Microscopic theory of atomic static displacements in substitutional binary alloys

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Abstract. A microscopic approach to considering the influence of atomic local static displacement (ASD) on binary alloy thermodynamic properties has been developed. An equation that permits the calculation of ASD amplitudes from first principles has been derived. The value of the ASD amplitude is shown to depend on the difference in the effective interatomic potentials of the alloy components. The expression for the alloy free energy, which takes the ASD into account, is obtained by the collective variables method. The theoretical results are illustrated by numerical calculations, performed for alloys of the K–Rb system. The dependence of the ASD squared, averaged over configurations, on temperature and alloy concentration has been investigated, in particular.

1. Introduction

As is well known, the formation of alloys is accompanied by atomic static displacements (ASD). These are caused by distinctions in the effective interaction potentials between ions of the alloy components [1]. The ASD have an essential effect on different alloy properties, in particular, on the x-ray and neutron scattering intensity [2]. The ASD define the dependence of the alloy lattice parameter on component concentration. That is why explicit account of the ASD is important in constructing a consistent microscopic theory of substitutional alloys.

The phenomenological theory of ASD in solid solutions has been developed [2, 3]. Its ideas are shown to be useful for interpretation of experiments related to the short-range order effects in multicomponent solid solutions [4]. But the problem of ASD or their Fourier components A_k determination has not yet been solved. The way to calculate A_k, based on the experimental information about elastic modulus and the lattice parameter dependence on alloy concentration, has been advanced in [2]. Complete information on these quantities is usually absent. A different approach for A_k calculations has been developed in [4]. The experimental values of the longitudinal and transverse acoustic velocities are used in this approach [4]. It is noteworthy that the ways to determine A_k developed in [2, 4] could be applied in the long-wave limit $k \to 0$ only, where k is the wavevector.

The Fourier components of ASD for dilute binary solutions have been calculated in [5] within the continuum approximation. An approach to determine A_k in substitutional binary alloys by the pseudopotential method has been proposed [6]. To realize it, one needs to divide phenomenologically the alloy lattice into sublattices and specify the probabilities of sublattice site occupation by atoms of two kinds. The problem of the consistent account of short-range order effects has not been solved in [6]. Thus, the construction of such a microscopic theory that would allow one to calculate the ASD without utilization of any experimental data is of great importance.

The method of collective variables [7] has been very fruitful for construction of a consistent microscopic alloy theory with atom thermal vibrations and ASD taken into account explicitly [8–10]. The basic ideas of the substitutional binary alloy thermodynamic property calculations by the collective variables method within the rigid-lattice approximation have been presented in [8, 9]. This paper extends the ideas of [1]. The developed theory possesses the following feature: the problems of alloy lattice dynamics, ASD and thermodynamic property investigations are solved within the same approach, based on the collective variables method; see also [1, 8–10].

This paper is organized in the following way: the calculation of the alloy partition sum by the collective variables method with explicit account of the ASD is given in section 2; the equations for the A_k determination are derived in section 3; section 4 illustrates the efficiency of the developed theory.

2. The alloy partition sum

Consider a substitutional binary alloy. The atoms of two kinds A and B are placed arbitrarily on N crystal lattice sites. Their configuration is given by the set of numbers σ_R which equals $+1$ if the site R is occupied by the A atom and equals -1 otherwise.

The alloy Hamiltonian within the rigid-lattice and effective pair interionic interaction approximations has the form

$$H = \frac{1}{2N} \sum_{R_i,R_j} \left\{ \sum_q \left[\left(V_{\mathrm{AA}}(q) \frac{1+\sigma_{R_i}}{2} \frac{1+\sigma_{R_j}}{2} + V_{\mathrm{AB}}(q) \frac{1+\sigma_{R_i}}{2} \frac{1-\sigma_{R_j}}{2} \right. \right. \right.$$
$$\left. \left. \left. + V_{\mathrm{BA}}(q) \frac{1-\sigma_{R_i}}{2} \frac{1+\sigma_{R_j}}{2} + V_{\mathrm{BB}}(q) \frac{1-\sigma_{R_i}}{2} \frac{1-\sigma_{R_j}}{2} \right) \exp[iq(R_i - R_j)] \right] \right\}.$$

(1)

Here $V_{i,j}(q)$, $i, j = $ A, B, is the Fourier transform of the effective interaction between ions of i and j kinds, $V_{\mathrm{AB}}(q) = V_{\mathrm{BA}}(q)$. The explicit expressions for $V_{i,j}(q)$ are given in appendix 1.

The factor $\exp(iqR)$ in (1) could be expanded in power series of the static displacements δR

$$\exp(iqR) = \exp[iq(R^0 + \delta R)] = \exp(iqR^0)[1 + iq\delta R - \tfrac{1}{2}q^2(\delta R)^2 + \ldots]$$

(2)

where R^0 are the ideal lattice coordinates. One can restrict oneself to the square of δR in (2) if the ASD are small.

Let us write down δR in terms of the normal coordinates

$$\delta R_i = \frac{1}{\sqrt{N}} \sum_{k \in \mathrm{BZ}} [\delta R_k \exp(ikR_i^0) + \delta R_{-k} \exp(-ikR_i^0)]$$

(3)

and use the Fourier components of the occupation number σ_R

$$\hat{\rho}_k = \frac{1}{\sqrt{N}} \sum_R \sigma_R \exp(-ikR_i^0).$$

(4)

Vector k in (3) lies inside the first Brillouin zone (BZ). Equation (1) with allowance for (2)–(4) takes the form in a harmonic approximation

$$H = H_0(\hat{\rho}) + \sum_{k \in BZ} [H_1(k, \delta R_k, \hat{\rho}_k) + H_2(k, \delta R_k, \hat{\rho}_k)] \tag{5}$$

where

$$H_0(\hat{\rho}) = NV_0 + \sqrt{N} V_1 \hat{\rho}_0 + \tfrac{1}{2} \sum_{k \in BZ} V_2(k) \hat{\rho}_k \hat{\rho}_{-k} \tag{6}$$

is the Hamiltonian of an ideal lattice without displacements. The explicit expression for potentials V_0, V_1, $V_2(k)$ and their physical meaning are presented in appendix 1.

The addend $H_1(k, \delta R_k, \hat{\rho}_k)$ is linear in δR

$$
\begin{aligned}
H_1(k, \delta R_k, \hat{\rho}_k) &= \frac{i}{8} \sum_G \{(G - k)[V_{AA}(G - k) - V_{BB}(G - k)] \\
&\quad - (G + k)[V_{AA}(G + k) - V_{BB}(G + k)]\}(\delta R_k \hat{\rho}_{-k} - \delta R_{-k} \hat{\rho}_k) \\
&= (i/2) P_k (\delta R_k \hat{\rho}_{-k} - \delta R_{-k} \hat{\rho}_k).
\end{aligned}
\tag{7}
$$

Here G is the reciprocal lattice vectors. The structure of the third addend in (5) is the following [1]:

$$
\begin{aligned}
H_2(k, \delta R_k, \hat{\rho}_k) &= f^{(0)}(k) \delta R_k \delta R_{-k} + \frac{1}{\sqrt{N}} \sum_{k' \in BZ} f^{(1)}(k + k') \delta R_k \delta R_{k'} \hat{\rho}_{-k-k'} \\
&\quad + \frac{1}{N} \sum_{k', k'' \in BZ} f^{(2)}(k'') \delta R_k \delta R_{k'} (\hat{\rho}_{k''-k} \hat{\rho}_{-k''-k'} - \hat{\rho}_{k''-k-k'} \hat{\rho}_{-k''}).
\end{aligned}
\tag{8}
$$

Vectors k' and k'' lie inside the first BZ; $f^{(i)}(k)$ ($i = 0, 1, 2$) are the known functions given in appendix 2. Their form is similar to that of the coefficients of the square of the atomic thermal displacements in the alloy lattice dynamics problem; see [8, 10]. One can note that δR_k with different indices k are mixed in (8) because of the absence of translation invariance in disordered alloys.

The terms in H_1 (7) and H_2 (8) proportional to $\hat{\rho}_k$ and $\hat{\rho}_{k_1} \hat{\rho}_{k_2}$ are concerned with the long-range order and the short-range order effects, respectively. The ASD are random quantities in a disordered alloy. They are related to the component concentration fluctuations and the long- and short-range order fluctuations. This relationship has the simplest form in the Fourier representation [1, 2]

$$\delta R_k = i[(A_k/2)(\hat{\rho}_k - \sqrt{N} \delta_{0,k}) + (1/\sqrt{N}) B_k \hat{\rho}_k \hat{\rho}_{-k}] \tag{9a}$$

or in the more complex modification

$$\delta R_k = i \left(\frac{A_k}{2} (\hat{\rho}_k - \sqrt{N} \delta_{0,k}) + \frac{1}{\sqrt{N}} \sum_{k_1 \in BZ} B_{k+k_1} \hat{\rho}_{k+k_1} \hat{\rho}_{-k-k_1} \right) \tag{9b}$$

where A_k and B_k are unknown functions. The terms in (9a) proportional to $\hat{\rho}_k$ and $\hat{\rho}_k \hat{\rho}_{-k}$ are concerned with the concentration, long-range order and short-range order effects,

respectively. Values of $\hat{\rho}_k$ at $k \to 0$ relate, obviously, to the concentration fluctuations, while $\hat{\rho}_{k^*}$ with the indices k^* correspond to the absolute minimum of the ordering potential $V_2(R) = V_{AA}(R) + V_{BB}(R) - 2V_{AB}(R)$ Fourier transforms are connected with the long-range order in alloys [7, 8]. A simple relation exists between the Fourier transform $\langle \rho_k \rho_{-k} \rangle$ of the pair correlation function $\langle \sigma_R \sigma_{R'} \rangle$ and the Fourier components of the short-range order parameter [9]. Symbol $\langle \rangle$ denotes the configurational averaging. The approximation

$$\delta R_k = i(A_k/2)(\hat{\rho}_k - \sqrt{N}\delta_{0,k}) \qquad A_k = -A_k \tag{9c}$$

is used in the present paper. It means the direct influence of the short-range order effects on ASD are not taken into account.

Let us calculate the alloy partition sum by the collective variables method taking the ASD explicitly into account. The expression for the partition sum has the following form within this method [7–9]

$$Z = \int \cdots \int \exp(-\beta H)J(\rho) \prod_{k \in BZ} \mathrm{d}\rho_k. \tag{10}$$

Here $\beta = (k_B T)^{-1}$ is the inverse temperature, and

$$J(\rho) = \mathrm{Tr}_{[\sigma_R]} \prod_{k \in BZ} \delta\left(\hat{\rho}_k - \frac{1}{\sqrt{N}} \sum_R \sigma_R \exp(-ikR) \right)$$

$$\times \exp\left[-\beta\left(\mu_A \sum_R \frac{1+\sigma_R}{2} + \mu_B \sum_R \frac{1-\sigma_R}{2} \right) \right] \tag{11a}$$

is the transition Jacobian from the set of variables σ_R to the collective variables ρ_k space; see [7–9] for details. Symbol $\mathrm{Tr}_{[\sigma_R]}$ denotes that the trace in (11a) is taken over the eigenvalues of all σ_R, μ_i ($i = A, B$) is the chemical potential of metal i. The factor with the chemical potentials in the $J(\rho)$ takes into account that there are

$$N_A = \sum_R \frac{1+\sigma_R}{2} \qquad N_B = \sum_R \frac{1-\sigma_R}{2}$$

atoms of two kinds in the binary alloy. The presence of the chemical potentials in (11a) permits one to perform the trace operation at each site independently of the concrete configuration [9].

It is seen from (11a) that only the values of collective variables ρ_k equal to the occupation number σ_R Fourier components $\hat{\rho}_k$ will contribute to the transition Jacobian $J(\rho)$. Calculation of the transition Jacobian is described in detail in [7, 8]. The function $J(\rho)$ can be represented as an exponential infinite series

$$J(\rho) = \exp(NM_0)\varrho^N \exp\left(-\sqrt{N}a_1\rho_0 - \frac{a_2}{2!} \sum_{k \in BZ} \rho_k \rho_{-k} \right.$$

$$\left. - \frac{a_3}{3!} \sum_{k_1,k_2,k_3 \in BZ} \rho_{k_1} \rho_{k_2} \rho_{k_3} \delta(k_1 + k_2 + k_3) - \cdots \right). \tag{11b}$$

The following notations are accepted in (11*b*):

$$M_0 = \ln \sum_{i=A,B} \exp(\beta\mu_i) \tag{12a}$$

$$Q = \int_{-\infty}^{\infty} \exp\left(2\pi i M_1\omega + \frac{(2\pi i)^2}{2!}M_2\omega^2 + \frac{(2\pi i)^3}{3!}M_3\omega^3 - \dots\right) d\omega \tag{12b}$$

$$a_1 = -\frac{\partial \ln Q}{\partial M_1} \qquad a_2 = a_1^2 - 2!\frac{\partial \ln Q}{\partial M_2} \tag{12c}$$

$$a_3 = a_1^3 + 3a_1a_2 - 3!\frac{\partial \ln Q}{\partial M_3} \dots \tag{12d}$$

$$M_n = \frac{\partial^n}{\partial h^n} \ln[\exp(-\beta\mu_A - h) + \exp(-\beta\mu_B + h)]|_{h=0} \qquad n = 1, 2, \dots. \tag{12e}$$

Here M_n ($n = 0, 1, 2, 3, \dots$) are cumulants and the quantities a_i ($i = 1, 2, 3, \dots$) are the coefficients of the transition Jacobian. As follows from (12*b*)–(12*e*) a_i are complex functions of the chemical potentials.

It was shown in [7, 8] that the thermodynamic properties of binary alloys can be described adequately within the framework of the collective variables method by a Gaussian approximation in the temperature region $T > T_c$, where T_c is the order–disorder phase transition temperature. In the Gaussian approximation the transition Jacobian $J(\rho)$ can be calculated in analytical form. Putting accordingly into this approximation $M_3 = M_4 = \dots = 0$ in (12*b*) one obtains

$$Q_G = \left(\frac{1}{2\pi M_2}\right)^{1/2} \exp\left(\frac{M_1^2}{2M_2}\right) \qquad a_1 = \frac{M_1}{M_2} \qquad a_2 = \frac{1}{M_2} \qquad a_3 = a_4 = \dots = 0. \tag{13}$$

In view of (10), (11), (13) and (5)–(9) the partition function in the Gaussian approximation of the collective variables method takes the form

$$Z = Q^N \exp(-N\beta V_0) \exp(NM_0) \int \dots \int \exp\{-\sqrt{N}(a_1 + \beta V_1 + \tfrac{1}{2}P_0A_0)\rho_0$$

$$- \frac{1}{2}\sum_{k\in BZ}[a_2 + \beta V_2(k) - P_kA_k + \frac{1}{2}A_k f^{(0)}(k)A_k(\hat{\rho}_k - \sqrt{N}\delta_{0,k})$$

$$\times (\hat{\rho}_{-k} - \sqrt{N}\delta_{0,-k})] + \frac{1}{\sqrt{N}}\sum_{k_1,k_2,k_3\in BZ}\tfrac{1}{4}A_{k_1}f^{(1)}(k+k_2)A_{k_2}(\hat{\rho}_{k_1} - \sqrt{N}\delta_{0,k_1})$$

$$\times (\hat{\rho}_{k_2} - \sqrt{N}\delta_{0,k_2})\rho_{k_3}\delta(k_1 + k_2 + k_3)$$

$$+ \frac{1}{N}\sum_{k_1,k_2,k_3\in BZ}\tfrac{1}{4}A_{k_1}f^{(2)}(k_3)A_{k_2}(\hat{\rho}_{k_1} - \sqrt{N}\delta_{0,k_1})(\hat{\rho}_{k_2} - \sqrt{N}\delta_{0,k_2})$$

$$\times [\rho_{k_3-k_1}\rho_{-k_3-k_2} - \rho_{k_3-k_1-k_2}\rho_{-k_3}]\} \prod_{k\in BZ} d\rho_k. \tag{14}$$

Let us simplify (14) to calculate the partition sum analytically. One can replace ρ_{k_3} and $\rho_k \rho_{k'}$ in the last two terms of (14) by their averages within the framework of the Gaussian approximation:

$$\rho_{k_3} \rightarrow \langle \rho_{k_3} \rangle \qquad \rho_k \rho_{k'} \rightarrow \langle \rho_k \rho_{k'} \rangle \tag{15}$$

where $\langle \rho_{k_3} \rangle$, $\langle \rho_k \rho_{k'} \rangle$ are the Fourier components of one-particle and pair distribution functions, respectively. One should emphasize that according to the definition of the collective variables ρ_k (see (8)), $\langle \rho_{k_3} \rangle$ and $\langle \rho_k \rho_{k'} \rangle$ are the Fourier transforms of the reference system distribution functions $\langle \sigma_R \rangle$ and $\langle \sigma_R \sigma_{R'} \rangle$, respectively. The alloy rigid lattice without any displacements is the reference system.

At temperatures above the order–disorder phase transition point $\langle \rho_{k_3} \rangle$ and $\langle \rho_k \rho_{k'} \rangle$ are defined within the Gaussian approximation by [8, 9]:

$$\langle \rho_0 \rangle = \sqrt{N}(c_A - c_B) \qquad \langle \rho_k \rangle \equiv 0 \qquad k \neq 0 \tag{16}$$

$$\langle \rho_0^2 \rangle = \langle \rho_0 \rangle^2 + \frac{M_2}{1 + \beta V_2(0)M_2} \qquad \langle \rho_k \rho_{k'} \rangle = \frac{M_2}{1 + \beta V_2(k)M_2}\delta(k + k') \tag{17}$$

where $e_i = N_i/N$ is the concentration of i atoms, $i = A, B$.

One can rewrite the expression for the partition sum (14) using (15)–(17) and the results of [10]:

$$Z = Q^N \exp(-N\beta \tilde{V}_0) \exp(NM_0) \int \dots \int \exp\{-\sqrt{N}(a_1 + \beta \tilde{V}_1)\rho_0$$
$$- \tfrac{1}{2} \sum_{k \in BZ} [a_2 + \beta \tilde{V}_2(k, A_k)]\rho_k \rho_{-k}\} \prod_{k \in BZ} d\rho_k. \tag{18}$$

Here

$$\tilde{V}_0 = V_0 + \tfrac{1}{4}A_0 \Phi^{(0)} A_0 \tag{19a}$$

$$\tilde{V}_1 = V_1 + \tfrac{1}{2}P_0 A_0 - \tfrac{1}{2}A_0 \Phi^{(0)} A_0 \tag{19b}$$

$$\tilde{V}_2(k, A_k) = V_2(k) - P_k A_k + \tfrac{1}{2}A_k \Phi^{(0)} A_k \tag{19c}$$

are the addends of the alloy Hamiltonian, renormalized by the ASD, and $\Phi^{(0)}$ is the force constant matrix of the correlated average crystal (CAC). The expression for $\Phi^{(0)}$ is given in [10]; see also appendix 2. One can get familiarized with the CAC term value in [10]. The approximation (15), made within the Gaussian one, allows one to get (18) and (19). It is noteworthy that in the force constant matrix $\Phi^{(0)}$ the pair correlations (the short-range order effects) are explicitly taken into account through $\langle \rho_k \rho_{-k} \rangle$ owing to this approximation; see (A14). It means one could go beyond the framework of the single-site methods calculating the eigenvalues of $\Phi^{(0)}$ [10]. The integration variables are separated in (18). Thus, the partition sum can be easily calculated and the alloy free energy per atom, $F = -\ln Z/(\beta N)$, is defined by the following formula:

$$F(T, \mu) = -\beta^{-1}M_0 + \tilde{V}_0 + \frac{1}{2}\frac{\tilde{V}_2(0)M_1^2 - 2\tilde{V}_1 M_1 - \beta \tilde{V}_1^2 M_2}{1 + \beta \tilde{V}_2(0, A_k)M_2}$$

$$+ \frac{\beta^{-1}}{2N} \sum_{k \in BZ} \ln[1 + \beta \tilde{V}_2(k, A_k)M_2]. \tag{20}$$

The free energy (20) is a function of temperature and chemical potentials. More suitable variables are temperature and concentration. Transition to new variables can be performed by the Legendre transformation

$$F(T, c) = F(T, \mu) - \sum_{i=A,B} \mu_i N_i \tag{21}$$

where the chemical potentials are defined by

$$c_i = N_i/N = \partial F/\partial \mu_i \qquad i = A, B. \tag{22}$$

3. Equation for the ASD amplitudes

The equilibrium values of the ASD amplitudes are determined from the condition of the alloy free energy extremum with respect to A_k

$$\frac{\partial F}{\partial A_k} = \frac{1}{1 + \beta \tilde{V}_2(k, A_k) M_2} \frac{\partial \tilde{V}_2(k, A_k)}{\partial A_k} = 0. \tag{23}$$

We consider temperatures above the order–disorder phase transition point T_c. The quantity $1 + \beta \tilde{V}_2(k, A_k) M_2 \neq 0$ at $T > T_c$. Then, the system of equations

$$\sum_{\beta} \Phi^{(0)}_{\alpha, \beta} A_k^\beta = P_k^\alpha \qquad \alpha, \beta = x, y, z, \qquad k \in \text{BZ} \tag{24}$$

determining the Cartesian components of the vector A_k, follows from (23) and (19c).

To solve (24), expand the A_k and P_k in the complete set of some functions. The polarization vectors $\epsilon_{k\lambda}$ of the CAC vibrations could be used as such a complete set of basis functions. The $\epsilon_{k\lambda}$ are the eigenvectors of the dynamic matrix $\Phi^{(0)}$:

$$\Phi^{(0)} \epsilon_{k\lambda} = \tilde{M} \bar{\omega}^2_{k\lambda} \epsilon_{k\lambda} \tag{25}$$

where $\tilde{M} = \sum_{i=A,B} M_i c_i$ is the average ion mass and $\bar{\omega}_{k\lambda}$ is the frequency of CAC; see [8, 10] for details.

Then

$$A_k = \sum_{\lambda} A_{k\lambda} \epsilon_{k\lambda} \qquad P_k = \sum_{\lambda} P_{k\lambda} \epsilon_{k\lambda}. \tag{26}$$

Here $A_{k\lambda}$, $P_{k\lambda}$ are the expansion coefficients and $\lambda = 1, 2, 3$ is the polarization index.

Let us substitute (26) in (24) and take (25) into account. The following solutions of (24) are obtained:

$$A_{k\lambda} = (P_k \epsilon_{k\lambda})/\tilde{M} \bar{\omega}^2_{k\lambda} \tag{27a}$$

or, see (26),

$$A_k = \sum_{\lambda} \frac{(P_k \epsilon_{k\lambda})}{\tilde{M} \bar{\omega}^2_{k\lambda}} \epsilon_{k\lambda}. \tag{27b}$$

Let us analyse the result (27) in detail. In the first place the formula (27b) corroborates the Krivoglaz conclusion that the waves of the static displacements are only longitudinal ones along the principal symmetry directions [100], [110] and [111] in alloys [2]. Such a deduction has been made in [2] on the basis of qualitative considerations. Let us prove it analytically. One can notice from (7) that the vectors P_k and k are parallel: $P_k \| k$. The vibrations of the CAC are pure longitudinal or transverse ones along the [100], [110] and [111] directions [8]: $\epsilon_{kL} \| k$ and $\epsilon_{kT_1} \perp k$ and $\epsilon_{kT_2} \perp k$. It means the transverse modes do not contribute to the $A_{k\lambda}$. That is why $A_k \| k$; see (27b). Besides, it is easy to find the asymptotic behaviour of the ASD amplitudes A_k in the long-wave limit $k \to 0$. So long as $P_k \simeq k$ (see (7)) and $\bar{\omega}_{k\lambda} \simeq k$, then $|A_k| \simeq k^{-1}$ at $k \to 0$. This result confirms the similar finding made in [2] within the phenomenological approach.

One can conclude from (27) and (7) that the ASD are small if the effective inter-ionic potentials of the alloy components are similar: $V_{AA}(q) \simeq V_{BB}(q)$. Really, $P_k \equiv 0$ at $V_{AA}(q) = V_{BB}(q)$ and then $A_k = 0$. This conclusion allows one to understand at the microscopic level the nature of the well known phenomenological Hume–Rothery rules [11].

What are the peculiarities of the developed theory? It is a microscopic approach. All quantities in the RHS of (27) could be calculated from first principles. It is noteworthy that the expression for the P_k (7) as well as for the potentials $\tilde{V}_0$, $\tilde{V}_1$, $\tilde{V}_2(k)$, renormalized by the ASD, have been derived for the first time. It permits one to investigate the ASD influence on alloy thermodynamic properties consistently.

Knowledge of the ASD amplitudes A_k permits one to calculate the quantities $\langle \delta R \rangle$ and $\langle \delta R^2 \rangle$, where symbol $\langle \rangle$ denotes the configurational averaging with the correlation functions (16), (17) of the reference system rigid lattice. The ASD δR_i with (3) and (9) takes the form

$$\delta R_i = \frac{1}{\sqrt{N}} \sum_{k \in BZ} \frac{iA_k}{2} [\exp(ikR_i^0)(\hat{\rho}_k - \sqrt{N}\delta_{0,k}) - \exp(-ikR_i^0)(\hat{\rho}_{-k} - \sqrt{N}\delta_{0,-k})]. \quad (28)$$

Then, the average value of δR_i is equal at temperatures $T > T_c$ to

$$\langle \delta R_i \rangle = 2c_B \lim_{k \to 0} [A_k(kR_i^0)]. \quad (29)$$

Equation (16) has been used in the derivation of (29). The projection of $\langle \delta R_i \rangle$ on the R_i vector direction in $|R_i^0|$ units and with allowance for (27) is described by the formula

$$\frac{\langle \delta R_i \rangle n_{R_i^0}}{|R_i^0|} = 2c_B \lim_{k \to 0} \left(\sum_\lambda \frac{(P_k \epsilon_{k\lambda})(\epsilon_{k\lambda} n_{R_i^0})}{\bar{M}\bar{\omega}_{k\lambda}^2} (kn_{R_i^0}) \right). \quad (30)$$

Here $n_{R_i^0}$ is the unit vector in the R_i^0 direction: $R_i^0 = |R_i^0| n_{R_i^0}$. The square of the ASD, averaged over configurations, is defined as

$$\langle \delta R^2 \rangle = \langle \delta R \rangle^2 + \frac{1}{N} \sum_{k \in BZ} A_k^2 \langle \rho_k \rho_{-k} \rangle \quad (31)$$

where $\langle \rho_k \rho_{-k} \rangle$ is given by (17). Equation (30) describes lattice parameter alteration caused by the presence of B component in the alloy. One should take such an alloy component as a kind of B that $c_B \leqslant 0.5$. The quantity (31) belongs to the important alloy characteristics. It defines the alloy Debye–Waller factor.

4. The atomic static displacements in K–Rb alloys

The ASD in alloys of K–Rb system have been investigated to illustrate the developed theory. Solid solutions of disordered alloys $K_x Rb_{1-x}$ exist in the high-temperature region [11]. The $K_x Rb_{1-x}$ alloys have a body-centred cubic (BCC) structure at $T > T_c$. The alloy lattice parameter d obeys Vegard's law

$$d = d_A c_A + d_B c_B \tag{32}$$

where d_i ($i = A, B$) is the parameter of pure metal i. It means that the alloys of K–Rb system are similar to ideal solutions at high temperatures.

The vector P_k (7) determines the amplitudes of the ASD in alloys; see (27). The behaviour of the P_k along the principal symmetry directions of the Brillouin zone is shown in figure 1 for two $K_{0.9}Rb_{0.1}$ and $K_{0.1}Rb_{0.9}$ alloys. The P_k has been calculated according to the formulae (7), (A1), (A2) and (A6), (A7). One can conclude the P_k behaves equally at different concentrations in the $K_x Rb_{1-x}$ alloys. The value of $|P_k|$ is small: $\simeq 10^{-4}$ au. By the way, the P_k is equal to zero in the high-symmetry points of the Brillouin zone; see figure 1. Figures 2 and 3 present the ASD amplitude A_k behaviour along the principal symmetry directions. It is seen that A_k is a weak function of concentration in $K_x Rb_{1-x}$ solutions. The weak dependence of A_k on alloy concentration means that relationship (9c) is adequate for the K–Rb system. The A_k displays the most interesting behaviour in the [111] direction, but the largest values of it are in the [100] direction; compare figures 2 and 3. The $|A_k| \simeq k^{-1}$ in the long-wave limit: $k \to 0$.
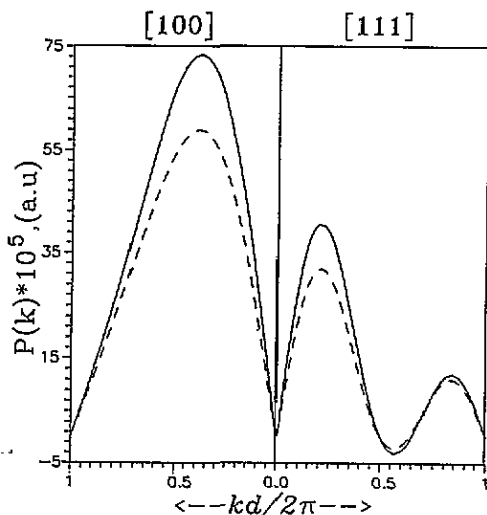

Figure 1. The vector $P(k)$ (7) projections on the principal symmetry directions for the $K_{0.9}Rb_{0.1}$ (———) and $K_{0.1}Rb_{0.9}$ (- - - -) alloys.
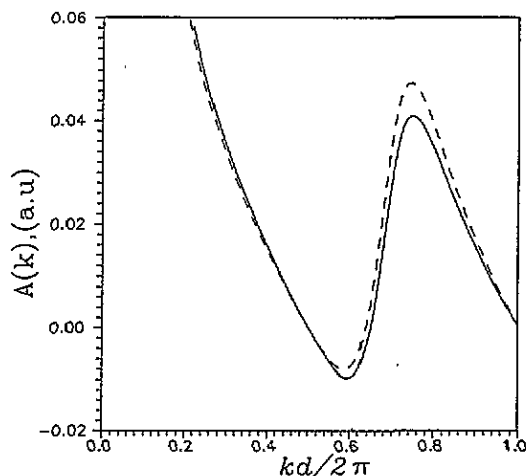
Figure 2. The amplitudes of the atomic static displacements in the [111] direction for the $K_{0.9}Rb_{0.1}$ (———) and $K_{0.1}Rb_{0.9}$ (- - - -).

The square of the ASD, averaged over configurations, has been calculated with a view to (31), (27), (17) and (A5). The equilibrium volume of the reference system unit cell is supposed to obey Vegard's law; see (32). Figure 4 shows the dependence of $\langle \delta R^2 \rangle$
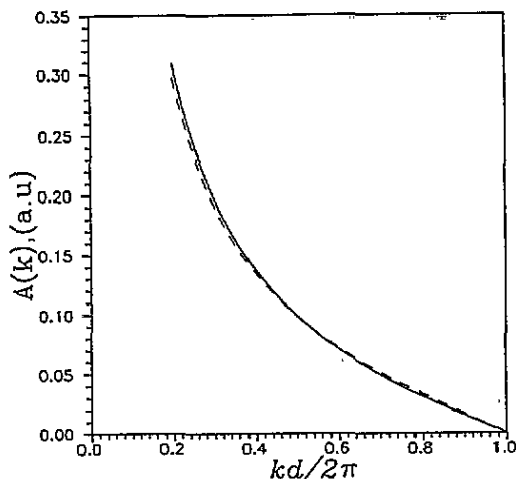
Figure 3. The amplitudes of the ASD in the [100] direction; notations are the same as in figure 2.
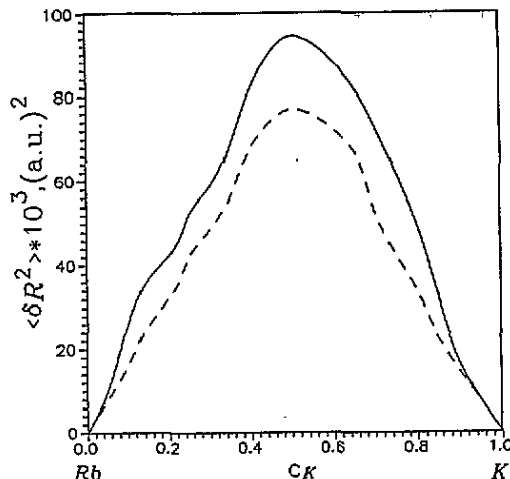
Figure 4. Dependence of the atomic static displacement squared, averaged over configurations, for the second coordination sphere atoms at $T = 80$ K (———) and $T = 200$ K (----).

on concentration at two temperatures in K–Rb solutions. One can note that deviations from Vegard's law are small in K–Rb solutions. They are the largest in the equiatomic alloys. As the temperature decreases, the $\langle \delta R^2 \rangle$ increase; see figure 4. This result confirms numerically the statement that alloys of K–Rb system are like ideal solutions, especially at high temperatures. One can notice that the first derivative of $\langle \delta R^2 \rangle$ with respect to the alloy concentration is not a regular function for K–Rb solutions at both temperatures investigated. More accurate consideration of $K_x Rb_{1-x}$ physical properties is desirable at concentrations x corresponding to these peculiarities, for example, at $x = 0.18$ and $T = 80$ K; see figure 4.

5. Conclusion

The approach suggested contains the following features. It is a microscopic theory that permits one to get some interesting results analytically. The next deductions are the most important.

(i) The waves of the static displacements are only longitudinal ones along the principal symmetry directions [100], [110] and [111] in alloys.

(ii) The ASD are small if the effective inter-ionic potentials of the alloy components are similar, i.e. $V_{AA}(q) \simeq V_{BB}(q)$.

(iii) The ASD amplitude A_k weak dependence on concentration in $K_x Rb_{1-x}$ solutions, obtained within the approximation (9c), allows one to conclude that the local environment effects on ASD could be small in alloys the equilibrium volume of which obeys Vegard's law.

The conclusion (iii) is valid in the high-temperature region above the order–disorder phase transition point. There still remains the more comprehensive problem to examine the ASD in the vicinity of the phase instability point where the pair correlation (the short-range

order) effects are displayed strongly. Besides, the numerical results of the ASD investigations depend on such parameters of the theory as electron–ion model pseudopotential, the electron dielectric function (function of local field), etc., used in the calculations (see appendices 1 and 2). All of the points mentioned above will be subjects of future research.

Acknowledgments

Appendix 1.

The Fourier transforms of the effective pair potential between ith and jth kind ions within the second order of pseudopotential perturbation theory can be expressed in atomic units as follows:

$$V_{ij}(q) = \frac{\Omega_0}{8\pi} q^2 \left(W_i W_j \frac{1 - \epsilon(q)}{\epsilon(q)} + \frac{16\pi}{\Omega_0^2} \frac{z_i z_j}{q^4} \exp(-q^2/4\eta) \right). \tag{A1}$$

Here $\Omega_0 = \Omega/N$ is the equilibrium volume per atom, $W_i(q)$ the bare pseudopotential form factor of an ith kind ion, $\epsilon(q)$ the conduction electron dielectric function, which contains the exchange and correlation corrections, z_j the jth kind ion charge, and η the Ewald parameter used to calculate the alloy electrostatic energy.

In the present paper a model pseudopotential, proposed in [12] with the form factor

$$W_i(q) = \frac{4\pi z_i}{\Omega_0} \frac{(2a_i - 1)(qr_i^0)^2 - 1}{q^2[1 + (qr_i^0)^2]^2} \qquad i = A, B \tag{A2}$$

is used as a bare pseudopotential, a and r^0 are the model pseudopotential parameters. The parameters a_i, r_i^0 are supposed to be the same in the alloy as in pure metal of i kind ($i = A, B$). Their values for K and Rb have been utilized in the present paper:

$$a_K = 2.671 \qquad r_K^0 = 0.689 \qquad z_K = 1$$
$$a_{Rb} = 2.293 \qquad r_{Rb}^0 = 0.779 \qquad z_{Rb} = 1.$$

The explicit expressions for V_0, V_1 and $V_2(k)$ (see (6) and (19)), obtained in the second order of pseudopotential perturbation theory, are [8, 9]

$$V_0 = \left(\frac{3}{10} k_F^2 + E_c \right) \bar{z} + \overline{W^{nc}} \bar{z} - \bar{z}^2 \left[\left(\frac{\eta}{\pi} \right)^{1/2} + \frac{\pi}{2\Omega_0 \eta} \right]$$
$$+ \frac{1}{8} \left(\frac{4\pi(z_A + z_B)^2}{\Omega_0} \sum_{G \neq 0} |S(G)|^2 \frac{\exp(-G^2/4\eta)}{G^2} \right.$$
$$\left. - \Omega_0 \sum_{G \neq 0} |S(G)|^2 \frac{\Pi(G)}{\epsilon(G)} [W_A(G) + W_B(G)]^2 \right) \tag{A3}$$

$$V_1(R) = \frac{1}{4}\left[\sum_{G \neq 0} \frac{S(G)\exp(iGR) + S^*(G)\exp(-iGR)}{2} \right.$$

$$\left. \times \left(\frac{4\pi(z_A^2 - z_B^2)}{\Omega_0} \frac{\exp(-G^2/4\eta)}{G^2} - \Omega_0 \frac{\Pi(G)}{\epsilon(G)}[W_A^2(G) - W_B^2(G)] \right) \right] \tag{A4}$$

$$V_2(k) = \frac{1}{2}\left(\frac{2\pi(z_A - z_B)^2}{\Omega_0} \sum_{G \neq 0} \frac{\exp(-|G+k|^2/4\eta)}{|G+k|^2} \right.$$

$$\left. - \frac{\Omega_0}{8\pi} \sum_G (G+k)^2 \frac{1-\epsilon(G+k)}{\epsilon(G+k)}[W_A(G+k) - W_B(G+k)]^2 \right). \tag{A5}$$

The following notations are accepted in (A3) to (A5): $k_F = (3\pi^2 \bar{z}/\Omega_0)^{1/3}$ is the Fermi momentum of electron gas, $\bar{z} = \sum_{i=A,B} z_i c_i$ the average ion valency in alloy, E_{xc} the exchange–correlation energy of the homogeneous interacting electron gas, $W_i^{nc} = \lim_{q\to 0}[W_i(q) + 4\pi z_i/\Omega_0]$ the non-Coulomb part of the pseudopotential form factor, $\overline{W^{nc}} = \sum_{i=A,B} W_i^{nc} c_i$, $S(q) = (1/N)\sum_R \exp(-iqR)$ the lattice structure factor, $S(q) = S^*(q)$, $\Pi(q)$ the polarization operator of electron gas, $\epsilon(q) = 1 + (4\pi/q^2)\Pi(q)$.

The dielectric function of Geldart and Vosko [13]

$$\epsilon(q) = 1 + \frac{4\pi}{q^2} \frac{\Pi_0(q)}{1 + G(q)\Pi_0(q)} \tag{A6}$$

with

$$\Pi_0(q) = \frac{k_F}{2\pi^2}\left(1 + \frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| \right) \qquad \eta = \frac{q}{2k_F} \tag{A7}$$

has been used in the calculation. Here $G(q)$ is the function of local field

$$G(q) = -\frac{q^2}{2(q^2 + \xi k_F^2)} \tag{A8}$$

with

$$\xi = \frac{2}{1 + 0.153(k_F\pi)^{-1}}. \tag{A9}$$

The expression for the exchange–correlation energy of the interacting electron gas

$$E_{xc} = -0.458/r_s - 0.115 + 0.031\ln(r_s) \qquad r_s = (3\Omega_0/4\pi z)^{1/3} \tag{A10}$$

is consistent via the parameter ξ with that for the static dielectric function owing to the exact relation between the polarization operator $\Pi(q)$ and the electron gas compressibility [13].

One can see from (A4), (A5) that $V_1(R)'$ indicates the difference between alloy component atomic characteristics, and $V_2(k)$ is the Fourier transform of the ordering potential $V_2(R) = V_{AA}(R) + V_{BB}(R) - 2V_{AB}(R)$. In cubic crystals $V_1(R) = \text{const}$, because of $S(G) \equiv 1$ and $\exp(iGR) \equiv 1$; see (A4).

Appendix 2.

The formulae for $f^{(i)}$ functions, entering (8), (14), are given below:

$$f^{(0)}(k) = \sum_{i,j=A}^{B} \left(\sum_{G} [(G+k)^2 V_{ij}(G+k) + (G-k)^2 V_{ij}(G-k) - 2(G)^2 V_{ij}(G)] \right)$$
(A11)

$$f^{(1)}(k+k') = \sum_{G} [(G+k)^2 \Delta V(G+k) + (G-k)^2 \Delta V(G-k) - (G)^2 \Delta V(G)$$
$$- (G+k+k')^2 \Delta V(G+k+k')]$$
(A12)

$$f^{(2)}(k) = \sum_{G} (G+k)^2 [V_{AA}(G+k) + V_{BB}(G+k) - 2V_{AB}(G+k)]$$
(A13)

where $\Delta V(q) = V_{AA}(q) - V_{BB}(q)$. The force constant matrix $\Phi^{(0)}$ of the correlated average crystal is a diagonal one in the wavevector representation with the matrix elements (see [8, 10])

$$\Phi_{kk}^{(0)} = \sum_{G} \left[(G+k)^2 \bar{V}^2(G+k) + (G-k)^2 \bar{V}^2(G-k) - 2(G)^2 \bar{V}^2(G) \right.$$
$$+ \frac{1}{4} \left(\sum_{k \neq k'} (G+k')^2 V_2(G+k') \langle \rho_{k'-k} \rho_{-k'+k} \rangle \right.$$
$$+ \sum_{k \neq -k'} (G-k')^2 V_2(G-k') \langle \rho_{k'+k} \rho_{-k'-k} \rangle$$
$$\left. \left. - 2 \sum_{k \neq 0} (G+k')^2 V_2(G+k') \langle \rho_{k'} \rho_{-k'} \rangle \right) \right]$$
(A14)

where

$$\bar{V}^2(q) = c_A^2 V_{AA}(q) + c_B^2 V_{BB}(q) + 2c_A c_B V_{AB}(q).$$
(A15)

The Fourier components of the short-range order parameter [9] are present in the matrix elements $\Phi_{kk}^{(0)}$ (A14). It means the spatial atomic pair correlations are explicitly taken into account in the force constant matrix $\Phi^{(0)}$ of CAC. The Cartesian components of the functions $f^{(i)}(k)$ and the force matrix $\Phi^{(0)}$ are defined in the way illustrated by the expression for $f_{\alpha\beta}^{(0)}(k)$ (see A11)

$$f_{\alpha,\beta}^{(0)}(k) = \sum_{i,j=A}^{B} \left(\sum_{G} [(G_\alpha + k_\alpha)(G_\beta + k_\beta) V_{ij}(G+k) + (G_\alpha - k_\alpha)(G_\beta - k_\beta) V_{ij}(G-k) \right.$$
$$\left. - 2G_\alpha G_\beta V_{ij}(G)] \right) \qquad \alpha, \beta = x, y, z.$$
(A16)

Here G_α, k_α are the Cartesian components of the reciprocal lattice vector G and wavevector k, respectively. The expression $A_k \Phi^{(0)} A_k$, presented in (19), means

$$A_k \Phi^{(0)} A_k = \sum_{\alpha,\beta=x,y,z} A_k^\alpha \Phi_{\alpha,\beta}^{(0)}(k) A_k^\beta.$$
(A17)

Thus all quantities necessary to perform the calculations are determined.

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