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STATISTICAL CALCULATION OF THE SELF-DIFFUSION COEFFICIENTS OF DISORDERED SUBSTITUTIONAL BINARY SOLID SOLUTIONS

É. T. Bruk-Levinson and L. P. Orlov

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We obtain and analyze approximate analytical expressions for the self-diffusion coefficients of a disordered substitutional binary solid solution.

A topical problem of the theory remains the microcopic justification for the phenomenological values of the transport coefficients including also the diffusion coefficient. All realistic substances are, in practice, solutions, i.e., to some degree, they must contain impurities. It is known [1, 2] that in this case, the diffusion coefficient is determined by the self-diffusion coefficients of the components. Consequently, the above problem reduces in practice to a statistical calculation of the self-diffusion coefficients.

In disordered substitutional binary solid solutions, the dominant mechanism of the diffusion processes is the monovacancy mechanism [3]. Noting the earlier results concerning self-diffusion in pure crystals with vacancies [4] and the structure of binary solid solution with vacancies [5, 6], this fact makes it possible to construct and realize an algorithm for the required statistical mechanical calculation of the self-diffusion coefficients of the components of the disordered substitutional solid solution. The starting premises of this algorithm are contained in the statistical method of conditional distributions [7] and in the random-walk theory in its statistical interpretation [8, 9].

SELF-DIFFUSION COEFFICIENTS OF A BINARY SYSTEM

For a crystalline binary system which consists of components A and B for the case of isotropic cubic lattice the self-diffusion coefficients are [8]

$$D_L = (1/6)\, k_L R^2 \quad (L = A,\ B), \tag{1}$$

where k_L is the jump frequency of atoms of type L, and R is the length of the jump (the nearest neighbor separation in the lattice). The elementary self-diffusion act in the monovacancy mechanism is a jump of an atom from an occupied site to a neighboring vacant site. This jump requires the overcoming of a potential barrier which is associated with the force field of other atoms. Consequently, the elementary acts of self-diffusion of an atom takes place only if the i-th site is filled, the j-th site is vacant and the atom on site i is activated with a sufficiently high kinetic energy which makes it possible for the atom to leave its site. This situation can be described by the probability density of observing in the neighborhood of site i near a point with coordinates $q_i{}^L$ an atom of type L with momentum in the interval from $\mathbf{p}_i^L$ to $\mathbf{p}_i^L + d\mathbf{p}_i^L$ in the neighborhood of site i near a point with coordinates $F_{ij}(\mathbf{q}_i^L,\ \mathbf{p}_i^L)$ under the condition that the neighboring site j is vacant. We denote this probability density by S_{ij}. The self-diffusion process contains contributions only from atoms which reach the boundary S_{ij} between the unit cells containing the filled and empty sites with a positive projection of the momentum $p_{i_z}{}^L$ onto the z axis which passes through the full and empty sites. Therefore, the jump frequency can be written as

$$k_L = (1/M_L) \sum_{j=1}^{z_1} \int_{-\infty}^{\infty} dp_{i_x}^L \int_{-\infty}^{\infty} dp_{i_y}^L \int_{0}^{\infty} dp_{i_z}^L \int_{S_{ij}} d\mathbf{q}_i^L\, p_{i_z}^L F_{ij}(\mathbf{q}_i^L,\ \mathbf{p}_i^L), \tag{2}$$

where M_L is the mass of an atom of type L, and z_1 is the number of nearest neighbors.

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Since the distributions of moments and coordinates of the atoms are independent in the classical equilibrium statistical mechanics, the probability density $F_{ij}(\mathbf{q}_i^L, \mathbf{p}_i^L)$ decomposes into independent factors

$$F_{ij}(\mathbf{q}_i^L, \mathbf{p}_i^L) = F_{ij}(\mathbf{q}_i^L) F(\mathbf{p}_i^L). \tag{3}$$

The first and second factors characterize the distribution in the configuration and momentum space, respectively. It is easy to obtain an explicit expression for the secnd factor. It represents the Maxwell distribution

$$F(\mathbf{p}_i^L) = [\beta/(2\pi M_L)]^{3/2} \exp\{-\beta(\mathbf{p}_i^L)^2/(2M_L)\} \tag{4}$$

at temperature $1/\beta$. The function $F_{ij}(\mathbf{q}_i^L)$, is an inherent component of the hierarchy of partial distribution functions in the formalism of conditional distributions [7].

STATISTICAL MODEL OF A DISORDERED BINARY CRYSTAL WITH VACANCIES

Let us suppose that a binary system of N_A atoms of type A and N_B atoms of type B occupies volume V. We divide this volume into $M(\geq N_A + N_B)$ geometrically identical cells of volume $w = V/M$ each. In the lowest approximation of the method of conditional distributions [7], the statistical description of the system under consideration can be restricted to such microstates of the binary crystal for which each cell is either empty or contains one atom of type L (L = A, B). From the physical viewpoint, by interpreting the cells as the Wigner—Seitz cells, the principle of selection of states then corresponds to the disordered binary substitutional solid solution with vacancies.

Once the volume of the system has been decomposed into cells and restrictions have been imposed on the selection of states, the following stage in the construction of the statistical model consists of introducing the sequence of distribution functions. The state of one cell is completely characterized by two unary distribution functions F_i and $F_i(\mathbf{q}_i^L)$. The first of these functions represents the probability that the cell is empty, and the second is the probability density that inside cell i, there is an atom of type L in the neighborhood of a point with coordinates $\mathbf{q}_i^L$. Clearly, for an infinite uniform system, F_i for any $i \in [1, M]$ is equal to the lattice concentration of vacancies m_0, i.e., to the ratio of the number of empty cells N_0 to the total number of cells M.

With allowance for all possible variants, the state of a pair of cells is characterized by three binary distribution functions F_{ij}, $F_{ij}(\mathbf{q}_i^L)$ and $F_{ij}(\mathbf{q}_i^L, \mathbf{q}_j^K)$. The function F_{ij} is equal to the probability that both cells i and j are simultaneously empty. The meaning of the function $F_{ij}(\mathbf{q}_i^L)$, (which is essential for the calculation of the self-diffusion coefficients as is clear from relation (3)), is that it determines the probability density that atom of type L is in the cell i in the neighborhood of a point with corodinates $\mathbf{q}_i^L$, and the cell j is empty. Finally, the function $F_{ij}(\mathbf{q}_i^L, \mathbf{q}_j^K)$ gives the probability density that an atom of type L is in cell i in the neighborhood of a point with coordinates $\mathbf{q}_i^L$ and, simultaneously, an atom of type K is in cell j in the neighborhood of a point with coordinates K.

Analogously, one can introduce also higher-order distribution function. However, this is not necessary if only pairwise interaction are taken into account.

By definition, the above unary and binary distribution functions satisfy the integral equations

$$F_i + \sum_{L=A,B} \int_i d\mathbf{q}_i^L F_i(\mathbf{q}_i^L) = 1,$$

$$F_{ij} + \sum_{L=A,B} \int_j d\mathbf{q}_j^L F_{ij}(\mathbf{q}_j^L) = F_i, \tag{5}$$

$$F_{ij}(\mathbf{q}_i^K) + \sum_{L=A,B} \int_j d\mathbf{q}_j^L F_{ij}(\mathbf{q}_i^K, \mathbf{q}_j^L) = F_i(\mathbf{q}_i^K). \tag{6}$$

The integration in the equations is carried out over the volume of the cell whose number is under the integral sign.

The unary distribution functions are related to the average-force potentials (AFP) $\varphi_i(\mathbf{q}_i)$ and quasipotentials (QP) φ_i by the following relations [5]:

$$F_i = (m_0/Q_0)\exp\{-\beta\varphi_i\}, \quad F_i(\mathbf{q}_i^K) = (m_K/Q_K)\exp\{-\beta\varphi_i(\mathbf{q}_i^K)\}, \tag{7}$$

where m_K are the lattice concentrations of states of the full cells which are equal to the ratio of the number of full cells N_K, containing one atom of type K, to the total number of cells M, and the normalization constants

$$Q_0 = \exp\{-\beta\varphi_i\},\ Q_K = \int_i d\mathbf{q}_i^K \exp\{-\beta\varphi_i(\mathbf{q}_i^K)\}.$$

Clearly, the sum of the lattice concentration of states of the filled cells and of the vacancy concentration is unity.

The structure of the binary distribution functions in the quasichemical approximation [7] which corresponds to the neglect of correlations between cells of order higher than second, has also a simple and unambiguous character [5]:

$$F_{ij} = \exp\{\beta[\varphi_{i,j} + \varphi_{j,i}]\} F_i F_j,\ F_{ij}(\mathbf{q}_i^K) = \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i^K) + \varphi_{j,i}]\} F_i(\mathbf{q}_i^K) F_j. \tag{8}$$

$$F_{ij}(\mathbf{q}_i^K, \mathbf{q}_j^L) = \exp\{\beta[\varphi_{i,j}(\mathbf{q}_i^K) + \varphi_{j,i}(\mathbf{q}_j^L) - \Phi(\mathbf{q}_i^K, \mathbf{q}_j^L)]\} F_i(\mathbf{q}_i^K) F_j(\mathbf{q}_j^L). \tag{9}$$

Relations (8) and (9) contain the potential of pairwise interactionof atoms of type K and L: $\Phi(\mathbf{q}_i^K, \mathbf{q}_j^L)$, and also the elementary components of AFP $\varphi_{i,j}(\mathbf{q}_i^K)$ and QP $\varphi_{i,j}$ which are related to the full AFP and QP by the additive relations [10]

$$\sum_{m \neq i}^{M} \varphi_{i,m}(\mathbf{q}_i^K) = \varphi_i(\mathbf{q}_i^K),\ \sum_{m \neq i}^{M} \varphi_{i,m} = \varphi_i. \tag{10}$$

The free energy of the system under consideration is [5]

$$F = -(M/\beta)[m_0 \ln(Q_0/m_0) + m_A \ln(Q_A/m_A) + m_B \ln(Q_B/m_B)].$$

It is a minimum for the lattice concentration of vacancies

$$m_0 = \exp\{-\beta[\varphi_i + Pw]\}, \tag{11}$$

where $P = -(\partial F/\partial V)_{\beta,m_0}$ represents the pressure.

Substitution of expressions (8) and (9) into Eqs. (5) and (6) with allowance for the relations (10) leads to a system of integral equations with respect to the elementary components of AFP and QP:

$$\exp\{-\beta\varphi_{i,j}\} = \exp\{\beta\varphi_{j,i}\} F_j + \sum_{L=A,B} \int_j d\mathbf{q}_j^L \exp\{\beta\varphi_{j,i}(\mathbf{q}_j^L)\} F_j(\mathbf{q}_j^L), \tag{12}$$

$$\exp\{-\beta\varphi_{i,j}(\mathbf{q}_i^K)\} = \exp\{\beta\varphi_{j,i}\} F_j + \sum_{L=A,B} \int_j d\mathbf{q}_j^L \exp\{\beta[\varphi_{j,i}(\mathbf{q}_j^L) - \Phi(\mathbf{q}_i^K, \mathbf{q}_j^L)]\} F_j(\mathbf{q}_j^L), \tag{13}$$

whose solution is eventually connected to computing the self-diffusion coefficient.

APPROXIMATE ANALYTICAL SOLUTION OF THE SYSTEM OF NONLINEAR INTEGRAL EQUATIONS

The system of equations (12)-(13) can be solved only numerically (see [7]). However, the problem is considerably simplified if we note the following two physical facts. First, the vacancy concentration m_0 in the binary crystal is very small and is equal, in the order of magnitude, to 10^{-4}-10^{-3} even at temperatures close to the melting temperature [11]. Second, by virtue of the predominant localization of the atoms in the sites of the crystal lattice, the unary distribution function $F_i(\mathbf{q}_i^K)$ must have a sharp maximum in a lattice point.

The structure of the system of equations (12)-(13) suggests the notation

$$\psi \equiv \exp\{-\beta\varphi\},\ K \equiv \exp\{-\beta\Phi\}.$$

In this notation, the system (12)-(13) takes the form

$$\psi_{i,j} = m_0/\psi_{j,i} + \sum_{L=A,B} m_L \Big[\int_j d\mathbf{q}_j^L \psi_j(\mathbf{q}_j^L)/\psi_{j,i}(\mathbf{q}_j^L)\Big] \Big/ \int_j d\mathbf{q}_j^L \psi_j(\mathbf{q}_j^L),$$

$$\psi_{i,j}(\mathbf{q}_i^K) = m_0/\psi_{j,i} + \sum_{L=A,B} m_L \Big[\int_j d\mathbf{q}_j^L K(\mathbf{q}_i^K, \mathbf{q}_j^L) \psi_j(\mathbf{q}_j^L)/\psi_{j,i}(\mathbf{q}_j^L)\Big] \Big/ \int_j d\mathbf{q}_j^L \psi_j(\mathbf{q}_j^L).$$

The smallness of the vacancy concentration makes it possible to seek the solution of the latter system of equations in the form of a power series in terms of m_0. In the first approximation we assume that $m_0 = 0$. Then $m_K = n_K = N_K/(N_A + N_B)$ and

$$\psi_{i,j} = \sum_{L=A,B} n_L \Big[\int_j d\mathbf{q}_j^L \psi_j(\mathbf{q}_j^L)/\psi_{j,i}(\mathbf{q}_j^L)\Big] \Big/ \int_j d\mathbf{q}_j^L \psi_j(\mathbf{q}_j^L), \tag{14}$$

$$\psi_{i,j}(\mathbf{q}_i^K) = \sum_{L=A,B} n_L \Big[\int_j d\mathbf{q}_j^L K(\mathbf{q}_i^K, \mathbf{q}_j^L)\psi_j(\mathbf{q}_j^L)/\psi_{j,i}(\mathbf{q}_j^L)\Big] \Big/ \int_j d\mathbf{q}_j^L \psi_j(\mathbf{q}_j^L). \tag{15}$$

Using the fact that the unary function is similar to the delta function one can use the Laplace method [12] in the calculation of the integrals on the right hand sides of relations (14) and (15). Restricting attention to the principal term of the asymptotic series, we obtain

$$\psi_{i,j} = \sum_{L=A,B} n_L/\psi_{j,i}(\mathbf{l}_j^L), \tag{16}$$

$$\psi_{i,j}(\mathbf{q}_i^K) = \sum_{L=A,B} n_L K(\mathbf{q}_i^K, \mathbf{l}_j^L)/\psi_{j,i}(\mathbf{l}_j^L), \tag{17}$$

where $\mathbf{l}_j^L$ are the coordinates of the lattice site.

Consequently, the elementary components of AFP and QP can be expressed in terms of the molar fractions of the components n_L, the interatomic interaction potentials $\Phi(\mathbf{q}_i^K, \mathbf{q}_j^L)$ and their proper values in the lattice points. To find these we set in (16) and (17) $\mathbf{q}_i^K = \mathbf{l}_i^K$ and simultaneously we introduce the notation

$$\psi_{i,j} = \psi_{j,i} \equiv \psi_0, \quad \psi_{i,j}(\mathbf{l}_i^K) = \psi_{j,i}(\mathbf{l}_j^K) \equiv \psi_K, \quad K(\mathbf{l}_i^K, \mathbf{l}_j^L) \equiv K_{KL}.$$

In the nearest-neighbor approximation we then obtain the system of equations

$$\psi_0 = \sum_{L=A,B} n_L/\psi_L\,,$$

$$\psi_K = \sum_{L=A,B} n_L K_{KL}/\psi_L\,,$$

whose solution has the form

$$\begin{aligned} \psi_A &= (n_A K_{AA} + n_B K_{AB}/\psi_{AB})^{1/2}, \\ \psi_B &= (n_A K_{AB}/\psi_{AB} + n_B K_{BB})^{1/2}, \end{aligned} \tag{18}$$

where

$$\psi_{AB} = \frac{(n_A - n_B)K_{AB}}{2n_A K_{AA}} \left\{1 + \left[1 + \frac{4n_A n_B K_{AA} K_{BB}}{(n_A - n_B)^2 K_{AB}^2}\right]^{1/2}\right\}.$$

It is important to emphasize that the obtained solutions are valid for any finite concentrations of components.

CALCULATION OF THE SELF-DIFFUSION COEFFICIENTS

Using expressions (2)-(4), (7) and (8), the jump frequency k_L can be written as, after integration over momenta,

$$k_L = z_1(2\pi\beta M_L)^{-1/2} m_0 n_L \psi_0^{-1} \int_{S_{ij}} d\mathbf{q}_i^L [\psi_i(\mathbf{q}_i^L)/\psi_{i,j}(\mathbf{q}_i^L)] \Big/ \int_i d\mathbf{q}_i^L \psi_i(\mathbf{q}_i^L). \tag{19}$$

Expression (19) contains two integrals: a two-dimensional integral over the common boundary of the cells S_{ij}, and a three-dimensional integral over the volume of cell i. Both these integrals can be calculated by the Laplace method.

The evaluation of the volume integral gives

$$\int_i d\mathbf{q}_i^L \psi_i(\mathbf{q}_i^L) = [2\pi/(\beta\sigma_L)]^{3/2} \psi_i(\mathbf{l}_i^L) = [2\pi/(\beta\sigma_L)]\, \psi_L^{12}, \tag{20}$$

where $\sigma_L = -\beta^{-1}\Delta \ln \psi_i(\mathbf{l}_i^L)/3$. The symbol Δ in the last expression denotes the Laplace operator.

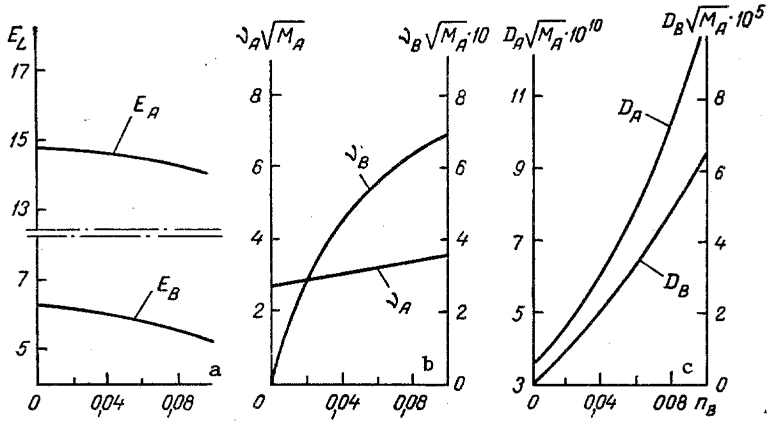

Fig. 1. Concentration dependence of the dimensionless activation energies E_L (a), effective frequencies ν_L (b) and the self-diffusion coefficients D_L (c) for the solution of argon in krypton.

In the integration over the boundary of the cell S_{ij}, it is necessary to take into account the maximum of the integrand $\psi_i(q_i^L)/\psi_{i,j}(q_i^L)$ in point with coordinates $s_i = (l_j - l_i)/2$, which lies in the center of the segment which connects the sites i and j. This function reaches maximum with respect to the neighborhood of the spoint with coordiantes s_i which belongs to the boundary of the cells. This is physically due to the fact that two neighboring positions of equilibrium are separated by an activation barrier. By positioning the coordinate axes x and y in the plane of the boundary between the cells i and j we obtain

$$\int_{S_{ij}} dq_{i_x}^L dq_{i_y}^L \psi_i(\mathbf{q}_i^L)/\psi_{i,j}(\mathbf{q}_i^L) = [2\pi/(\beta\sigma_L^{(s)})]\,\psi_i(\mathbf{s}_i^L)/\psi_{i,j}(\mathbf{s}_i^L), \tag{21}$$

where

$$\sigma_L^{(s)} = \beta^{-1}\{\nabla_{i_x}^2 \ln[\psi_i(\mathbf{s}_i^L)/\psi_{i,j}(\mathbf{s}_i^L)]\,\nabla_{i_y}^2 \ln[\psi_i(\mathbf{s}_i^L)/\psi_{i,j}(\mathbf{s}_i^L)]\}^{1/2}\,(\nabla_{i_x} \equiv \partial/\partial q_{i_x}).$$

The values of the functions $\psi(\mathbf{q}_i^K)$ and their derivatives in a point can be calculated by using the explicit expressions (15) for these quantities.

The obtained expressions (20) and (21) make it possible to write the jump frequency (19) in the traditional Arrhenius form

$$k_L = \nu_L \exp\{-\beta E_L\},$$

where the effective frequency is

$$\nu_L = z_1 n_L (\sigma_L/M_L)^{1/2} [\sigma_L/(2\pi\sigma_L^{(s)})]$$

and the activation energy for self-diffusion

$$E_L = \varphi_i + Pw + \{[\varphi_i(\mathbf{s}_i^L) - \varphi_{i,j}(\mathbf{s}_i^L)] - [\varphi_i(\mathbf{l}_i^L) - \varphi_{i,j}(\mathbf{l}_i^L)]\} + [-(\varphi_{i,j}(\mathbf{l}_i^L) + \varphi_{j,i})].$$

In accordance with (11), the quantity $g_V = \varphi_i + P_W$ in the last expression represents the formation energy of the vacancy. The remaining part of E_L can be interpreted as the activation energy for migration. This term again includes two terms: 1) In braces, there is the height of the potential barrier which is overcome by the atom when moving from the lattice point $\mathbf{l}_i^L$ to the saddle point $\mathbf{s}_i^L$; 2) In the square brackets, there is the binding energy of the atom and the vacancy when there is an atom in the lattice point (this quantity can be considered as a correction to the barrier height).

DISCUSSION OF THE RESULTS

To illustrate the obtained approximate analytical results we carried out a numerical calculation of the concentration dependence of the self-diffusion characteristics in the triple points of the pure matrix components using the Lennary-Jones 6-12 potential for the substitutional solid solutions of argon in krypton and krypton in argon. The first solution can be considered as a light impurity in the matrix of heavy atoms, and the second as a heavy impurity in the matrix of light atoms.

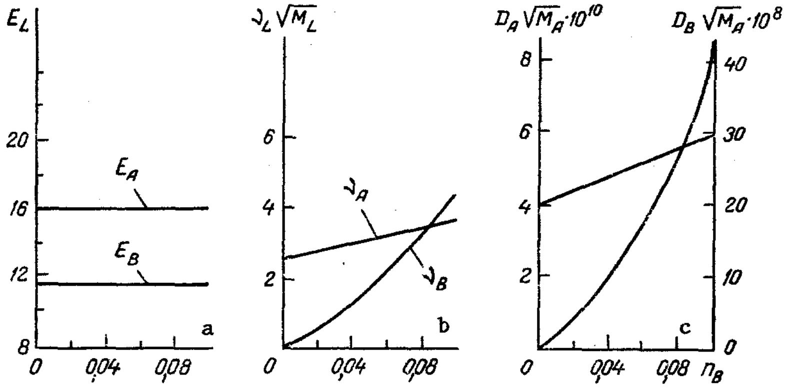

Fig. 2. Concentration dependence of the dimensionless activation energies E_L (a), effective frequencies ν_L (b) and the self-diffusion coefficients D_L (c) for the solution of krypton in argon.

The graphs shows that when a light impurity is added the activation energy for self-diffusion of both components decrease (Fig. 1a) and the effective frequencies increase (Fig. 1b). The self-diffusion coefficients of both components therefore increase with increasing concentration of the impurity particles (Fig. 1c), but they differ by five orders of magnitude.

The addition of a heavy impurity practically does not change the activation energy (Fig. 2a) but leads to an increase of the effective frequencies (Fig. 2b). As a result, the self-diffusion coefficients of both components also increase with increasing impurity concentration (Fig. 2c) and again differ considerably (approximately by three orders of magnitude).

NOTATION

Here, d_L is the self-diffusion coefficient of component 1: k_L, the jump frequency of atoms of type L; i and j, number the cells and lattice sites; $q_i^L = \{x_i^L, y_i^L, z_i^L\}$, coordinates of an atom of type L; $p_i^L = \{p_{i_x}^L, p_{i_y}^L, p_{i_z}^L\}$, components of momentum of atoms of type L; β inverse absolute temperature; w, volume of the unit cell; m_0, lattice concentration of vacancies; m_L, lattice concentrations of the states of cells which are filled with one atoms of type L; $\varphi_i(q_i^L)$, average-force potentials; φ_i, quasipotentials; $\Phi(q_i^K, q_j^L)$, potentials of the pairwise interaction of the atoms; P, pressure; and n_L, molar concentration of component L.

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