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q-space configurational energy and short-range order in alloys with atomic size mismatch

V. N. Bugaev,[1] H. Reichert,[1] O. Shchyglo,[1] A. Udyansky,[1] Y. Sikula,[1] and H. Dosch[1,2]
[1]*Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany*
[2]*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, 70569 Stuttgart, Germany*

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We present a *q*-space method for the incorporation of long-range strain fields into the statistical thermodynamics of binary alloys with atomic size mismatch. In this approach the configurational energy is parametrized via a set of potentials and generalized Kanzaki forces providing a powerful description of strain-induced many-body effects for systems with lattice distortions. We show how strain-induced interactions act on the topology of short-range-order patterns.

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Presently, the most general approach in the statistical mechanics of alloy systems on a given rigid ideal crystal lattice is based on a lattice model in which the configurational energy of a binary alloy $A_{1-c}B_c$ is described by a Hamiltonian represented as an exact real space expansion[1–5]

$$H(\{c_{\vec R}\})=V^{(0)}+\sum_{\vec R} V^{(1)}_{\vec R}c_{\vec R}+\frac{1}{2}\sum_{\vec R_1,\vec R_2} V^{(2)}_{\vec R_1,\vec R_2}c_{\vec R_1}c_{\vec R_2} + \frac{1}{6}\sum_{\vec R_1,\vec R_2,\vec R_3} V^{(3)}_{\vec R_1,\vec R_2,\vec R_3}c_{\vec R_1}c_{\vec R_2}c_{\vec R_3}+\cdots, \qquad (1)$$

where the occupation of lattice site $\vec R$ with atom A or B is labeled by the variable $c_{\vec R}=1$ (for B atom) and 0 (for the A atom). The set of effective interaction parameters $\{V^{(n)}\}n=1,2,3,\ldots$ are phenomenological constants which can be determined from electronic structure total energy calculations and then used in Monte Carlo simulations. $V^{(1)}$ denotes the site energy for injecting a B atom into the matrix, $V^{(2)}$ describes the two-body mixing potential, and $V^{(3)}$ quantifies the three-body interactions in the system (for details, see Ref. 6). This approach has been fruitfully used for the study of ground states, phase diagrams, and short-range order (SRO) in metallic and semiconductor alloys. Conversely, experimental SRO data are used in inverse Monte Carlo (IMC) techniques to determine concentration- and temperature-dependent effective pairwise interactions $\{V^{eff}_{\vec R}\}$,[7,8] which include contributions from the numerical mapping of all many-body interactions in Eq. (1) onto the set $\{V^{eff}_{\vec R}\}$. This set can then be used for the modeling of structural and thermodynamic properties of alloys. In the case of alloys with atomic size mismatch this accurate real-space approach should be improved by incorporating mechanical degrees of freedom which account for lattice distortions. Here we propose a *q*-space approach which allows us to overcome this problem by constructing an analytical procedure for the mapping of strain-induced many-body effects onto the two-body effective interactions. This procedure is based on the recently developed simple and accurate ring approximation.

Atomic size mismatch in alloys leads to mechanical relaxation of the crystal lattice that gives rise to a stochastic long-range field of static atomic displacements $\{\vec u_{\vec R}\}$. In this case, the chemical energy parameters $\{V^{(n)}\}$ in Eq. (1) should be replaced by $\{\tilde V^{(n)}\}\equiv\{V^{(n)}+\Delta V^{(n)}\}$ for a strain-induced contribution $\{\Delta V^{(n)}\}$ caused by the lattice distortions. By way of example, the contribution for the two-body effective interactions is given by[3,9,10]

$$\Delta V^{(2)}_{\vec R_1,\vec R_2}=-\sum_{\vec q}\ \vec\phi^{\,+}_{\vec q}\hat G_{\vec q}\vec\phi_{\vec q}e^{i\vec q(\vec R_1-\vec R_2)}+Q, \qquad (2)$$

where $\vec\phi_{\vec q}$ and $\hat G_{\vec q}$ are the Fourier components of the so-called Kanzaki forces and the lattice Greens function, respectively (see also Ref. 11). The latter appears in the theory of lattice dynamics and can be described in terms of force constants (the normalization constant Q is determined by the requirement of the absence of atomic self-interaction $\Delta V^{(2)}_{\vec R_1=\vec R_2}=0$). The summation over $\vec q$ in Eq. (1) and hereafter is carried out over the first Brillouin zone of the system. One important feature of $\Delta V^{(2)}_{\vec R_1,\vec R_2}$ is its infinite range of action which renders IMC and other purely real-space statistical thermodynamics as Monte-Carlo and the cluster-variation method based on the Hamiltonian in Eq. (1) to be inefficient for the study of the effects of atomic size mismatch in alloys. Notice also that the long-range strain-induced interaction exhibits a nonanalytic behavior of its Fourier component at $q=0$ (Γ point). Within the mixed-basis cluster expansion method[12,13] this problem is overcome to a certain extent by isolating this singularity and adding it as a separate term to Eq. (1). Doing so, the cluster energies $\{V^{(n)}\}$ are calculated for the relaxed state of the lattice and, therefore, the short-range part of the strain-induced interaction is included by mapping it into $\{V^{(n)}\}$ without explicit use of the force parameters described in Eq. (2).

Using the Kanzaki force approach[14,15] the set of (''chemical'') energy constants $\{V^{(n)}\}$ determined for the average lattice of the alloy is completed by the set of force constants $\{\phi^{(n)}\}$ responsible for the lattice displacements. Note that these artificial forces act on the average lattice in such a way that they cause the same displacements as in the actual lattice. In an adiabatic approximation, the condition of mechanical equilibrium allows then to express the static dis-

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placements $\{\vec{u}_{\vec{R}}\}$ in terms of the occupation variables $\{c_{\vec{R}}\}$. It is important to note that, even in the case of only pairwise chemical interactions, this procedure gives rise to many-body strain-induced interactions.[16] This naturally leads to a q-space simulation of the SRO in alloys with atomic size mismatch by means of the ring approximation.[17] In addition, it gives a simple and clear interpretation of the interaction in alloys by analytical "mapping" of the many-body contributions onto the effective two-body interactions.

In the presence of a displacement field caused by atomic size mismatch the Hamiltonian of the system can be represented as the sum of a chemical part determined for the undistorted lattice and an effective strain-induced part described in the quasiharmonic approximation[9] as follows:

$$H(\{c_{\vec{R}}\},\{\vec{u}_{\vec{R}}\})=H^{ch}(\{c_{\vec{R}}\})+H^{s\text{-}i}(\{c_{\vec{R}}\},\{\vec{u}_{\vec{R}}\}), \tag{3}$$

where H^{ch} is determined by Eq. (1) taking into account the pairwise chemical interaction only.[18] The strain-induced part of the Hamiltonian is then given by

$$\begin{aligned} H^{s\text{-}i}=&\frac{1}{2}\sum_{\vec{R}_1,\vec{R}_2}\vec{u}^{\,T}_{\vec{R}_1}\hat{\phi}^{(0)}_{\vec{R}_1-\vec{R}_2}\vec{u}_{\vec{R}_2}\\ &-\sum_{\vec{R}_1,\vec{R}_2}c_{\vec{R}_1}\vec{\phi}^{(1)T}_{\vec{R}_1-\vec{R}_2}\vec{u}_{\vec{R}_2}-\frac{1}{2}\sum_{\vec{R}_1,\vec{R}_2}c_{\vec{R}_1}\vec{\phi}^{(2)T}_{\vec{R}_1-\vec{R}_2}c_{\vec{R}_2}\vec{u}_{\vec{R}_2}, \end{aligned} \tag{4}$$

where the first term refers to the potential-energy change in the alloy due to the lattice distortions $\{\vec{u}_{\vec{R}}\}$ which are present even in a pure matrix. The second and the third terms are the potential-energy changes due to the displacement field induced by the injection of single B atoms into the alloy matrix and B atom pairs in the lattice, respectively. The symmetrical 3×3 matrix $\hat{\phi}^{(0)}_{\vec{R}_1-\vec{R}_2}=\|\partial^2\tilde{V}^{(0)}/\partial u^i_{\vec{R}_1}\partial u^j_{\vec{R}_2}\|_0$ [with $(i,j=x,y,z)$ as Cartesian coordinates] corresponds to the force ("spring") constants known from semiphenomenological models of lattice dynamics. The vectors $\vec{\phi}^{(n)}_{\vec{R}}=-\partial\tilde{V}^{(n)}/\partial\vec{u}_{\vec{R}}|_0$ with $n=1,2$ are the generalized Kanzaki forces.[19] The force constants $\{\phi^{(n)}\}$ in Eq. (4) as well as the potentials $\{V^{(n)}\}$ in Eq. (1) are determined for the undistorted state at a given alloy composition c. The associated q-space representation of Eq. (4) reads

$$\begin{aligned} H^{s\text{-}i}=&\frac{1}{2N}\sum_{ij}\sum_{\vec{q}}\phi^{(0)ij}_{\vec{q}}(u^i_{\vec{q}})^*u^j_{\vec{q}}\\ &-\frac{1}{N}\sum_{i}\sum_{\vec{q}}\phi^{(1)i}_{\vec{q}}c_{\vec{q}}(u^i_{\vec{q}})^*\\ &-\frac{1}{2N^2}\sum_{i}\sum_{\vec{k},\vec{q}}\phi^{(2)i}_{\vec{k}}(u^i_{\vec{q}})^*c_{\vec{k}}c_{\vec{q}-\vec{k}}. \end{aligned} \tag{5}$$

In mechanical equilibrium, i.e., $\partial H^{s\text{-}i}/\partial\vec{u}_{\vec{R}}=0$ for all $\{\vec{R}\}$, the (Cartesian) Fourier components of the displacement field read

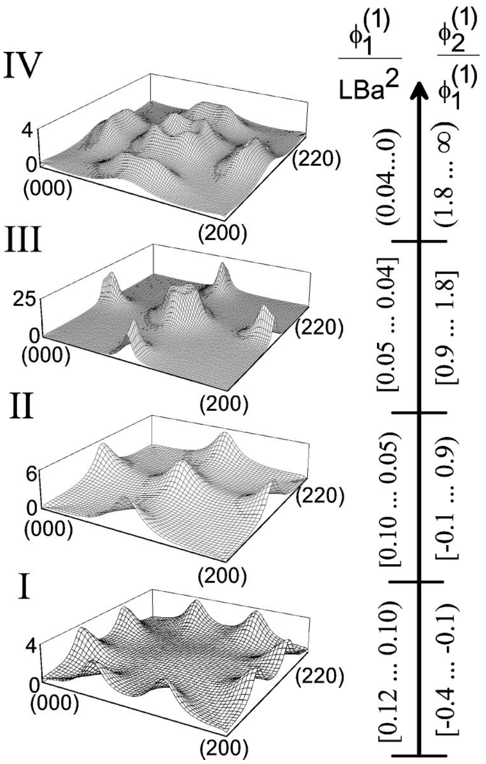

FIG. 1. Strain-induced effects on the topology of the SRO $\alpha_{\vec{q}}$. Four distinct SRO patterns (I–IV) are discernible as a function of the ratio $\phi_2^{(1)}/\phi_1^{(1)}$. Also shown is the corresponding $\phi_1^{(1)}$ rescaled by the factor LBa^2 where a is the lattice constant and $B=(c_{11}+2c_{12})$.

$$u^i_{\vec{q}}=A^i_{\vec{q}}c_{\vec{q}}+(2N)^{-1}\sum_{\vec{k}}B^i_{\vec{q},\vec{k}}c_{\vec{k}}c_{\vec{q}-\vec{k}}, \tag{6}$$

where

$$A^i_{\vec{q}}\equiv\sum_j G^{ij}_{\vec{q}}\phi^{(1)j}_{\vec{q}},\quad B^i_{\vec{q},\vec{k}}\equiv\sum_j G^{ij}_{\vec{q}}\phi^{(2)j}_{\vec{k}}.$$

Substituting Eq. (6) into Eq. (5) we obtain

$$\begin{aligned} H^{s\text{-}i}=&\frac{-1}{2N}\sum_{\vec{q}}\vec{\phi}^{(1)+}_{\vec{q}}\hat{G}_{\vec{q}}\vec{\phi}^{(1)}_{\vec{q}}c_{\vec{q}}c^*_{\vec{q}}\\ &-\frac{1}{4N^2}\sum_{\vec{q}_1,\vec{q}_2}(\vec{\phi}^{(2)+}_{\vec{q}_1}\hat{G}_{\vec{q}_2}\vec{\phi}^{(1)}_{\vec{q}_2}\\ &+\vec{\phi}^{(1)+}_{\vec{q}_1}\hat{G}_{\vec{q}_1}\vec{\phi}^{(2)}_{\vec{q}_2})c_{\vec{q}_1}c^*_{\vec{q}_2}c^*_{\vec{q}_1-\vec{q}_2}\\ &-\frac{1}{8N^3}\sum_{\vec{q}_1,\vec{q}_2,\vec{q}_3}\vec{\phi}^{(2)+}_{\vec{q}_1}\hat{G}_{\vec{q}_2}\vec{\phi}^{(2)}_{\vec{q}_3}c_{\vec{q}_1}c_{\vec{q}_2-\vec{q}_1}c^*_{\vec{q}_3}c^*_{\vec{q}_2-\vec{q}_3}. \end{aligned} \tag{7}$$

This Hamiltonian, which is one key result of this work, describes, in addition to two-body, three- and four-body strain-induced contributions to the atomic interactions. Note that in this *q*-space representation of the strain-induced interactions the radius of action is *a priori* not limited.

In the following we show how to take into account the many-body strain-induced interactions in the statistical mechanics of alloys. For this we use the ring approximation[17] which yields the Warren-Cowley SRO parameters

$$\alpha_{\vec{q}}=\left[1+\frac{c(1-c)}{k_BT}V_{\vec{q}}^{eff}\right]^{-1}, \tag{8}$$

where the projection of the many-body contributions onto the effective two-body potential is described by

$$V_{\vec{q}}^{eff}=W_{\vec{q}}^{(2)}+N^{-1}\sum_{\vec{k}}\left\{\frac{(1-2c)\Delta V_{\vec{k},\vec{q}-\vec{k}}^{(3)}-W_{\vec{k}}^{(2)}}{1+c(1-c)W_{\vec{k}}^{(2)}/(k_BT)}\right.$$
$$\left.-\frac{[c(1-c)\Delta V_{\vec{k},\vec{q}-\vec{k}}^{(3)}]^2+2c(1-c)(1-2c)W_{\vec{k}}^{(2)}\Delta V_{\vec{k},\vec{q}-\vec{k}}^{(3)}+(1-2c)^2W_{\vec{k}}^{(2)}W_{\vec{q}-\vec{k}}^{(2)}}{2k_BT[1+c(1-c)W_{\vec{k}}^{(2)}/(k_B)T][1+c(1-c)W_{\vec{q}-\vec{k}}^{(2)}/(k_BT)]}\right\} \tag{9}$$

with $W_{\vec{q}}^{(2)}\equiv\mu+\tilde{V}_{\vec{q}}^{(2)}$ where μ is determined by the constraint $N^{-1}\Sigma_{\vec{q}}\alpha_{\vec{q}}=1$. Here the two- and three-body strain-induced contributions read

$$\Delta V_{\vec{q}}^{(2)}=-\sum_{ij}(\phi_{\vec{q}}^{(1)i})^{*}(G_{\vec{q}}^{ij})\phi_{\vec{q}}^{(1)j}, \tag{10}$$

$$\Delta V_{\vec{q}_1,\vec{q}_2}^{(3)}=6\sum_{ij}[(\phi_{\vec{q}_1}^{(1)i})^{*}(G_{\vec{q}_1}^{ij})\phi_{\vec{q}_2}^{(2)j}+(\phi_{\vec{q}_1}^{(2)i})^{*}(G_{\vec{q}_2}^{ij})\phi_{\vec{q}_2}^{(1)j}],$$

and the four-body contribution is neglected.[20] It directly follows from Eq. (9) that, in the absence of strain-induced interactions, i.e., for all $\Delta V^{(n)}=0$, $V_{\vec{q}}^{eff}$ is a function of concentration which is symmetrical with respect to the interchange of the components of the alloy (i.e., replacing c by $1-c$). By adding three-body strain-induced interactions, $V_{\vec{q}}^{eff}$ becomes an explicitly asymmetric function of concentration[21] (notice that the three-body contribution is small in the vicinity of the equiatomic composition). This also renders the SRO parameters $\alpha_{\vec{q}}$ asymmetric with respect to equiatomic concentration. It may also be the reason for the asymmetry in the concentration dependence of other structural and thermodynamic descriptions of alloys such as the phase diagram and the free energy.

When the denominator in Eq. (8) approaches zero as a function of concentration or temperature, the disordered state of the alloy loses its stability with respect to some ordered structures.[3,9] Therefore, the value of $V_{\vec{q}}^{eff}$ can be considered as a measure of stability of the alloy at a given temperature and concentration. At a wave vector $\vec{q}_o$ associated with such a structural instability the function $V_{\vec{q}}^{eff}$ then reaches its absolute minimum. In the high-temperature limit $(|\tilde{V}|\ll kT)V_{\vec{q}}^{eff}$ takes the simple, temperature-independent form

$$V_{\vec{q}}^{eff}=\tilde{V}_{\vec{q}}^{(2)}+N^{-1}(1-2c)\sum_{\vec{k}}\Delta V_{\vec{k},\vec{q}-\vec{k}}^{(3)}. \tag{11}$$

In this limit the contribution of the three-body strain-induced interaction in $V_{\vec{q}}^{eff}$ disappears for the equiatomic composition $c=0.5$.

In comparison with experimental results it is most important to reproduce the topology of the SRO parameters $\alpha_{\vec{q}}$. In order to demonstrate the potential of this approach we have applied our formalism to fcc alloys. In some of these systems the SRO maxima exhibit a splitting along certain crystallographic directions. In the following we show that the topology of the SRO is an explicit feature of strain-induced interactions. For the calculations the chemical interaction is assumed to be pairwise and short-range with nearest neighbors $V_1=100$ meV and next-nearest neighbors $V_2=-25$ meV resulting in an ordered ground state with $\{100\}$ concentration waves. The force constants $\{\phi^{(0)}\}$ were calculated within a microscopic model of the lattice dynamics[22] using experimental values for the elastic constants of $\mathrm{Cu_3Au}$. We introduce strain-induced two-body interactions by applying Kanzaki forces $\vec{\phi}_1^{(1)}$ and $\vec{\phi}_2^{(1)}$ in the first and second shells, respectively. The absolute value of the forces $\phi_1^{(1)}$ and $\phi_2^{(1)}$ are linked by the relation

$$L=\frac{1}{3(c_{11}+2c_{12})\Omega}\sum_{s}\sum_{\vec{R}_s}\vec{R}_s\vec{\phi}_{\vec{R}_s}^{(1)} \tag{12}$$

where c_{ij} are the elastic constants, Ω is the volume of the unit cell, and L is the lattice expansion coefficient. The summation is carried out over the first two atomic coordination shells $s=1,2$. The SRO $\alpha_{\vec{q}}$ is calculated at a temperature of $T=700$ K. Figure 1 shows four different types of SRO patterns $\alpha_{\vec{q}}$ in the $(h,k,0)$ plane as a function of the parameter $\phi_2^{(1)}/\phi_1^{(1)}$. The calculations demonstrate nicely that the topology of the SRO is strongly dependent on the ratio $\phi_2^{(1)}/\phi_1^{(1)}$.[23] Furthermore the obtained SRO distributions have in fact been observed in various fcc systems, such as, e.g., for the parameter range III which is $\mathrm{Cu_3Au}$-like. This demonstrates that strain-induced effects, in addition to well-established electronic ‘‘nesting’’ effects, can also contribute essentially to the formation of split peaks in SRO patterns. Other recent experimental and theoretical results show rather convincingly that the adequate description of the long-range part of the interaction in the alloy $Cu_{83}Mn_{17}$ (Ref. 24) requires only three force constants $\phi^{(0)}$ and one Kanzaki force $\phi_1^{(1)}$ in the first coordination shell. This demonstrates the rapid convergence of the results with the number of force constants in this case.

In conclusion, we have presented an explicit q-space method for the incorporation of strain-induced effects caused by atomic size mismatch into the statistical mechanics of alloys. It contributes via effective many-body strain-induced interactions $\{\Delta V^{(n)}\}$ which can be parametrized by a limited number of force parameters $\{\phi^{(n)}\}$ instead of an infinite set $\{V^{(n)}\}$ (e.g., in the case of IMC procedures, see also Ref. 22). Via the ring approximation the introduced three-body strain-induced interactions may naturally be used for calculating SRO and other structural and thermodynamic features of alloys with atomic size mismatch. Note that the numerical accuracy of our procedure for mapping the many-body strain-induced interactions onto two-body effective interactions is limited especially by the accuracy of the ring approximation which is known to decrease at low alloy concentration and in the vicinity of the phase transformation temperature.[17] For the semiphenomenological calculation of $V_{\vec{q}}^{eff}$ the number of parameters $\{\phi^{(n)}\}$ can be limited by using a convergence criterion for the calculated $\alpha_{\vec{q}}$ in comparison with corresponding experimental diffuse scattering data. The determination of the forces $\{\phi^{(n)}\}$ requires the successive introduction of force constants for more distant coordination shells until convergence is reached within the methodical error bars. The sets $\{V^{(n)}\}$ and $\{\phi^{(n)}\}$ can also be calculated from first principles. For the calculation of $\{V^{(n)}\}$ three approaches can be used, the Connolly-Williams method,[4] generalized perturbation methods,[25] and mean-field concentration functional theory.[26]

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[18] Chemical many-body interactions are neglected at this point in order to simplify the following line of reasoning. In principle, it is not difficult but cumbersome to incorporate them into the formalism.

[19] $n=1$ corresponds to the conventional Kanzaki forces; $n=2$ takes into account the coupling between pairs of atoms and the lattice distortions (nonlinear contribution, see also Ref. 16).

[20] Note, that the interaction potential in Eq. (10) must be normalized in order to exclude the self-interaction of atoms.

[21] An implicit asymmetry with respect to concentration may arise in the two-body strain-induced interaction in the case of concentration-dependent forces $\{\phi\}$.

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