Journal of Engineering Physics and Thermophysics, Vol. 65, No. 2, 1993

PHASE EQUILIBRIUM AND INTERPHASE TRANSITION LAYER AS AN ORDERING PROBLEM

P. T. Bruk-Levinson and I. Yu. Murokh

UDC 548.7

The model of a binary ordering alloy, developed previously based on the conventional distribution method, is used for describing spatially inhomogeneous multiphase equilibrium systems of gas-solid, liquid-gas or crystal-liquid types, including the structure of an interphase transition layer. General results are illustrated by specific predictions for a two-phase crystal-gas system.

The classical problems of structural ordering of crystal systems [1, 2] are classified with macroscopically homogeneous systems, irrespective of whether order-disorder phase transitions are of the first or the second kind. In this case, the phase transition is characterized by redistribution of particles of two sorts over two sublattices, "inserted" into each other from the viewpoint of their spatial arrangement.

In the current study the model of a binary ordering alloy with point defects [3-5], developed previously based on the conventional distribution model [10], is used for describing spatially inhomogeneous multiphase equilibrium systems of gas-solid, liquid-gas, or crystal liquid type, including the structure of an interphase transition layer.

Although numerous results at both the phenomenological [6] and macroscopic [7] levels were obtained in describing phase transitions of the first kind of the sublimation, evaporation, or melting type, for a long time there was no answer to the fundamental question of whether it is possible to describe, within the framework of Gibbs statistical mechanics, all phase transitions of the first kind in a simple molecular system, including triple and critical points. The basic difficulties consists in the fact that the statistical mechanical description of various phases employs different approximations that do not join one another when the attempt is made to "match" the solutions for an inhomogeneous system.

The relatively simple van der Waals equation proves to be a good approximation only for a liquid-vapor system. Taking account of subsequent virial coefficients involves considerable technical difficulties and does not give an adequate description of all states of aggregation of a substance [8]. Lee and Yang [9] obtained an equation of state, similar to the van der Waals equation, in the average field approximation when considering the Izing model for a lattice gas, in which atoms correspond to an "upward spin" state, and vacancies at the points of a regular lattice correspond to a "donwward spin" state.

We note [10], in which based on the conventional distribution method within the framework of a quasichemical approximation the possibility of a unified description of all phase transitions of the first kind in a one-component system was demonstrated for the first time. The parameters were identified from the coordinates of the points of a common tangent to an isotherm of the free energy as a function of the molecular volume (points of equal pressure).

The main idea of the approach developed lies in considering, analogously to the ordering alloy model, the one-component multiphase system as a two-component mixture of real (sort A particles) and fictitious (sort 0 particles) atoms by describing, as a function of thermodynamic parameters of the system, the particle redistribution over two sublattices, which are spatially divided by a certain boundary in this case. Here the order parameter, equal to the difference of probabilities of detecting a given atom on one or the other side of the boundary, actually reflects the difference in density between the phases under study.

Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute of the Belarussian Academy of Sciences," Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 65, No. 2, pp. 198-206, August, 1993. Original article submitted April, 23, 1992.

1062-0125/93/6502-0776$12.50 ©1994 Plenum Publishing Corporation

I. Phase Equilibrium. Consider a system of N pairwise interacting sort A particles, located in the volume V at the temperature T (the NVT ensemble). We break down the entire volume of the system into $M = M^{(1)} + M^{(2)} \geq N$ geometrically identical nonoverlapping cells of volume $w = V/M$, $M^{(1)}$ of which refer to cells of the first type and $M^{(2)}$ to cells of the second type. We will assume that the cell centers form ordered lattices in spatially divided phases of the corresponding type and not more than one particle can reside in each cell. We denote the concentration of the μ-type cells by $\nu^{(\mu)} = M^{(\mu)}/M$ ($\mu = 1, 2$), and introduce the cell concentrations of sort A particles and vacancies:

$$m_A = N/M,\ m_0 = (M - N)/M = N_0/M, \tag{1}$$

where

$$w = v(1 - m_0),\ m_A = 1 - m_0, \tag{2}$$

where $v = V/N$ is the volume per particle.

The probabilities of finding a particle of sort K = 0, A (the index 0 corresponds to a vacancy) at a point of type $\mu = 1, 2$ are written in the form

$$P_K^{(\mu)} = N_K^{(\mu)}/M^{(\mu)}, \tag{3}$$

where $N_K^{(\mu)}$ is the number of sort K particles located in μ-type cells, and

$$\sum_{K=0,A} N_K^{(\mu)} = M^{(\mu)},$$

and, therefore,

$$\sum_{K=0,A} P_K^{(\mu)} = 1,\ \mu = 1,\ 2. \tag{4}$$

For describing the equilibrium state of this system we introduce the order parameter

$$\eta = P_A^{(1)} - P_A^{(2)} = (P_A^{(1)} - m_A)/\nu^{(2)} = P_0^{(2)} - P_0^{(1)}, \tag{5}$$

which characterizes structural differences of the coexisting phases. Thus, for example, in the crystal state ($\mu = 1$) the vacancy concentration is small ($P_0^{(1)} << 1$), amd whereas in the gas phase the particle concentration is small ($P_A^{(1)} << 1$), therefore the two-phase crystal-gas system may be regarded within this model as an almost completely ordered system with $\eta \approx 1$. In the case of crystal-liquid and liquid-gas phase equilibria, the order parameter assumes intermediate values ($0 < \eta < 1$). Obviously, the condition $\eta = 0$ is essential for the existence of a critical point.

Studies [3-5] showed that the conventional distribution method allows for the contributions of thermal oscillations of particles to both the free energy of the system and the phase transition (phase equilibrium) parameters, and therefore the order parameter considered accounts not only for quantitative differences in the states of aggregation of a substance (the particle concentration in one or another phase) but also for qualitative changes in the dynamic state of the particles (the probability density distribution over the cell volume).

It follows from Eqs. (3) and (5) that

$$m_K = \sum_{\mu=1,\ 2} \nu^{(\mu)} P_K^{(\mu)}. \tag{6}$$

We point out that only the average specific volume v is specified in this model, whereas the real volumes $v^{(\mu)}$ allocated to a particle in each phase and the ratio of the volumes occupied by each phase are not known in advance and are related to P_K^{μ} and w, which are determined in a self-consistent way from the condition of a minimum free energy of the system:

$$v^{(\mu)} = w/P_A^{(\mu)} \Rightarrow v^{(1)}/v^{(2)} = P_A^{(2)}/P_A^{(1)}, \tag{7}$$

$$\nu = \nu^{(1)}/\nu^{(2)} = \frac{v^{(1)}(v^{(2)} - v)}{v^{(2)}(v - v^{(1)})}. \tag{8}$$

Studies [4, 5] introduced basic equations to describe a three-component (particles of sorts A and B and vacancies) ordering alloy. In this sense, the system considered describes a model of a two-component (sort A particles and vacancies) alloy, for which all relations obtained previously remain valid.

Therefore, the chain of integral equations for conventional partial distribution functions (DF) of the two-component system is written as follows:

$$\begin{gathered}
F_{i(\mu)} = P_0^{(\mu)}, \qquad \int\limits_{w_{i(\mu)}} di_A^{(\mu)} F_{i(\mu)}(i_A^{(\mu)}) = P_A^{(\mu)}, \\
F_{i(\mu)} = F_{i(\mu)j(\alpha)} + \int\limits_{w_{j(\alpha)}} dj_A^{(\alpha)} F_{j(\alpha)i(\mu)}(j_A^{(\alpha)}), \\
F_{i(\mu)}(i_A^{(\mu)}) = F_{i(\mu)j(\alpha)}(i_A^{(\mu)}) + \int\limits_{w_{j(\alpha)}} dj_A^{(\alpha)} F_{i(\mu)j(\alpha)}(i_A^{(\mu)}, j_A^{(\alpha)}),
\end{gathered} \tag{9}$$

where $F_{i(\mu)}(i_K^{(\mu)})$ defines the probability density of detecting a sort K particle near the point $i_K^{(\mu)}$) on condition that the remaining cells contain not more than one particle, and $F_{i(\mu)\,j(\mu)}(i_K^{(\mu)}, j_L^{(\alpha)})$ defines a similar probability density for two particles in two cells.

The DFS may be represented in exponential form, reflecting their "Gibbsian" origin, and in the quasichemical approximation they reduce to the form

$$\begin{gathered}
F_{i(\mu)j(\alpha)} = P_0^{(\mu)} P_0^{(\alpha)} \exp\{\beta(\varphi_{i(\mu),j(\alpha)} + \varphi_{j(\alpha),i(\mu)})\}, \\
F_{i(\mu)j(\alpha)}(i_A^{(\mu)}) = P_0^{(\alpha)} F_{i(\mu)}(i_A^{(\mu)}) \exp\{\beta(\varphi_{i(\mu),j(\alpha)}(i_A^{(\mu)}) + \varphi_{j(\alpha),i(\mu)})\}, \\
F_{i(\mu)j(\alpha)}(i_A^{(\mu)}, j_A^{(\alpha)}) = F_{i(\mu)}(i_A^{(\mu)}) F_{j(\alpha)}(j_A^{(\alpha)}) \times \\
\times \exp\{-\beta[\Phi(i_A^{(\mu)}, j_A^{(\alpha)}) - \varphi_{i(\mu),j(\alpha)}(i_A^{(\mu)}) - \varphi_{j(\alpha),i(\mu)}(j_A^{(\alpha)})]\},
\end{gathered} \tag{10}$$

where $\varphi_{i(\mu),j(\alpha)}(i_K^{(\mu)})$ are the elementary average-force potentials (AFPs), characterizing the averaged action of a particle in the j-th cell on a particle in the i-th cell, $\Phi(i_K^{(\mu)}, j_L^{(\alpha)})$ is the interatomic potential, and β is the inverse temperature.

We now write, in conformity with [4, 5], expressions for the configuration integral and the free energy:

$$\begin{gathered}
Q_M = \Big\{ \prod_{\mu=1,2} \Big[\prod_{K=0,A} (Q_K^{(\mu)}/P_K^{(\mu)})^{P_K^{(\mu)}} \Big]^{\nu(\mu)} \Big\}^M, \\
F = Mf = -(M/\beta) \ln \Big\{ \prod_{\mu=1,2} \Big[\prod_{K=0,A} (Q_K^{(\mu)}/P_K^{(\mu)})^{P_K^{(\mu)}} \Big]^{\nu(\mu)} \Big\},
\end{gathered} \tag{11}$$

where the free energy per cell is

$$f = -\beta^{-1} \sum_{\mu=1,2} \nu^{(\mu)} \sum_{K=0,A} P_K^{(\mu)} \ln(Q_K^{(\mu)}/P_K^{(\mu)}), \tag{12}$$

the normalization constants have the form

$$\begin{gathered}
Q_0^{(\mu)} = \exp\{-\beta\varphi_{i(\mu)}\}, \\
Q_A^{(\mu)} = \int\limits_{w_{i(\mu)}} di_A^{(\mu)} \exp\{-\beta\varphi_{i(\mu)}(i_A^{(\mu)})\},
\end{gathered} \tag{13}$$

and the total AFPs are the sums of elementary AFPs:

$$\varphi_{i^{(\mu)}} = \sum_{l^{(\tau)} \neq i^{(\mu)}} \varphi_{i^{(\mu)}, l^{(\tau)}}, \quad \varphi_{i^{(\mu)}}(i_A^{(\mu)}) = \sum_{l^{(\tau)} \neq i^{(\mu)}} \varphi_{i^{(\mu)}, l^{(\tau)}}(i_A^{(\mu)}). \tag{14}$$

The conventional extremum of Eq. (11) must be found taking into account that, unlike a real ordering alloy, the cell concentrations $\nu^{(\mu)}$ are not known beforehand. Varying the free energy with respect to $\nu^{(\mu)}$ brings about an additional, as compared with [4], condition, imposed on thermodynamic parameters of the system, which also determines the existence of phase equilibrium.

As a result we obtain

$$\sum_{\mu=1,2} \nu^{(\mu)} \ln (Q_0^{(\mu)}/P_0^{(\mu)}) = \beta P w, \tag{15}$$

$$Q_A^{(1)} P_A^{(2)} / (Q_A^{(2)} P_A^{(1)}) = Q_0^{(1)} P_0^{(2)} / (Q_0^{(2)} P_0^{(1)}), \tag{16}$$

$$Q_0^{(1)}/P_0^{(1)} = Q_0^{(2)}/P_0^{(2)}, \tag{17}$$

where $P = -(\partial f/\partial w)_\beta$ is the pressure, which is defined from the virial theorem [10]:

$$\beta P w = 1 - m_0 - (\beta/6M) \sum_{i^{(\mu)}} \sum_{j^{(\alpha)}} \int_{w_{i^{(\mu)}}} d i_A^{(\mu)} \int_{w_{j^{(\alpha)}}} d j_A^{(\alpha)} \Phi (i_A^{(\mu)}, j_A^{(\alpha)}) \times$$
$$\times (|i_A^{(\mu)} - j_A^{(\alpha)}|) F_{i^{(\mu)} j^{(\alpha)}} (i_A^{(\mu)}, j_A^{(\alpha)}). \tag{18}$$

Substituting Eq. (17) into Eq. (15) leads to equations

$$\ln (Q_0^{(\mu)}/P_0^{(\mu)}) = \beta P w \quad (\mu = 1,\ 2), \tag{19}$$

which exactly coincide with the relation derived in [11] for homogeneous systems of arbitrary density and express the equality of pressures and temperatures under the conditions of phase equilibrium. In this case, Eq. (16) corresponds to the equality of chemical potentials.

Together with relations (2)-(10), Eqs. (16)-(19) form a closed system, whose solution at prescribed thermodynamic parameters of the two-phase system (β, v) allows a complete description of the phase equilibrium characteristics (P, $v^{(\mu)}$, $\nu^{(\mu)}$ and $P_K^{(\mu)}$).

As the simplest example, we will examine phase equilibrium in the crystal-gas system. It is assumed that there is no interphase interaction $\varphi_{i^{(\mu)}, j^{(\alpha)}}(i_A^{(\mu)}) = \varphi_{i^{(\mu)}, j^{(\alpha)}} = 0, \mu \neq \alpha$) and then Eqs. (10) can be solved separately for each phase.

Setting $P_0^{(1)} = 0$ for the crystal phase ($\mu = 1$) in the first approximation and using the Laplace method to calculate integrals [12], up to the leading asymptotic term we obtain

$$\psi_{i^{(1)}, j^{(1)}} = P_A^{(1)} / \psi_{j^{(1)}, i^{(1)}} (\bar{j}_A^{(1)}), \quad \psi_{i^{(1)}, j^{(1)}} (i_A^{(1)}) = P_A^{(1)} K / \psi_{j^{(1)}, i^{(1)}} (\bar{j}_A^{(1)}), \tag{20}$$

where

$$\psi_{j^{(1)}, i^{(1)}} = \exp \{ -\beta \varphi_{j^{(1)}, i^{(1)}} \},$$

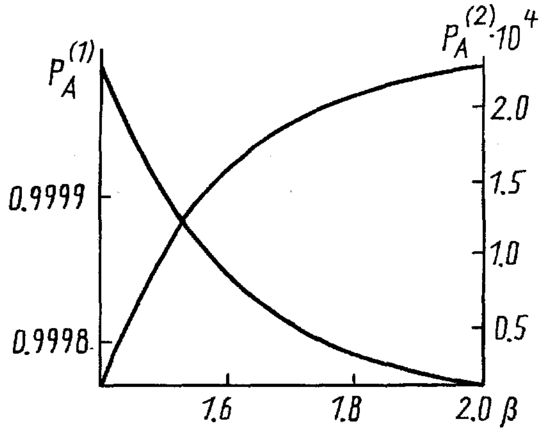
$$\psi_{j^{(1)}, i^{(1)}} (\bar{j}_A^{(1)}) = \exp \{ -\beta \varphi_{j^{(1)}, i^{(1)}} (\bar{j}_A^{(1)}) \}, \quad K = \exp \{ -\beta \Phi (i_A^{(1)}, \bar{j}_A^{(1)}) \}.$$

Substitution of $j_A^{(1)} = \bar{j}_A^{(1)}$ ($\bar{j}_A^{(1)}$ denotes the coordinates of the crystal lattice point) into Eq. (20) yields ($P_A^{(1)} \approx 1$)

$$\psi_{j^{(1)}, i^{(1)}} (\bar{j}_A^{(1)}) = K^{1/2}, \quad \psi_{j^{(1)}, i^{(1)}} = K^{-1/2}. \tag{21}$$

In the same approximations, with consideration of the interaction of nearest neighbors, from Eqs. (13) and (14) it follows that

$$Q_A^{(1)} = \exp \{ -\beta \varphi_{i^{(1)}} (\bar{i}_A^{(1)}) \} = [\psi_{i^{(1)}, j^{(1)}} (\bar{i}_A^{(1)})]^z = K^{z/2},$$



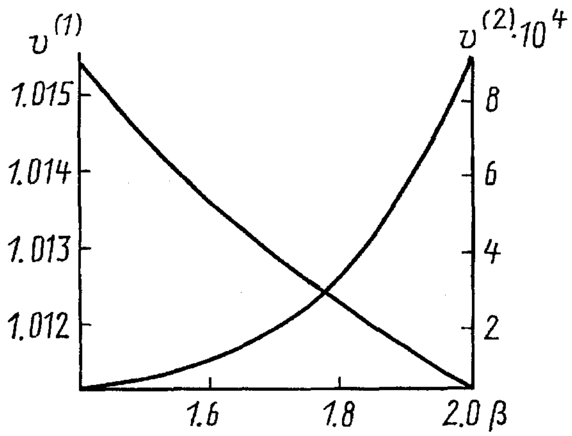


Fig. 1. Probability of finding sort A particles in cells of type 1 and 2 vs the inverse temperature β on the curve of solid-gas equilibrium.

Fig. 2. Specific volumes of the solid and gas phases vs the inverse temperature β on the curve of solid-gas equilibrium.

$$Q_A^{(1)} = \exp\{-\beta\varphi_{i^{(1)}}\} = [\psi_{i^{(1)},j^{(1)}}]^z \doteq K^{-z/2}, \tag{22}$$

where z is the number of nearest neighbors.

For the gas phase ($\mu = 2$), in the ideal gas approximation $P_A^{(2)} \ll 1$ we have

$$Q_A^{(2)} \approx Q_0^{(2)} \approx 1. \tag{23}$$

Substituting Eqs. (23) and (22) into Eqs. (16)-(18) and taking into account Eq. (4), we obtain

$$\begin{gathered} P_A^{(1)} = P_0^{(2)} = K^{z/2}/(K^{z/2}+1), \quad P_A^{(2)} = P_0^{(1)} = 1/(K^{z/2}+1), \\ \beta P w = \ln(1 + K^{-z/2}). \end{gathered} \tag{24}$$

On the other hand, in the same approximations, from Eq. (18) it follows that

$$\beta P w = P_A^{(1)} - \beta Z/6\, [P_A^{(1)}]^2\, \Phi'(r)\, r, \tag{25}$$

for the condensed phase, where r is the spacing between nearest neighbors.

We note that Eq. (25) is quadratic with respect to $P_A^{(1)}$ and, for $P_A^{(1)} \ll 1$ it reduces to the equation of state for an ideal gas

$$\beta P w = P_A^{(2)} = \tilde{P}_A^{(1)}.$$

Then we may write

$$P_A^{(1)} + P_A^{(2)} = 6\Phi'(r)\, r/\beta Z,$$

whence for particles with the Lennard-Jones interaction potential we have

$$r = [48\beta/(24\beta - 1)]^{1/6}. \tag{26}$$

Thus, Eqs. (7), (8), (24), and (26) fully describe the equilibrium state in the crystal-gas two-phase system. Figures 1-3 present calculated results for crystals of inert gases with an fcc lattice ($w = r^3/\sqrt{2}$). Qualitative agreement between the temperature dependences of the system parameters and experimental data [13] is noted. A strong discrepancy in the value of the specific volume of the gas phase is explained by the underestimated particle concentration because of relatively rough approximations in solving the integural equations.

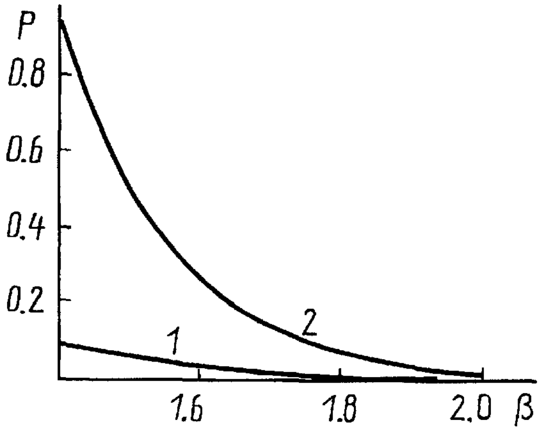


Fig. 3. Pressure vs the inverse temperature on the curve of solid-gas equilibrium: 1) prediction; 2) experiment [13].

II. Interphase Transition Layer. The scheme developed above allows a prediction of thermodynamic characteristics of two-phase systems, provided each phase is homogeneous. In reality, however, the interface causes local parameters of the system ($P_K^{(\mu)}$) to deviate from their statistical means over the volume, i.e., causes spatial inhomogeneity within each phase.

In principle, the interface has this effect on each molecular layer, which asymptotically approaches zero with distance from the surface of phase contact. At the same time, it is evident that, for particles with a short-range potential, the "penetration depth" is comparable in order of magnitude with the effective radius of interaction. In other words, the phase interaction manifests itself in the existence of a transition region of width amounting to a few molecular layers (excluding, of course, the vicinity of the liquid-vapor critical point).

Despite significant advances made in understanding the fine structure of the interphase (a coarsening transition [14] and an order-disorder transition [15, 16]), the statistical theory of the interphase transition layer is still far from complete even in the case of simple one-component systems. As was pointed out above, this is primarily due to the necessity of simultaneously describing two phases of a substance.

Having modified the developed formalism so that nonequivalence of molecular layers located at different distances from the interface is taken into account, it is possible to construct a statistical scheme for describing the transition region.

We break down the entire volume of the system into $M \geq N$ geometrically identical nonoverlapping cells of volume $w = V/M$ and define the probability of finding a particle of sort $K = 0, A$ in a cell belonging to layer $\mu = 1, 2, \ldots, T$ in the form

$$P_K^{(\mu)} = N_K^{(\mu)}/M_s, \tag{27}$$

where $N_K^{(\mu)}$ is the number of sort K particles residing in the μ-th layer, and M_s is the number of particles in a layer (not dependent on μ). Here

$$\sum_{K=0,A} N_K^{(\mu)} = M_s \Rightarrow \sum_{K=0,A} P_K^{(\mu)} = 1, \tag{28}$$

$$\sum_{\mu=1}^{T} N_A^{(\mu)} = N, \quad M = TM_s. \tag{29}$$

The chain of integral equations for conventional partial distribution functions of such a system formally corresponds to relations (9); the difference is that the Greek symbols (μ, α) refer to the number of the molecular layer. The expressions for the configuration integral and the free energy acquire the form

$$Q_M = \left\{ \prod_{\mu=1}^{T} \left[\prod_{K=0,A} \left(Q_K^{(\mu)}/P_K^{(\mu)}\right)^{P_K^{(\mu)}} \right] \right\}^{M_s},$$

TABLE 1. Probability of Finding a Sort A Particle in a Cell Belonging to the α-th Molecular Layer in the Crystal-Gas Transition Region as a Function of the Inverse Temperature β (α = 1 corresponds to the volume-average particle concentration in the gas phase and α = 5, in the crystal phase)

β	α				
	1	2	3	4	5
1.0	$2.49844 \cdot 10^{-3}$	0.111579	0.758927	0.989311	0.997214
1.1	$1.37142 \cdot 10^{-3}$	0.123269	0.827761	0.995341	0.998544
1.2	$7.52528 \cdot 10^{-4}$	0.118333	0.862979	0.997680	0.999220
1.3	$4.12860 \cdot 10^{-4}$	0.106756	0.886139	0.998791	0.999578
1.4	$2.26495 \cdot 10^{-4}$	0.093142	0.904148	0.999362	0.999770
1.5	$1.24254 \cdot 10^{-4}$	0.778678	0.998764	0.999873	0.999875
1.6	$6.81664 \cdot 10^{-5}$	0.865056	0.999621	0.999931	0.999931
1.7	$3.73973 \cdot 10^{-5}$	0.907953	0.999851	0.999962	0.999962
1.8	$2.05174 \cdot 10^{-5}$	0.934401	0.999935	0.999979	0.999979
1.9	$1.12569 \cdot 10^{-5}$	0.951983	0.999970	0.999988	0.999988
2.0	$6.17625 \cdot 10^{-6}$	0.964183	0.999985	0.999993	0.999993

$$F = M_s \sum_{\mu=1}^{T} f^{(\mu)} = -(M_s/\beta) \ln \left\{ \prod_{\mu=1}^{T} \left[\prod_{K=0,A} (Q_K^{(\mu)}/P_K^{(\mu)})^{P_K^{(\mu)}} \right] \right\}, \tag{30}$$

where the free energy per cell in the μ-th layer is

$$f^{(\mu)} = -\beta^{-1} \sum_{K=0,A} P_K^{(\mu)} \ln (Q_K^{(\mu)}/P_K^{(\mu)}), \tag{31}$$

and the normalization constants and the potentials of average forces are determined from Eqs. (13) and (14).

In contrast to Eq. (11), the free energy in Eq. (30) is a function of the particle and vacancy concentration in each molecular layer. Varying the free energy by the above scheme with allowance for relations (28) and (29) leads to the following equilibrium conditions:

$$Q_0^{(\mu)} P_A^{(\mu)} / (Q_A^{(\mu)} P_0^{(\mu)}) = \text{const} \ \ (\mu = 1,\ 2,\ \ldots,\ T). \tag{32}$$

It is assumed here that the transition layer slightly affects the volume characteristics of the system, and relations (16) and (18), obtained for them, remain valid. Then Eq. (32) can be recast as

$$Q_0^{(\mu)} P_A^{(\mu)} / (Q_A^{(\mu)} P_0^{(\mu}) = Q_0^{(\gamma)} P_A^{(\gamma)} / (Q_A^{(\gamma)} P_0^{(\gamma)}), \tag{33}$$

where the superscript γ denotes the number of a layer in one or another phase sufficiently far from the interface.

Thus, the solation of the system of equations (16)-(19) determines the volume characteristics of the phase equilibrium $P_K^{(\gamma)}$, and solation of the system of equations (9)-(14) determines the intermediate probabilities of the transition layer.

We again carry out specific calculations for the crystal-gas system. Suppose that main changes due to the interface occur in the structure of the surface layers of the crystal. Then, using the Laplace method to compute the integrals in Eq. (30), up to the leading asymptotic term we obtain

$$\begin{gathered} \psi_{i^{(\mu)}, j^{(\alpha)}} = P_0^{(\alpha)} / \psi_{i^{(\alpha)}, j^{(\mu)}} + P_A^{(\alpha)} / \psi_{j^{(\alpha)}, i^{(\mu)}} (\overline{j}_A^{(\alpha)}), \\ \psi_{i^{(\mu)}, j^{(\alpha)}} (i_A^{(\mu)}) = P_0^{(\alpha)} / \psi_{i^{(\alpha)}, j^{(\mu)}} + P_A^{(\alpha)} K / \psi_{j^{(\alpha)}, i^{(\mu)}} (\overline{j}_A^{(\alpha)}), \end{gathered} \tag{34}$$

where

$$\psi_{j^{(\alpha)},i^{(\mu)}} = \exp\{-\beta\varphi_{j^{(\alpha)},i^{(\mu)}}\};$$

$$\psi_{j^{(\alpha)},i^{(\mu)}}(\bar{j}_A^{(\alpha)}) = \exp\{-\beta\varphi_{j^{(\alpha)},i^{(\mu)}}(\bar{j}_A^{(\alpha)})\}; \quad K = \exp\{-\beta\Phi(i_A^{(\mu)}, \bar{j}_A^{(\alpha)})\}.$$

Substituting $i_A^{(\mu)} = \bar{i}_A^{(\mu)}$ into Eq. (34) results in a closed system of equations for the unknowns $\psi_{j^{(\alpha)},i^{(\mu)}}(\bar{j}_A^{(\alpha)}) = \psi^A_{\alpha,\mu}$, $\psi_{j^{(\alpha)},i^{(\mu)}} = \psi^0_{\alpha,\mu}$, which can only be solved for the following combinations of them:

$$\begin{gathered}\psi^A_{\mu,\alpha}\psi^A_{\alpha,\mu} = KP_A^{(\alpha)} + P_0^{(\alpha)}\psi_{\alpha\mu},\\ \psi^0_{\mu,\alpha}\psi^0_{\alpha,\mu} = P_A^{(\alpha)}/\psi_{\alpha\mu} + P_0^{(\alpha)},\end{gathered} \tag{35}$$

where

$$\psi_{\alpha\mu} = \psi^A_{\alpha,\mu}/\psi^0_{\alpha,\mu} = [P_{\alpha\mu} + \{P^2_{\alpha\mu} + 4KP_A^{(\alpha)}P_0^{(\alpha)}\}^{1/2}]/(2P_0^{(\alpha)}),$$

$$P_{\alpha\mu} = P_0^{(\alpha)} - P_A^{(\alpha)} - (K-1)(P_A^{(\alpha)} - P_A^{(\mu)})$$

In the same approximations, without consideration of vibrational degrees of freedom the normalization constants of Eq. (13) take the form

$$\begin{gathered}Q_A^{(\alpha)} = \exp\{-\beta\varphi_{j^{(\alpha)}}(\bar{i}_A^{(\alpha)})\} = \prod_{\mu=1}^{T} [\psi^A_{\alpha,\mu}]^{z_\mu^{(\alpha)}},\\ Q_0^{(\alpha)} = \exp\{-\beta\varphi_{j^{(\alpha)}}\} = \prod_{\mu=1}^{T} [\psi^0_{\alpha,\mu}]^{z_\mu^{(\alpha)}},\end{gathered} \tag{36}$$

where $z_{(\mu)}^{(\alpha)}$ is the number of nearest neighbors located in the μ-th layer around a point in the α-th layer.

From Eqs. (22)-(24) it follows that

$$Q_0^{(\gamma)}P_A^{(\gamma)}/(Q_A^{(\gamma)}P_0^{(\gamma)}) = K^{-z/2}, \tag{37}$$

whence, with allowance for Eqs. (33) and (36), we obtain

$$P_A^{(\alpha)}/P_0^{(\alpha)} = K^{-z/2}Q_A^{(\alpha)}/Q_0^{(\alpha)} = K^{-z/2}\prod_{\mu=1}^{T}[\psi_{\alpha\mu}]^{z^\alpha_\mu}. \tag{38}$$

Near the surface of a crystal with an fcc lattice, relation (38) for the planes (001) in the approximation of nearest neighbors reduces to the form

$$P_A^{(\alpha)}/P_0^{(\alpha)} = K^{-z/2}\prod_{\mu=\alpha-1}^{\alpha+1}[\psi_{\alpha\mu}]^4. \tag{39}$$

The system of equations obtained was solved numerically by an iteration method. The values of $P_K^{(\alpha)}$ (K = 0, A) obtained in the previous section were taken for boundary conditions. The calculated results are presented in Tablel 1.

NOTATION

N, number of particles; M, number of cells; w, volume of a cell; V, volume of the system; $\nu^{(\mu)}$ ($\mu = 1, 2$), concentration of μ-type cells (concentration of points of the μ-th sublattice); m_K (K = 0, A), cell concentrations of particles, the index 0 denotes a vacancy; $P_K^{(\mu)}$, probability of finding particles in a μ-type cell; f, free energy per cell; $F_{i^{(\mu)}}(i_K^{(\mu)})$, probability density of finding a sort K particle near the point $i_K^{(\mu)} \in W_{i^{(\mu)}}$ (belonging to the i-th μ-type cell); $F_{i^{(\mu)}j^{(\alpha)}}(i_K^{(\mu)}, j_L^{(\alpha)})$, probability density of finding a sort K particle near the point $i_K^{(\mu)} \in W_{i^{(\mu)}}$ and a sort

L particle near the point $j_K^{(\alpha)} \in W_{j^{(\alpha)}}$; $Q_K^{(\mu)}$, normalization constants; $\varphi_{i^{(\mu)}}(i_K^{(\mu)})$, $\varphi_{i^{(\mu)}j^{(\alpha)}}(i_K^{(\mu)}, j_L^{(\alpha)})$, potentials of average forces; $\Phi(i_K^{(\mu)}, j_K^{(\mu)})$, potential energy of interaction of a particle pair; β, inverse temperature.

REFERENCES

1. M. A. Krivoglaz and A. A. Smirnov, Theory of Ordering Alloys [in Russian], Moscow (1958).
2. J. Ziman, Disorder Models [Russian translation], Moscow (1982).
3. P. T. Bruk-Levinson, Statistical Theory of Real Crystals [in Russian], Minsk (1989).
4. P. T. Bruk-Levinson and I. Yu. Murokh, Dokl. Akad. Nauk BSSR, **34**, No. 11, 1005-1008 (1990).
5. P. R. Bruk-Levinson and I. Yu. Murokh, in: Thermal Physics of Condensed Media: Structure and Properties [in Russian], Minsk (1990), pp. 65-82.
6. K. Crockstone, Physics of the Liquid State [Russian translation], Moscow (1978).
7. I. Z. Fisher, Statistical Theory of Liquids [in Russian], Moscow (1961).
8. L. D. Landau and E. M. Lifshits, Statistical Physics [in Russian], Moscow (1976).
9. C. N. Yang and T. D. Lee, Phys. Rev., **87**, No. 3, 404-419 (1952).
10. L. A. Rott, Statistical Theory of Molecular Systems [in Russian], Moscow (1979).
11. P. T. Bruk-Levinson and V. V. Belov, "Statistical theory of equilibrium properties of a substance of arbitrary density," Preprint No. 3, Heat and Mass Transfer Institute, Belorussian Academy of Sciences, Minsk (1983).
12. M. V. Fedoryuk, Steepest Descent Method [in Russian], Moscow (1977).
13. G. L. Pollack, Rev. Mod. Phys., **36**, No. 3, 748-791 (1964).
14. H. Van Beiren and I. Nolden, Usp. Fiz. Nauk, **161**, No. 7, 133-172 (1991).
15. X.-M. Zhu and H. Zabel, Acta Cryst., **46A**, 86-94 (990).
16. E. I. Kats and M. I. Tribelskii, Zh. Éksp. Tekh. Fiz., **98**, No. 1, 196-210 (1990).