of the energy $|E_e^{(2)}(\mathbf{k})|$ per atom can be much larger than $|E_e(\mathbf{k})|$. Second, by choosing a suitable long- or short-range order in the disposition of the ordered regions and their phase, it is possible to "split up" the superstructure site $\mathbf{G}'$ into a group of sites $\mathbf{G}' \pm \mathbf{q}_n$ and, just as in the case of long-period structures, lower by the same token the electron energy if the minimum of $E_e(\mathbf{k})$ is shifted somewhat relative to $\mathbf{G}'$ and

$$E_e(\mathbf{G}'+\mathbf{q}_n)+E_e(\mathbf{G}'-\mathbf{q}_n)-2E(\mathbf{G}')<0$$

(the possibility of formation of heterogeneous states as a result of this mechanism was qualitatively discussed earlier in Ref. 14). Third, appreciable local deformations which occur when the concentration is redistributed in solutions with noticeably different atomic radii of the components shift the vectors $\mathbf{G}'$ for the small ordered regions relative to the reciprocal-lattice sites of the homogeneously ordered phase, and this can also decrease $E_e$ and stabilize the heterogeneous states.

The essential role of amplitude modulation of the local order in the considered case of systems in which the ordering takes place as a pronounced first-order phase transition with variation of $\eta$ from 0 to $\approx 1$ is connected with the character of the $\varphi(\eta)$ dependence plotted in Fig. 1 for such systems. The presence of a second maximum or of a section with a small slope at $\eta = \eta_m \sim 1$ besides the minimum at $\eta = 0$, and the strong increase of $\varphi(\eta)$ at intermediate $\eta$, favor the formation of sections with $\eta(r) \approx \eta_m$ and $\eta = 0$ (or $\eta \ll 1$).

To reveal more illustratively the physical causes of formation of equilibrium heterogeneous states and to investigate their structure and characteristics, we investigate below simple models of such states. First, in Secs. 1 and 2 we consider the change of the electron energy upon formation of a heterogeneous state, and determine its thermodynamic potential. This is followed by investigation of the equilibrium characteristics of the heterogeneous state for cases of uncorrelated and strongly correlated ordered regions in metallic solid solutions, in which substitutional (Secs. 3–5) and displacive (Sec. 6) ordering takes place.

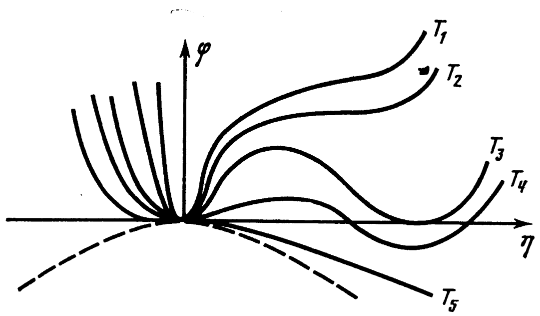
## 1. ELECTRON ENERGY OF SOLUTION

The potential energy $V(\mathbf{r})$ of a conduction electron in a binary disordered solution $A$–$B$ in the customarily employed additive approximation can be written as a sum of contributions of individual atoms:

$$V(\mathbf{r})=\overline{V}(\mathbf{r})+\Delta V(\mathbf{r}),$$

$$\Delta V(\mathbf{r})=\sum_{s=1}^{N}(c_s-c)\,[V_A(\mathbf{r}-\mathbf{R}_s)-V_B(\mathbf{r}-\mathbf{R}_s)]. \qquad (1)$$

Here $N$ is the number of lattice sites, $\overline{V}(\mathbf{r})$ is the potential



energy of the electron in a ideal crystal consisting of "average" atoms, $\mathbf{R}_s$ is the radius vector of the $s$th atom (static displacements of the atoms are assumed small and are disregarded), $c_s$ takes on values 1 or 0 if atom $A$ or $B$, respectively, is located on site $s$, $c = \langle c_s \rangle$ is the concentration of the atoms $A$, and $V_A(\mathbf{r})$ and $V_B(\mathbf{r})$ are the interaction energies of the electron with atoms $A$ and $B$. Changing over from $c_s - c$ to Fourier components $c_k$, we can represent $\Delta V(\mathbf{r})$ in the form of a sum over the reciprocal-lattice cell:

$$\Delta V(\mathbf{r})=\sum_{\mathbf{k}} c_{\mathbf{k}} v_{\mathbf{k}}(\mathbf{r})\,e^{-i\mathbf{k}\mathbf{r}}, \quad c_{\mathbf{k}}=\frac{1}{N}\sum_{s}(c_s-c)\,e^{i\mathbf{k}\mathbf{R}_s},$$
$$v_{\mathbf{k}}(\mathbf{r})=\sum_{s}[V_A(\mathbf{r}-\mathbf{R}_s)-V_B(\mathbf{r}-\mathbf{R}_s)]\,e^{i\mathbf{k}(\mathbf{r}-\mathbf{R}_s)}. \qquad (2)$$

If the difference $|V_A - V_B|$ is small compared with the Fermi energy $E_F$, the electron energy can be determined by perturbation theory. The configuration part of this energy, which depends on $c_s$, appears in the second-order approximation and reduces to a sum of contribution of separate waves $c_k v_k$:

$$E_e^{(2)}=\frac{1}{2}N\sum_{\mathbf{k}} w^{(2)}(\mathbf{k})\,|c_{\mathbf{k}}|^2, \qquad (3)$$

where, in the single-electron approximation,

$$w^{(2)}(\mathbf{k})=-\frac{2}{N}\sum_{\varkappa\mathbf{G}}|v_{\mathbf{k}}(\varkappa,\varkappa+\mathbf{k}+\mathbf{G})|^2\,\frac{n(E_\varkappa)-n(E_{\varkappa+\mathbf{k}+\mathbf{G}})}{E_{\varkappa+\mathbf{k}+\mathbf{G}}-E_\varkappa}. \qquad (4)$$

Here $\mathbf{G}$ are the reciprocal-lattice vectors, $E_\varkappa$ is the energy of an electron with wave vector $\varkappa$ in the expanded-band scheme, $n(E_\varkappa)$ are the Fermi occupation numbers, $v_{\mathbf{k}}(\boldsymbol{\kappa}, \boldsymbol{\kappa}+\mathbf{k}+\mathbf{G})$ is the matrix element $v_{\mathbf{k}}(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r})$ on the Bloch wave functions $(\boldsymbol{\kappa}|$ and $|\boldsymbol{\kappa}+\mathbf{k}+\mathbf{G})$, corresponding to the potential $\overline{V}(\mathbf{r})$.

As already noted, greatest interest attaches to the singularity of $w(\mathbf{k})$ in the region where $\mathbf{k}+\mathbf{G}$ is close to the Fermi-surface diameter $2\mathbf{k}_F$ which joins its parallel sections. The singular part of $\mathrm{w}^{(2)}(\mathbf{k})$, designated $W^{(2)\prime}(\mathbf{k})$, is determined by only one term in the sum (4) over $\mathbf{G}$ (with $\mathbf{G} \approx 2\mathbf{k}_F - \mathbf{k}$). The character of the singularity manifests itself more strongly the more flattened these sections[15,16]: a singularity of the type $\delta k_z \ln(C_1|\delta k_z|)$ appears for spherical sections, of the type $(\delta k_z)^{1/2}$ (at $\delta k_z > 0$) for cylindrical, while of the type $\ln(C_2|\delta k_z|)$, for almost flat ones where $\delta\mathbf{k} = \mathbf{k}+\mathbf{G}-2\mathbf{k}_F$, the $\mathbf{k}_z$ axis is parallel to the normal to these sections, and $C_1$ and $C_2$ are constants.

Allowance for the interelectron interaction leads to replacement of $\mathbf{w}^{(2)\prime}(\mathbf{k})$ by $\tilde{w}^{(2)}(\mathbf{k})$, where for a homogeneous electron liquid with dielectric constant $\varepsilon(\mathbf{k})$ we have in the random-phase approximation

$$\begin{gathered}\tilde{w}^{(2)\prime}(\mathbf{k})=w^{(2)\prime}(\mathbf{k})/\varepsilon(\mathbf{k}+\mathbf{G}),\\ \varepsilon(\mathbf{k})=1+u_e(\mathbf{k})P(\mathbf{k}),\quad u_e(\mathbf{k})=4\pi e^2/k^2.\end{gathered}\tag{5}$$

Here $\mathbf{G}\approx 2\mathbf{k}_F-\mathbf{k}$ and $P(\mathbf{k})$ is determined by Eq. (4) with $v_\mathbf{k}=1$. In a number of cases, in the region of singularity of $w(\mathbf{k})$ the dielectric constant $\varepsilon(\mathbf{k})\approx 1$, and the singularity is mainly connected with the numeraor and not with the denominator of (5). When account is taken of the inhomogeneity of the electron liquid and of exchange and correlation effects, the expression for $\tilde{w}(\mathbf{k})$ becomes more complicated, but the qualitative singularities of the electron energy, which are described by (3)–(5), remain in force.

Expressions (3) and (4) are valid only in the limit of low perturbation amplitudes $c_\mathbf{k}v_\mathbf{k}$. For $\mathbf{k}+\mathbf{G}\approx 2\mathbf{k}_F$ a perturbation with finite amplitude leads to mixing of the electron states $\boldsymbol{\kappa}\approx-\mathbf{k}_F$ and $\boldsymbol{\kappa}+\mathbf{k}+\mathbf{G}\approx\mathbf{k}_F$, which have close energies $E_\varkappa\approx E_{\varkappa+\mathbf{k}+\mathbf{G}}\approx E_F$, and to a restructuring of the spectrum in the actual "singular" region that makes the main contribution to the singular part of $w(\mathbf{k})$. Allowance for this restructuring of the spectrum can be carried out with the aid of generalized perturbation theory and changes $w(\mathbf{k})$ significantly compared with the result of ordinary perturbation theory.[13,17]

The quantity $w'(\mathbf{k})$, which determines the singular part of the change of the electron energy $(1/2)Nw'(\mathbf{k})|c_\mathbf{k}|^2$, a change connected with the perturbation $v_k(\mathbf{r})c_k$, depends on $U^2=v_k{}^2|c_\mathbf{k}|^2$, where $v_\mathbf{k}^2$ is equal to $|v_\mathbf{k}(\boldsymbol{\kappa},\boldsymbol{\kappa}+\mathbf{k}+\mathbf{G})|^2$ averaged in some manner over $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}+\mathbf{k}+\mathbf{G}$, and located in the singular region ($\mathbf{k}+\mathbf{G}\approx 2\mathbf{k}_F$). As $U\to 0$, $w'(\mathbf{k})$ tends to $w^{(2)\prime}(\mathbf{k})$ [Eq. (4)], but at finite $U$ it differs substantially from $w^{(2)\prime}(\mathbf{k})$. Explicit expressions for $w'(\mathbf{k})$ in the case of a small interelectron interaction [$\varepsilon(\mathbf{k})\approx 1$] were obtained in Refs. 13 and 17 for different shapes of the Fermi surface. Let, e.g., the main contribution to $w'(\mathbf{k})$ be made by its flattened regions with areas $S_\mathbf{k}$, namely spherical sections with large curvature radii and with small height $\tilde{k}$, and let the parameters $U$, $E_m=\hbar v_z\tilde{k}$, and $\delta E=\hbar v_z\delta k_z$ ($v_z$ is the projection of the electron velocity on the direction normal to the flattened section $k_z$) be small compared with $E_F$, but let the ratios of the parameters be arbitrary. Then, according to Ref. 17,

$$\begin{aligned}w'(\mathbf{k})=\frac{v_0S_\mathbf{k}v_\mathbf{k}{}^2}{2\pi^3\hbar|v_z|h}\Big[&g(t)+g(h-t)\\ &-\frac{1}{4}h+\frac{1}{2}h\ln\frac{U}{2\hbar|v_z|k_F}\Big].\end{aligned}\tag{6}$$

Here $v_0$ is the volume of the unit cell,

$$\begin{gathered}h=E_m/U,\quad t=\delta E/U,\quad g(t)={}^1/_6t^3\ \text{at}\quad|t|\leqslant 1,\\ g(t)={}^1/_6\{t^3-(t^2+2)(t^2-1)^{1/2}\operatorname{sign}t\\ +3t\ln[|t|+(t^2-1)^{1/2}]\}\ \text{at}\quad|t|>1.\end{gathered}\tag{7}$$

At sufficiently small $U\ll|\delta E|$ and $U\ll|E_m-\delta E|$, expression (6) coincides with the result of perturbation theory and is proportional to $U^2$:

$$\begin{aligned}w^{(2)\prime}(\mathbf{k})=-\frac{v_0S_\mathbf{k}v_\mathbf{k}{}^2}{4\pi^3\hbar|v_z|}\Big[&-\frac{\delta k_z}{\tilde{k}}\ln\frac{|\delta k_z|}{\tilde{k}}-\frac{\tilde{k}-\delta k_z}{\tilde{k}}\ln\frac{|\tilde{k}-\delta k_z|}{\tilde{k}}\\ &+1+\ln\frac{k_F}{\tilde{k}}\Big].\end{aligned}\tag{8}$$

At $U\sim|\delta E|$, however, (i.e., at relatively small $U\ll E_F$, if $|\delta k_z|\ll k_F$), $w'(\mathbf{k})$ and $w^{(2)\prime}(\mathbf{k})$ differ substantially. The expressions for $w'$ and $w^{(2)\prime}$ for a more general form of flattened and cylindrical Fermi surfaces are given in Ref. 17. For a set of perturbation waves with different $\mathbf{k}$, the change of the electron energy $E_e$ can be determined in the form of the sum (3) over $\mathbf{k}$, if the differences $k_z$ are large compared with $U/\hbar|v_z|$. In this sum, however, it is necessary to replace $w^{(2)}(\mathbf{k})$ by $w(\mathbf{k})$.

## 2. CHANGE OF THERMODYNAMIC POTENTIAL UPON FORMATION OF THE HETEROGENEOUS STATE

The long-range effects that lead to heterogenization, are due to the rapidly changing singular part $w'(\mathbf{k})$ of the energy $w(\mathbf{k})$ (connected with the presence of a Fermi surface or with the sharp extremum of $v_\mathbf{k}^2$). Introducing the smooth function $\theta(\mathbf{k})$, which is equal to unity in the singular region and decreases rapidly outside this region, we can formally break up $w(\mathbf{k})$ into $w'(\mathbf{k})$ and a smooth part $w^{(0)}(\mathbf{k})=w(\mathbf{k})-\theta(\mathbf{k})w'(\mathbf{k})$. The latter leads only to short-range indirect-interaction forces. We denote the corresponding contribution to the density of the thermodynamic potential $\varphi$ together with the energy of the direct interaction of the atoms and the entropy term by $\varphi^0(c,\eta)$. It depends locally on the order parameter $\eta(\mathbf{r})$ and on the concentration $c(\mathbf{r})$. Adding the singular part of the electron energy, we write $\varphi$ in the form

$$\varphi=\varphi^0+\varphi_e',\quad \varphi_e'=\frac{1}{2v_0}\sum_\mathbf{k}w'(\mathbf{k})\theta(\mathbf{k})|c_\mathbf{k}|^2.\tag{9}$$

In a homogeneously ordered solution, the main contribution to the sum for $\varphi_e'$ is made by $\mu'$ sites of the reciprocal lattice $\mathbf{G}'$, which appear upon ordering and lie in the singular region. For these sites $c_\mathbf{k}=\xi\eta/2$, where, e.g., in the case of an $L1_2$ lattice and $\mathbf{G}'=\langle 110\rangle$, we have $\mu'=12$ and $\xi=\frac{1}{2}$, while in the case $L1_0$ we have $\mu'=4$ and $\xi=1$ (the contribution of the terms with $\mathbf{k}\neq\mathbf{G}$ can be neglected, inasmuch as for these terms $|c_\mathbf{k}|^2\propto N^{-1}$, and the volume of the singular region in which $\theta(\mathbf{k})=1$ is small). Therefore for homogeneous ordering we have

$$\varphi(c,\eta)=\varphi^0(c,\eta)+\varphi_{hom}',\quad \varphi_{hom}'=\mu'\xi^2w'(\mathbf{k})\eta^2/8v_0.\tag{10}$$

In a disordered solution (which contains no ordered regions), $\varphi=\varphi^0(,0)$. To determine the thermodynamic potential of the heterogeneous state we consider the simplest model, assuming that in the ordered regions the order parameter $\eta(\mathbf{r})=\eta$ is constant, and outside these regions $\eta=0$, and that the dimensions $D_0$ and the shapes of all ordered regions are the same. Since in solutions the inhomogeneous ordering should be accompanied by inhomogeneous redistribution of the composition, the concentration $c$ in the ordered regions is replaced by a certain quantity $\delta c = c - c_0$, relative to the average concentration $c_0$, and in disordered regions it is replaced by

$$\delta c' = c' - c_0 = -\delta c p/(1-p),$$

where $p$ is the volume fraction of the ordered regions. In this model, the difference between $\varphi$ of the heterogeneous state $\varphi_{\text{het}}$ and that of the disordered solution $\varphi(c_0, 0)$ can be written in the form

$$\begin{gathered}
\Delta\varphi = \varphi_{het} - \varphi(c_0, 0) = p\psi(c, \eta, p) + \gamma S + \delta\varphi_e', \\
\delta\varphi_e' = \varphi'_{e\,het} - p\varphi'_{e\,hom}, \\
\psi(c, \eta, p) = \varphi(c, \eta) - \varphi(c_0, 0) \\
+ [(1-p)/p][\varphi(c', 0) - \varphi(c_0, 0)] \\
\approx \varphi(c, \eta) - \varphi(c_0, 0) \\
-\frac{\partial\varphi(c_0, 0)}{\partial c_0}(c - c_0) + \frac{1}{2}\frac{p}{1-p}\frac{\partial^2\varphi(c_0, 0)}{\partial c_0^2}(c - c_0)^2; \quad S = \zeta\frac{p}{D_0}.
\end{gathered} \tag{11}$$

Here $\gamma S$ is the surface energy of the ordered regions per unit volume (with a total area $S$; $\zeta \sim 1$), and $\delta\varphi_e'$ is the difference between the singular part of the heterogeneous and homogeneous systems with identical $\eta$. In the approximate formula for $\psi$ we have discarded the higher-order terms of the expansion in $\delta c'$.

The quantity $\delta\varphi_e'$ is determined according to (9) by the values of $c_{\mathbf{k}}$ in the singular region at small $\mathbf{q} = \mathbf{k} - \mathbf{G}'$. The latter are connected with the $\mathbf{q}$th Fourier components $\eta(\mathbf{r})$, and in the model considered we have

$$\begin{gathered}
c_{\mathbf{k}} = \frac{1}{2V}\xi\int \exp(i\mathbf{q}\mathbf{r})\eta(\mathbf{r})\exp[i\Phi(\mathbf{r})]d\mathbf{r} = \frac{1}{2V}\xi\eta s(\mathbf{q})p(\mathbf{q}); \\
p(\mathbf{q}) = \sum_{\mathbf{R}_m}\exp[i\mathbf{q}\mathbf{R}_m + \mathbf{G}'\mathbf{d}(\mathbf{R}_m)], \quad s(\mathbf{q}) = \int s(\mathbf{r})\exp(i\mathbf{q}\mathbf{r})d\mathbf{r}.
\end{gathered} \tag{12}$$

Here $V$ is the crystal volume, $s(\mathbf{r}) = 1$ inside the ordered region with $\mathbf{R}_m = 0$ and $s(\mathbf{r}) = 0$ outside this region, $\mathbf{R}_m$ is the radius vector of the center of the $m$th ordered region, and account has been taken of the fact that when it is shifted by a certain vector of the lattice of the disordered crystal $\mathbf{d}(\mathbf{R}_m)$, the phase $\exp(i\mathbf{G}'\cdot\mathbf{r})$ of the wave is replaced by $\Phi = \mathbf{G}'\cdot\mathbf{d}(\mathbf{R}_m)$.

Separating in (9) the constant part $w'(G')$ from $\mathbf{w}'(k)$, and taking into account (10) and the relation

$$\int |s(\mathbf{q})|^2|p(\mathbf{q})|^2 d\mathbf{q} = 8\pi^3 pV,$$

we represent $\delta\varphi_e'$ in the form

$$\begin{gathered}
\delta\varphi_e' = \delta\varphi_1' + \delta\varphi_2' + \delta\varphi_3', \quad \delta\varphi_1' = -K_1 p\eta^2, \quad K_1 = \xi^2\mu'\delta w_1/8v_0, \\
\delta\varphi_2' = -\frac{\xi^2\mu'\eta^2}{64\pi^3 v_0 V}\Big[\int \delta w_2(\mathbf{q})|s(\mathbf{q})|^2|p(\mathbf{q})|^2\theta(\mathbf{k})d\mathbf{q} \\
-\frac{\tilde{D}_0}{D_0}\int \delta w_2(\mathbf{q})\lim_{\tilde{D}_0\to\infty}|s(\mathbf{q})|^2|p(\mathbf{q})|^2\theta(\mathbf{k})d\mathbf{q},
\end{gathered} \tag{13}$$

$$\delta\varphi_3' = -\frac{\xi^3 p\eta^2}{8v_0}\sum_{\mathbf{G}'}\frac{\partial w'(\mathbf{G}')}{\partial G_i'}u_{ij}G_j' = -K_3 p\eta^2,$$

$$\delta w_1 = w'_{hom}(\mathbf{G}') - w'_{het}(\mathbf{G}'), \qquad \delta w_2(\mathbf{q}) = w'_{het}(\mathbf{G}') - w'_{het}(\mathbf{G}' + \mathbf{q}).$$

Here $\delta\varphi_1'$ takes into account the change of $w'(\mathbf{G}')$ and of the specific electronic energy on going to small disordered regions, owing to the decrease of the harmonic $U$ of the perturbed potential energy [$w'_{\text{hom}}$ corresponds to $U = v_{G'}\xi\eta/2$, and $s'_{\text{het}}$ for small $D_0$ and $p$ corresponds to the limit $U \to 0$, i.e., $w'_{\text{het}}(\mathbf{G}') = w^{(2)\prime}(\mathbf{G}')$], $\delta\varphi_2'$ takes into account its change due to the smearing of the peak $|c_{\mathbf{G}'}|^2$ in the heterogeneous state, and $\delta\varphi_3'$ is due to the shift of this peak, caused by deformation of the ordered regions $u_{ij}$ $(i, j = x, y, z)$. In the formula for $\delta\varphi_2'$, the limit in the second term corresponds to the larger size of the particles $\tilde{D}_0$ (at a given $p$ and under the similarity transformation of the structure). This term is approximately [neglecting the dependence of $\delta w_2(\mathbf{q})$ on $D_0$] proportional to $1/D_0$ and takes into account the need for subtracting the contribution $\delta\varphi_2'$ to the surface energy, which is already included in the so defined singular part of the term $\gamma S$ in (11).[1]

Equations (11)–(13) determine $\Delta\varphi$ as a function of $p$, $\eta$, and $c$. In the equilibrium state

$$\begin{gathered}
\frac{\partial\Delta\varphi}{\partial c} = 0, \quad \frac{\partial\Delta\varphi}{\partial\eta} = 0, \quad \frac{\partial\Delta\varphi}{\partial p} = 0, \quad \frac{\partial\Delta\varphi}{\partial D_0} = 0, \\
\delta_2(\Delta\varphi) > 0, \quad \min\Delta\varphi < 0,
\end{gathered} \tag{14}$$

where $\delta_2(\Delta\varphi)$ is the second variation of the funciton $\Delta\varphi$ $(p, \eta, c)$.

## 3. UNCORRELATED ORDERED REGIONS

We consider first the simplest case, when the ordered regions are not distorted and the function $\delta w_2(\mathbf{q}) + \delta w_2(-\mathbf{q})$ is sufficiently small. In this case one can neglect the terms $\delta\varphi_2'$ and $\delta\varphi_3'$ in (13), and the heterogeneous state gains electron energy only because of the term $\delta\varphi_1'$, which does not depend on the location of the ordered regions, i.e., the ordered regions can be regarded as uncorrelated.[2] The positive (if $\gamma > 0$) contribution $\gamma S$ to $\Delta\varphi$ can be decreased by increasing the dimension of the ordered regions $D_0$. The growth of $D_0$, however, is limited by the fact that the difference between $w'(\mathbf{G}')$ for the ordered regions and for the homogeneously-ordered crystal manifest themselves only at small $D_0 \lesssim D_0'$, when the additional potential produced by the ordered regions can be regarded as a small perturbation. If, however, the ordered regions are large, the wave functions in their volume are the same as in a bulk crystal, and $\delta w_1 = 0$. Using the known estimates of the region of applicability of perturbation theory, (see §45 in Ref. 18), we can find that for the equal-axis particles

$$D_0' \sim E_F d/v_{\mathbf{k}} \quad \text{at} \quad \delta k_z D_0' \leqslant 1, \tag{15}$$

where $d$ is the lattice constant, i.e., $D_0' \sim (5\text{–}10)d$. The considerable decrease of $\delta w_1$ for ordered regions of noticeably large size makes their formation unlikely.

At sufficiently small $D_0$ and as $p \to 0$ in formula (13) we have $u'_{\text{het}} = w^{(2)'}$ and $w'_{\text{hom}}(\mathbf{G}')$ corresponds to $U_{\text{hom}} = v_{G'}\xi\eta/2$. For a qualitative estimate of the dependence of $\delta w_1$ on $p$ we can put $U_{\text{het}} = pU_{\text{hom}}$. In the case considered $\delta\varphi'_e/p$ and $\psi(c, p, \eta)$ in (11) are then minimal as $p \to 0$. The quantity $\psi(c, \eta, 0)$ decreases with decreasing temperature and is lower than the temperature $T'_0$, for which

$$\psi(c, \eta, 0)+\xi\gamma/D_0-K_1\eta^2=0 \quad (T=T_0'), \tag{16}$$

according to (11), $\Delta\varphi < 0$, and the heterogeneous state is thermodynamically favored. The temperature $T'_0$ can be considerably higher than the point $T_0$ of transition to the homogeneous ordered state [at which $\Delta\varphi = \psi(c_0, \eta, 1)$]. For example, for a solution with structure $L1_0$, which has flattened spherical sections of the Fermi surface, at the values of the parameters

$$U_{hom}=2E_m=4\delta E=0.7\text{ eV}, \quad \hbar^2 k_F^2/2m_0=7\text{ eV},$$
$$S_{\mathbf{k}}=\pi k_F^2/4, \quad v_z=\hbar k_F/m_0$$

(i.e., $\bar{k} = 0.1k_F$, $\delta k_z = k_F/40$), we have according to (6)–(8) and (13) $v_0K_1 \approx 0.06$ eV. Such an increase of the effective ordering energy raises at $\psi \gg \zeta\,|\gamma|/D_0$ the point $T'_0$ to $\approx 600$ K above $T_0$ even in the absence of other factors that stabilize the heterogeneous state (see below). When the temperature drops below $T'_0$ a decrease of $\psi$ leads to a continuous increase of $p$ from the value $p = 0$. However, allowance for the term $\delta\varphi'_2$ together with $\delta\varphi'_1$ makes correlation between the particles energywise favorable at considerable $p$, and can lead to a jumplike change of $p$ at the point $T = T'_0$.

## 4. ROLE OF CORRELATION OF ORDERED REGIONS

If the function $\delta w_2(\mathbf{q})q^{-2}$ is not small, the correlation in the arrangement of the ordered regions becomes significant. The role of the correlation is particularly large in the case considered below, when $\mathbf{G}'$ lands in the region where the plot of $w(\mathbf{k})$ has negative curvature, so that $\delta w_2(\mathbf{q}) > 0$ and $\delta\varphi'_2 < 0$. Choosing in suitable fashion the arrangement and the phases of the particles, it is possible to split the peak $|c_{G'}|^2$ by increasing $|\delta\varphi'_2|$ and lowering in this case $\delta\varphi'_e$.

To estimate the value of $\delta\varphi'_2$ we use a model in which the ordered regions are periodically arranged in space (the role of nonperiodicity will be discussed below). In such a model, only $p(\mathbf{q})$ with $q = \mathbf{q}_n$ differ from zero, where $\mathbf{q}_n$ corresponds to a lattice of ordered regions, and the integral with respect to $\mathbf{q}$ in (13) reduces to a sum over $\mathbf{q}_n$. By way of example we consider solutions with fcc lattices and with concentrations in the region $c_0 \approx 1/4$, which have in the ordered state an $L1_2$ structure ($Cu_3Au$). Four types of ordered regions of such a structure are possible, with the following different shifts

$$\mathbf{d}_1=0, \quad \mathbf{d}_2=(\mathbf{a}_1+\mathbf{a}_2)/2, \quad \mathbf{d}_3=(\mathbf{a}_1+\mathbf{a}_3)/2, \quad \mathbf{d}_4=(\mathbf{a}_2+\mathbf{a}_3)/2$$

and with corresponding phases $\Phi = \mathbf{G}'\cdot\mathbf{d}$. Analysis shows that a three-dimensional periodic structure of ordered regions usually leads to a smaller value of $\delta\varphi'_2$ than a one-dimensional one. It has cubic symmetry and an identical number of ordered regions with different phases in a cell.

We assume that a cubic cell with edge length $D$ contains $\nu'$ ordered regions of cubic shape with edge lengths $D_0$. It follows from (12) that the nonzero $p(\mathbf{q}_n)s(\mathbf{q}_n)$ and the corresponding $\mathbf{q}_n$ are defined by the formulas

$$\mathbf{q}_n=\frac{2\pi}{D}\sum_{i=1}^{3} n_i\mathbf{e}_i, \quad |p(\mathbf{q})s(\mathbf{q})|^2$$
$$=\frac{8\nu'^2V}{\pi^3}\delta(\mathbf{q}-\mathbf{q}_n)\prod_i\frac{\sin^2\pi x n_i}{n_i^2}, \quad x=\frac{D_0}{D}, \tag{17}$$

where $|\mathbf{e}_i| = 1$ and $\mathbf{e}_i \| \langle 100\rangle$, while $n_i$ are integers determined by the structure. Thus, if the ordered regions form an fcc lattice ($\nu' = 4$) consisting of four simple cubic lattices with different $\mathbf{d}$, then $\delta\varphi'_2$ is a minimum when the sublattices (000), $(D/2, D/2, 0)$, $(D/2, 0, D/2)$, and $(0, D/2, D/2)$ correspond to shifts $\mathbf{d}_1$, $\mathbf{d}_4$, $\mathbf{d}_2$, and $\mathbf{d}_3$. In this case, e.g., in the vicinity of the site $\mathbf{G}' = (110)$, the numbers $n_1$ and $n_3$ for $p(\mathbf{q}_n) \neq 0$ should be even, while $n_2$ should be odd (or vice versa).

Assume for the sake of argument that the vectors $\mathbf{G} + \mathbf{G}'\langle 110\rangle$ are close to $2\mathbf{k}_F$ (as in alloys based on copper), and assume that $\delta w_2(\mathbf{q})$ have sufficiently sharp maxima and almost constant values $\max \delta w_2(q)$ on large sections of planes or cylinders perpendicular to the vectors $\pm\mathbf{k}_F$ and located at a short distance $\mathbf{k}_0$ away from the site $\mathbf{G}'$. This makes it possible to retain in the integral (sum) (13) only terms for which $\mathbf{q}_n$ land on the indicated surfaces. For an fcc lattice of ordered regions with different $\mathbf{d}$, these terms correspond to the sets $(n_1, n_2) = (1,0)\ (2, -1) \ldots$ with $n_1 + n_2 = 1$ for a plane, or to the pair (1,0), (0,1) for a cylinder and any even (or odd) $n_3$, with $\delta\varphi'_2$ a minimum at $\sqrt{2}\pi/D \approx k_0$. Summing in (13) over such $\mathbf{q}_n$ with allowance for (17), we retain only the rapidly varying part $\delta w_2(\mathbf{q}) \approx \delta w_2^{(2)}(\mathbf{q})$ with peak height $W$ (the contributions of the smooth part in the two integrals in (13) cancel out) and include the second integral of (13), which is proportional to $S$, in the surface energy $\gamma S$ (without changing thereby the designations $\gamma$ and $\delta\varphi_2$). As a result we find that in this case $\delta\varphi_2$, $p$, $S$, and $D$ are given by

$$\delta\varphi_2=-K_2\eta^2 p f_{1,2}(x), \quad K_2=\frac{3W}{4\pi^2 v_0},$$
$$f_1(x)=\frac{1}{x}\left(1-\frac{\sin 2\pi x}{2\pi x}\right) \quad (x<1); \tag{18}$$
$$f_2(x)=2\sin^2\pi x, \quad p=\nu' x^3, \quad S=6\nu'/D, \quad D=\sqrt{2}\pi/k_0,$$

where the functions $f_1(x)$ and $f_2(x)$ correspond respectively to plane and cylindrical sections of the Fermi surface.

The quantity $|\delta\varphi_2|$ takes on somewhat smaller value if the sublattices (000), $(D/2, D/2, 0)$, $(D/2, 0, D/2)$, and $(0, D/2, D/2)$ correspond to the shifts $\mathbf{d}_1$, $\mathbf{d}_2$, $\mathbf{d}_3$ and $\mathbf{d}_4$ [the numbers $n_1$ and $n_2$ for the site $\mathbf{G} + \mathbf{G}' = (110)$ are then even or odd], but in this case $D$ is doubled, i.e., the surface energy is decreased. In this case we have

$$f_1(x)=\frac{1}{4x}\left(1-\frac{\sin 4\pi x}{4\pi x}\right) \quad \text{at} \quad x<\frac{1}{2},$$

$$f_1(x)=\frac{1}{4x}\left[1+\frac{\sin 4\pi x}{4\pi x}+\frac{1-2x}{x}\cos 4\pi x\right] \quad \text{at} \quad x>\frac{1}{2},$$

$$f_2(x)=\frac{\sin^4 \pi x}{\pi^2x^2}, \qquad D=\frac{2\sqrt{2}\,\pi}{k_0}. \tag{19}$$

Equations (18) and (19) describe also the case of a cubic lattice of ordered regions, consisting of four bcc sublattices with different $\mathbf{d}$. It must only be taken into account that in this case $\nu'=8$. Just as in the case of uncorrelated ordered regions, Eqs. (18) and (19) for $\delta\varphi_2$ are valid only at $D_0<D_0'$ in the region of applicability of perturbation theory. When $D_0$ exceeds $D_0'$ (15) noticeably, the wave functions of the electrons inside the ordered regions (with the exception of the subsurface layer) become the same as in the bulk crystal, thereby weakening greatly the interaction of the ordered regions. Formally this corresponds to a considerable decrease of $f_{1,2}(x)$ at $x=D_0/D>D_0'/D$.

Although the expressions presented for $\delta\varphi_2$ were obtained for a model of a periodic structure of ordered regions, actually practically the same gain in electron energy can be obtained by establishing a short-range order of the ordered regions. It suffices only for the function $|c_{\mathbf{k}}|^2$ (12) to have a sufficiently sharp peak with a width less than $k_0$. If, e.g., the short-range order of the ordered regions can be described as an aggregate of small quasicrystals of a lattice of ordered regions with dimensions $2D$, and $D$ is connected with $k_0$ by Eq. (19), then the width of the $|c_{\mathbf{k}}|^2$ peak amounts to $k_0/3$. An even sharper peak is obtained in the paracrystal model.[19] This means that if the $\delta w_2(\mathbf{q})$ peak is not very sharp, then the difference $\delta\varphi_2'$ for long- or short-range order of the ordered regions is small. Therefore the heterogeneous state corresponds apparently to a short-range order in the arrangement of the ordered regions. The considered example of negative curvature of $w'(\mathbf{k})$ in the region $\mathbf{k}\approx\mathbf{G}'$ (i.e., $W>0$), the neighboring ordered regions should be in antiphase. If, however, the curvature of $w'(\mathbf{k})$ is positive (i.e., $W<0$), then they have identical phases.

## 5. ANALYSIS OF THE HETEROGENEOUS STATE

Equations (11), (13), (18), and (19) specify the value of $\Delta\varphi(c,\eta,p)$. By determining the equilibrium concentration $c=c(\eta,p)$ in the ordered regions from the condition $\partial\Delta\varphi/\partial c=0$, we can represent $\Delta\varphi$ as a function of $\eta$ and of $p=\nu'x^3$:

$$\Delta\varphi(\eta,p)=p[\psi(\eta,p)+6\gamma/xD-K_1(p)\eta^2 \\ -K_2\eta^2f(x)-K_3\eta^2], \quad \gamma=\gamma(\eta,\delta). \tag{20}$$

Here $\psi(\eta,p)=\psi[c(\eta,p),\eta,p]$, and $\gamma$ depends on the distance $\delta$ between the edges of the neighboring ordered regions, i.e., on $p$ (the mutual approach of the ordered regions hinders the spatial relaxation of the order and of the composition), increasing strongly at $\delta\sim d$ (usually $D\sim 5d$, i.e., at $\nu'=4$ we have $\delta\approx 4d$ at $p=1/16$ and $\delta\approx 1.5d$ at $p=1/4$).

The dependence of $\psi(\eta,p)+6\gamma/xD$ on $\eta$ is described by curves of the type shown in Fig. 1, while the negative term in (20) depend quadratically on $\eta$ and lead to an additional contribution to the ordering energy. They lower the resultant plots of $\Delta\varphi$ against $\eta$ (for a given $p$). Just as in the case of ordinary homogeneous ordering, at sufficiently high temperatures $\psi$ is large, $\Delta\varphi>0$ at all $x$ and $\eta$, and the heterogeneous state is thermodynamically not profitable. However, starting with a certain temperature $T_0'$, at which the $\Delta\varphi(\eta,p)$ curve for the optimum value $p=p_0$ touches the abscissa axis at the point $\eta_0\sim 1$ (as the curve does for $T=T_3$ in Fig. 1), we have $\min\Delta\varphi<0$ and the heterogeneous state becomes the thermodynamically equilibrium state.

Inasmuch as at small $p$ we have $K_1=K_1^{(0)}-K_1^{(2)}p^2$, and $f(x)\propto p^{1/3}$ (or $f(x)\propto p^{2/3}$), a finite fraction of ordered regions appears in the model with correlated arrangement of the ordered regions and $K_2>0$ (in contrast to the case $K_2=0$) even at $T=T_0'$. Therefore the transition into the heterogeneous state should be regarded as a smeared-out (owing to the finite dimensions of the ordered regions) first-order phase transition. The value of $p_0$ is determined by the relation between $K_1^{(2)}$, $K_2$, $D^{-1}\partial\gamma/\partial p$, and $\partial x/\partial p$. A typical estimate of $p_0$ is the interval3) $p_0\approx 0.05$–$0.2$. The distance between the ordered regions is a maximum (i.e., $\gamma S$ is a minimum) in the considered fcc lattice of ordered regions with different $\mathbf{d}(\nu'=4)$, and in the region $T\approx T_0'$ such a lattice apparently describes a heterogeneous state at $K_2>0$.

With decreasing temperature, $x$ decreases, $\Delta\varphi$ can be negative at larger $p$, and as seen from (20) the minimum of $\Delta\varphi$ corresponds to ever larger $p$ and $\eta$. When the value of $\psi$ decreases strongly noticeably below $T_0'$ (and can then become negative), the growth of $p$ is limited only by the strong increase of $\gamma$ at small $\delta$, by the decrease of $K_1(p)$, and by the growth of $\psi$ with $p$, so that $p$ can reach values $\sim 1$. It becomes thermodynamically more profitable in the region $p\sim 1$ to have a short-range order of the ordered regions, which corresponds not to a lattice with $\nu'=4$ (and $p\leqslant 1/2$) but to a more closely packed lattice with $\nu'=8$ (and $p\leqslant 1$) or to a layered structure. The transitions between the structures with different short-range order of the ordered regions or with different $D$ should be regarded as smeared first-order phase transitions.

After reaching a certain temperature $T_0$, at which

$$\Delta\varphi(\eta,p)=\psi(c_0,\eta_0,1)\equiv\varphi(c_0,\eta_0)-\varphi(c_0,0), \tag{21}$$

the solution goes over into a homogeneously ordered state with an order parameter $\eta_0$ less than $\eta$. For systems with $p(T_0)\ll 1$, the points $T_0$ determined by the usual equilibrium condition (in the absence of a heterogeneous state) $\varphi(c_0,\eta)=\varphi(c_0,0)$ and by the condition (21) are close. If, however, $p(T_0)\sim 1$, then (21) leads to noticeably smaller $T_0$.

At large $K_1$, $K_2$, and $K_3$ the interval of the existence of the heterogeneous state $T_0'-T_0$ can be sufficiently large and comparable in order of magnitude with $T_0$. For example, estimating $K_1$ for the alloy $Cu_3Au$ and assuming that its Fermi surface is the same as that of copper, we can find that $v_0K_1\approx 0.01$ eV at $E_F=7$ eV, $v_{G'}=1$ eV, and $\delta K_z=0.05\,k_F$ [exact estimates of $v_{G'}$ and $K_1$, $K_2$, and $K_3$ are made difficult by the insufficient information on the wave functions of the electrons and by the smearing of the $\delta w_2(\mathbf{q})$ peak]. Using the results of the calculations of $P(\mathbf{k})$ for Cu (Ref. 9) we can obtain the estimate $v_0K_2f(x)\approx 0.02$–$0.03$ eV at $x\approx 1/4$. The quantity $k_3$, connected with the deformations in the ordered regions, e.g., at $u_{ii}=-0.03$, amounts according to (13) and Ref. 9 to4) $\approx 0.02$ eV. All these factors act in the same direction and, jointly with the effects that are caused by the inhomogeneity of $\eta(\mathbf{r})$ and $c(\mathbf{r})$ in the ordered regions, can lead to values $T_0' - T_0 \approx 800$–1000 K ($T_0 = 667$ K in $Cu_3Au$).

The type of local order in the ordered regions above $T_0$ is not necessarily the same as at $T < T_0$. Thus, in the ordered regions of an $AB_3$ solution, owing to the redistribution of the concentration, the local order can correspond to the structure $L1_0$ (with large $|\delta\varphi_1'|$), or a mixed heterogeneous state can arise, containing ordered regions of the type both $L1_2$ and $L1_0$. At sufficiently large $p$ and $\eta$, owing to the third-order terms in the expansions of $\delta\varphi_e'$ in terms of $v_{\mathbf{k}}/E_F$, the stable regions may turn out to be those with structure $DO_{22}$, having vectors $\mathbf{G}'$ of the type $(1\,\frac{1}{2}\,0)$ and (010) (the triangle made up of the vectors $(1\,\frac{1}{2}\,0)$, $(\bar{1}\,\frac{1}{2}\,0)$, and (010) is almost inscribed in the Fermi surface; see footnote 1).

The small ordered regions should lead to certain singularities of diffuse scattering of x rays in the vicinity of the sites $\mathbf{G}'$, e.g., to the appearance of "crosses" of four maxima in the directions [100] and [010] near the (110) site for the structure of the ordered regions corresponding to eq. (18), or of two maxima in the [110] direction for the structure of ordered regions corresponding to (19). These singularities were observed experimentally in Cu-Au (Refs. 20 and 1). It appears that the foregoing results make it possible to explain the general picture of the distribution of the scattering intensity, to understand the physical nature of the heterogeneous state observed in diffraction and electron-microscopy investigations of a number of systems,[1,2,21] to obtain correct estimates of the sizes of the ordered regions, to explain the type of the resultant local order ($L1_2$, $L1_0$, and $DO_{22}$ in $Cu_3Au$, Ref. 1) and the ratios of the phases of the neighboring ordered regions, as well as the large temperature interval of existence of the heterogeneous state and the presence of smeared-out phase transitions $T_0 < T < T_0'$, connected with the restructuring of the local order and of the structure of the ordered regions.[1]

## 6. HETEROGENEOUS STATES IN DISPLACEMENT-TYPE PHASE TRANSITION

In a number of transition-metal solutions with bcc lattices, a first-order phase transition takes place with formation of a trigonal $\omega$ phase on account of the displacements of pairs of atomic planes of the (111) type relative to one another, by a distance $u_0 \approx \sqrt{3}d/12$, while each third plane remains immobile. They can be described by a static displacement wave[22]

$$\mathbf{u}_s = \mathbf{u}_0 \sin(\mathbf{G}'\mathbf{R}_s + \Phi), \qquad \mathbf{u}_0 \| \mathbf{G}' = (2\pi/d)\,({}^2/_3\,{}^2/_3\,{}^2/_3), \quad (22)$$

where the phase shifts $\Phi = 0$, $2\pi/3$, and $4\pi/3$ for the three possible subvariants of the $\omega$ phase differ in the numbers of the undisplaced atomic planes $3n + 0, 1, 2$.

In a certain range of compositions, in place of the homogeneous $\omega$ phase there is produced a heterogeneous state containing alternating sections of $\omega$ and bcc phases.[3–6] When explaining its existence, Cook[23] has advanced an interesting idea that an important role is played by the slight incommensurability of these phases, which leads to modulation of the displacement wave. In the local theory, however, this factor is by itself insufficient for the appearance of the observed amplitude-modulated heterogeneous state in place of the phase-modulated structure that contains only ordered domains of different subvariants.[12,24]

The existence of the observed heterogeneous state can be understood by taking into account the nonlocal effects considered above, which are of quantum origin and are due to the very strong dependence of the electron energy $w'(\mathbf{k})$ at $\mathbf{k} \approx \mathbf{G}'$. (Such a dependence was obtained in numerical calculations for the Zr–Nb system[25,26].)

Using a heterogeneous-state model in which the amplitude $\mathbf{u}_0$ is constant in the ordered regions (in sections of the $\omega$ phase), we can determine its electron energy from Eqs. (9) and (12), in which $c_{\mathbf{k}}$ is replaced by the modulus $i\mathbf{u}_{\mathbf{k}}$ of the Fourier component of the displacements, and $\xi\eta$ is replaced by $u_0$, as well as taking into account the fact that now $v_{\mathbf{k}}(\mathbf{r})$ in expressions (4)–(8) for $w(\mathbf{k})$ contains in place of the difference $V_A(\mathbf{r} - \mathbf{R}_s) - V_B(\mathbf{r} - \mathbf{R}_s)$, as in Eq. (2), the term $-i\mathbf{e}V(\mathbf{r} - \mathbf{R}_s)$, where $\mathbf{e} = \mathbf{u}_0/u_0$. Accordingly, $\delta\varphi_e'$ is determined by Eqs. (13), in which $\xi\eta$ is replaced by $u_0$ and $s(q)$ correspond to the nonequilibrium form of the ordered regions (since the symmetry of the problem is lower than cubic).

We shall simulate the heterogeneous state by a lattice of ordered regions in which both the unit cells and the ordered regions themselves are parallepipeds with edge lengths $D_i$ and $D_{0i} = x_i D_i$. At $\delta w_2(\mathbf{q}) > 0$, the quantity $\delta\varphi_2$ can be made minimal if alternating ordered regions of different subvariants, with phases $\Phi$ equal to 0, $2\pi/3$, and $4\pi/3$, are placed along the axis $Z \| \mathbf{u}_0 \| [111]$ for the given variant of the $\omega$ phase. For such a lattice, the only $p(\mathbf{q})$ that differ from zero are those with $q_z = q_{nz}$, where $q_{nz} = 2\pi n_z/D_z$ ($n_z = 3l + 1$, $l$ is an integer). We consider for the sake of argument systems in which the bcc phase $\delta w_e(\mathbf{q})$ has a sharp peak of almost constant height $W$ on a large section of the (111) plane of $\mathbf{k}$-space, located a short distance $k_0$ away from $\mathbf{G}'$ (in the direction away from the origin). It can be connected with the flattened or cylindrical sections of the Fermi surface.[25,26] The main contribution to $\delta\varphi_2$ is made by the two sites $\mathbf{G}'$ (111) and $(\bar{1}\bar{1}\bar{1})$ $(\mathbf{u}_0 \cdot \mathbf{G}')^2$ and $v_{\mathbf{G}'}$ are noticeably smaller for the other $\mathbf{G}'\{111\}$). Assuming that in the integral (sum) (13) the only important terms are those with $n_z = 1$, for which the $\mathbf{q}_{\mathbf{n}}$ land on the indicated plane, we find that the minimum of $\delta\varphi_2$ is located at $D_z = 2\pi/k_0$ and is equal to

$$\delta\varphi_2' = -K_2 u_0^2 p \frac{\sin^2 \pi x_z}{x_z}, \qquad K_2 = \frac{3W}{4\pi^2 v_0}, \qquad x_z = \frac{D_{0z}}{D_z}. \quad (23)$$

Equations (13) for $\delta\varphi_1'$ and $\delta\varphi_3'$ and (23) for $\delta\varphi_2'$ determine $\delta\varphi_e'$ and, according to (11), also $\Delta\varphi$. If $K_1$, $K_2$, and $K_3$ are large enough, then $\min\Delta\varphi < 0$ and the heterogeneous state is more stable than the bcc phase. In transition metals, $P(\mathbf{k})$ in (5) is usually large and $\varepsilon(\mathbf{k}) - 1 \sim 1$. Therefore $\tilde{w}_{\mathrm{het}}^{(2)\prime}(\mathbf{G}')$ can be greatly increased relative to $w_{\mathrm{hom}}^{(2)\prime}(\mathbf{G}')$, if the heterogeneous state contains ordered regions that are strongly elongated along the [111] axis and have thicknesses $D_{0\perp} \sim d$ and much larger lengths $D_{0z}$. The sites $\mathbf{G}'$ (or $\mathbf{G}' + \mathbf{k}_0$) for the ordered regions are then smeared out into disks of width

$\sim\pi/D_{0\perp}$, as a result of which the average value of $k^2 = G'^2 + k_\perp^2$ increases by 1.5–3 times, and $u_e(\mathbf{k})\sim k^{-2}$ in (5) decreases strongly while $P(\mathbf{k})$ remains almost unchanged, and it is this which leads to the strong increase of $\widetilde{w}^{(2)\prime}(\mathbf{G}')$ in the heterogeneous state. This increase becomes even more abrupt for $\widetilde{w}'(\mathbf{G}')$ because $U_{\text{het}} < U_{\text{hom}}$ at small $p$. This factor can make the values of $K_1$ and $|\delta\varphi_1|$ in (13) large, and together with $\delta\varphi_2'$ (23) it stabilizes the heterogeneous state that contains elongated ordered regions. We note that for perturbation theory to be applicable at small $\delta k_z$ it is necessary to satisfy a condition of the type (15)

$$D_{0z}<E_F d/v_{\mathbf{k}}, \quad \text{if} \quad D_{0\perp}{}^2>D_{0z}E_m d/E_F\zeta_{\mathbf{k}},$$

or

$$D_{0\perp}<(E_m/v_{\mathbf{k}}\zeta_{\mathbf{k}})^{1/2}d, \quad \text{if} \quad D_{0\perp}{}^2<D_{0z}E_m d/E_F\zeta_{\mathbf{k}} \qquad (\zeta_{\mathbf{k}}=S_{\mathbf{k}}d^2).$$

It can be seen from (23) that $\delta\varphi_2'$ is a minimum at the largest possible $x_z = 1/3$, i.e., at $D_{0z} = D_z/3$. However, the dimensions of the ordered regions $D_{0z}$, and especially $D_{0\perp}$, and their fraction $p$, are strongly limited by the indicated dependences of $U_{\text{het}}$ and $\widetilde{w}_e'$ on $p$ and $D_{0\perp}$, by the growth of $\psi$ with $p$ [see (11)] because of the redistribution of the concentration (this redistribution is quite strong, since usually $dT_0/dc\sim 10^4$ K), and also by the abrupt increase of the surface energy of the lateral boundaries of the ordered regions as they come closer together. The joint action of these factors makes the fraction $p\sim 10^{-1}$ small in the temperature region where the heterogeneous state is produced. With decreasing temperature, $\psi$ decreases and therefore $p$ and the "order parameter" $u_0$ increase until a transition takes place at $T = T_0$ into the homogeneous $\omega$ phase. Just as in the case considered above, the interval $T_0' - T_0$ can be large ($\sim 10^2$–$10^3$ K), and the order in the arrangement of the ordered regions is short- rather than long-range.

Thus, the considered simplified model (which does not claim to describe the subtle details of the construction of the sections of the $\omega$ phase and of the transition layers of the bcc matrix) provides a qualitative explanation of the physical nature and of the general picture of heterogeneous state with $\omega$-phase particles, a state observed in a number of studies.[3–6]

## CONCLUSION

Various types of heterogeneous states are possible, due to the interaction of conduction electrons with inhomogeneities of the order. In semiconducting systems they are the result of kinetic factors or of the lowering of the bottom of the conduction band and of the redistribution of the electrons in the region of the changed parameter of the medium, while the dimensions of the ordered regions are limited by the growth of the Coulomb energy.[27–29] It follows from the foregoing results that the heterogeneous states with characteristic inhomogeneity scales $\sim\pi|\mathbf{G}' - 2\mathbf{k}_F|^{-1}$ can arise also in metallic systems with $\mathbf{G}'\gtrsim 2\mathbf{k}_F$, especially if their Fermi surfaces contain flattened or cylindrical sections. It is thus possible to understand the physical nature of the inhomogeneous local order observed in a number of systems with first-order phase transitions of the substitution and displacement type.[1–6,30,31]

We note that in liquid metals there can also be realized heterogeneous states consisting of small ordered crystal-structure regions (not necessarily the same as in the solid metal), alternating with liquid sections. The factors that lower the electron energy of the heterogeneous state $E_e$, indicated in the introduction, should manifest themselves also in liquid metals if $G'\gtrsim 2k_F$ and $G' < 2k_F$, although to a lesser degree because of the spherical shape of the Fermi surface. The "splitting" of the $\mathbf{G}'$ sites in the heterogeneous state can also lower $E_e$ strongly if the minimum of the pseudopotential $v(\mathbf{k})$ lies at $k\approx G'$ (as in indium). If the resultant surface energy is not very high, these factors can lead to stability of the heterogeneous state in a certain interval above $T_{\text{melt}}$. In liquid alloys, the heterogeneous state should be additionally stabilized by the redistribution of the composition.

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[1] It should be noted that at not very small $v_{\mathbf{k}}/E_F$ an important role can be played by singular contributions to $\delta\varphi_e'$ due to higher orders of perturbation theory. For example, the contribution of the third order, while containing an extra factor $v_{\mathbf{k}}/E_F$, has a more abrupt singularity that manifests itself when the triangle made up of the superstructure vectors $\mathbf{G}_1'$, $\mathbf{G}_2'$, and $\mathbf{G}_3'$ is almost inscribed in the Fermi surface.

[2] The quantities $\delta(w_1)(\mathbf{q})$ and $\delta w_2(\mathbf{q})$, and consequently also $\delta\varphi_1'$ and $\delta\varphi_2'$, given the function $w(\mathbf{k})$, are related as can be seen from (6)–(8). If we neglect the dependence of $v_{\mathbf{k}}^2$ on $\mathbf{k}$, we find in this example, for the considered case when $\mathbf{G}'$ lands in the region of small curvature of the function $w'(\mathbf{k})$, that $\delta w_1 < 0$ and $\delta\varphi_1' > 0$. Usually, however, $v_{\mathbf{k}}^2$ depends strongly on $\mathbf{k}$, so that the interval of small bending of $w'(\mathbf{k})$ can be shifted into the region of the minimum of $w'(\mathbf{k})/v_{\mathbf{k}}^2$, where $\delta w_1 > 0$ is a maximum.

[3] If $K_2$ is much larger than the other parameters, $p_0$ corresponds to the maximum of $f(x)$ and, according to (18), if $x_0 < D_0'/D$, then $x_0 = 1/2$, i.e., $p_0 = 1/2$. However, if this value of $Dx_0$ exceeds $D_0'$ (15), the aforementioned decrease of $f(x)$ at $x > D_0'/D$, owing to the violation of the applicability of perturbation theory, leads to a decrease of $x_0$ (to a value $\sim D_0'/D$) and accordingly to a strong decrease of $p_0$. In addition, if $\gamma$ depends strongly on $\delta$ (i.e., on $p$), $\Delta\varphi$ may be smaller (because of the decrease of $\gamma/D$) if the ordered regions make up a lattice with double the period and $f(x)$ is determined by Eq. (19). In this case $x_0 = 1/4$ and $p_0 = 1/16$. Usually $K_1^{(2)}\sim K_2$, and consequently (and also because of the increase of $\psi(\eta, p)$ and $\gamma$ with increasing $p$) the cited values of $p_0$ should even decrease.

[4] In elastically isotropic crystals, the local redistribution of the atoms does not change the elastic energy, and the strain $u_{ii} = \Gamma v_0^{-1}(\partial v_0/\partial c)(c - c_0)$ (where $\Gamma\approx 2/3$) is determined only by the change of the concentration in the ordered region itself. In real elastically anisotropic crystals, appreciable strains of the ordered region can be due to the change of the concentration in the disordered matrix at the boundary with the ordered region. Particularly favorable from the point of view of lowering $\delta\varphi_e'$ in $Cu_3Au$ is the appearance of ordered regions with $L1_0$ structure on the boundaries of the ordered regions with $L1_2$ structure. They lead to considerable strains of the ordered regions $L1_2$, which have the required sign. Such configurations were observed in experiment.[1] We note that a considerable redistribution of the concentration, which facilitates the heterogenization, can be particularly easily reached near a two-phase region on the phase diagram.

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[1] R. Bardhan and J. B. Cohen, Acta Crystallogr. **A32**, 579 (1976).
[2] R. Sinclair and G. Thomas, J. de Phys. **38**, C7, 165 (1977).
[3] S. C. Moss, D. T. Keating, and J. Axe, Phase Transformations, L. E. Cross, ed., Pergamon, 1973, p. 179.
[4] W. Lin, H. Spalt, and B. W. Batterman, Phys. Rev. **B13**, 5158 (1976).

[5] J. D. Axe, D. T. Keating, and S. C. Moss, Phys. Rev. Lett. **35**, 530 (1975).

[6] T. S. Kuan and S. L. Sass, Phil. Mag. **36**, 1473 (1977).

[7] Ya. I. Frenkel', Zh. Eksp. Teor. Fiz. **9**, 952 (1939).

[8] H. Sato and R. S. Toth, Phys. Rev. **124**, 1833 (1961).

[9] M. Tachiki and K. Teramoto, J. Phys. Chem. Sol. **27**, 335 (1966).

[10] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).

[11] L. N. Bulaevskii, Usp. Fiz. Nauk **115**, 263 (1975); **120**, 259 (1976) [Sov. Phys. Usp. **18**, 131 (1975); **19**, 836 (1976)].

[12] W. L. McMillan, Phys. Rev. **14**, 1496 (1976).

[13] I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. **47**, 336 (1964) [Sov. Phys. JETP **20**, 223 (1965)].

[14] M. A. Krivoglaz, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 403 (1976) [JETP Lett. **24**, 368 (1976)].

[15] A. M. Afanas'ev and Yu. Kagan, Zh. Eksp. Teor. Fiz. **43**, 1456 (1962) [Sov. Phys. JETP **16**, 1030 (1963)].

[16] L. M. Roth, H. J. Zeiger, and T. A. Kaplan, Phys. Rev. **149**, 519 (1966).

[17] D. A. Vul' and M A Krivoglaz, Fiz. Met. Metallov. **52**, 1127 (1981).

[18] L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Nonrelativistic Theory, Pergamon, 1977.

[19] R. Hoseman and S. N. Bachi, Direct Analysis of Matter by Diffraction, North-Holland, 1962.

[20] S. C. Moss, Phys. Rev. Lett. **22**, 1108 (1969).

[21] K. Ohshima and J. Harada, Sci. Rep. Res. Inst. Tohoku Univ. **A29**, Suppl. 1, 123 (1981).

[22] J. M. Sanchez and D. de Fontaine, J. de Phys. **38**, C7, 444 (1977).

[23] H. E. Cook, J. Appl. Cryst. **8**, 132 (1975).

[24] R. J. Pynn, J. Phys. F, **8**, 1 (1978).

[25] H. W. Myron, A. J. Freeman, and S. C. Moss, Sol. St. Commun. **17**, 1467 (1980).

[27] A. I. Larkin and D. E. Khmel'nitskiĭ, Zh. Eksp. Teor. Fiz. **55**, 2345 (1968) [Sov. Phys. JETP **28**, 1245 (1969)].

[28] M. A. Krivoglaz, ibid. **63**, 670 (1972 [**36**, 354 (1973)].

[29] M. A. Krivoglaz and A. I. Karasevskiĭ, Fiz. Tverd. Tela (Leningrad) **16**, 1458 (1974); **17**, 2565 (1975) [Sov. Phys. Solid State **16**, 934 (1974); **17**, 1709 (1975)]; Zh. Eksp. Teor. Fiz. **69**, 297 (1965) [Sov. Phys. JETP **42**, 153 (1966)].

[30] S. Hashimoto and H. Iwasaki, Phys. Stat. Sol. (a) **51**, 673 (1979).

[31] H. Bouchiat, E. Dartyge, P. Monod, and M. Lambert, Phys. Rev. **B23**, 1375 (1981).

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