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# Effect of static displacements of the host atoms on short-range order in the hydrogen subsystem of Ni–H solution

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## Abstract

The temperature and concentration dependences of the short-range order (SRO) parameters and their Fourier transform in H subsystem distributed on the octahedral interstices of fcc Ni are analysed, taking into account both direct (electrochemical) and indirect (strain-induced) contributions into the H–H interaction. The parameters of the electrochemical H–H interaction are estimated within the framework of the semiempirical approximation for atom–atom potentials. In order to calculate the energy parameters of the H–H strain-induced interaction, the Matsubara–Kanzaki–Krivoglaz lattice-statics method is applied. We demonstrate that, in the framework of the considered model, the strain-induced part mainly contributes to the total H–H interatomic mixing potential. For a description of the H–H SRO, the high-accuracy analytical (so-called ring) approximation is used. It is revealed that, for all considered values of the H concentration $c = 0.10$, 0.25 and 0.50, the H–H SRO Fourier transform is characterized by a strong peak at the origin of the reciprocal space when the temperature approaches its critical value. In real space, the H–H SRO parameters are characterized by a strong correlative attraction for the first coordination shell and demonstrate oscillations with an increase in the radius of the coordination shells.

## § 1. Introduction

Solid solutions of the H isotopes, namely hydrogen (H), deuterium (D) and tritium (T), in fcc metals such as $\alpha$-Ni, $\gamma$-Fe and Pd have been studied by many experimental research groups during the last 70 years (Gel'd *et al.* 1985, Ageev *et al.* 1987, Fukai 1993). The ability for H isotopes on octahedral interstices of some fcc metals to remain in the condition of a solid solution (i.e. in the disordered state) at high concentrations and low temperatures without the formation of precipitations of a hydride phase as well as the phenomenon of anomalous electrical resistance have been the starting points of extensive experimental researches. These researches were done by means of investigation of the diffuse neutron scattering intensity, the temperature dependence of the electrical resistance, the nuclear magnetic resonance (NMR) spectra and the internal friction in the denoted systems.

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One of the actual metal-physics problems under investigation consists of a study of the structural and energy state of H (D) atoms in a solid solution (i.e. in a disordered interstitial alloy) M–H and in the non-stoichiometric subhydrides $MH_c$ ($c \leqslant \frac{1}{2}$) of a crystalline interstitial phase on the basis of a metal M with the fcc crystal structure (e.g. M = Pd, α-Ni, γ-Fe, etc). In particular, it is important to reveal the correlation between the structural type, the electronic properties (e.g. the character of chemical bonds) and the other physical properties (e.g. the thermal stability) of such an alloy. However, there are still few systematic quantitative studies of the statistical–thermodynamic and structural properties of alloys in question.

The purpose of the present paper is to study the most favourable macroscopically homogeneous short-range ordered distributions of H atoms within the octahedral interstices of fcc Ni in a wide temperature–concentration region. For the obtained results to be experimentally adequate, it is important to take into consideration correctly the deviations in the actual structure of a solid solution from the ideal structure due to the interatomic correlations. So, for a description of the short-range order (SRO), the high-accuracy analytical (so-called ring) approximation (Chepulskii 1998, Chepulskii and Bugaev 1998a,b,c) is used (§ 2).

The H–H and H–M interactions are the major control factors of the behaviour of H atoms in an interstitial M–H alloy. The set of possible configurational types of H atom distribution around the M atoms depends on the character of such interactions. The achievement of the aim of the present paper is impossible without knowledge of the atomic interactions. Thus, the determination of such interactions is an actual problem. A number of ways (the so-called inverse methods) for this determination are based on the use of experimental data. However, the integral results of thermal measurements do not allow us to extract unequivocally information about the local interactions of the interstitial H atoms, if the corresponding energies are considered as fitting parameters within the framework of any configurational model. In some cases, there is scope for more detailed detection of the local environments of M atoms by H atoms inside a fcc M–H alloy, for example by neutron diffraction or NMR studies. However, until now, reliable estimations carried out on the basis of model analysis of the corresponding spectra are absent, even taking account only the nearest-neighbour H–H interactions.

In the present paper, the parameters of the direct electrochemical H–H interaction are estimated within the framework of the semiempirical approximation for atom–atom potentials (Mirskaya *et al.* 1974, Molodkin *et al.* 1992, Tatarenko and Tsinman 1992) (§ 3.1). We also take into account the indirect (strain-induced) contributions to the H–H interaction arising as a result of elastic relaxation of metal crystal lattice in the presence of interstitial H atoms within it. In order to calculate the energy parameters of the H–H strain-induced interaction, the Khachaturyan (1967) theory used within the framework of the Matsubara (1952)–Kanzaki (1957)–Krivoglaz (1958) lattice-statics method is applied (see § 3.2 and also the reviews by Krivoglaz (1969, 1996), Khachaturyan (1978, 1983), Peisl (1978) and Bugaev and Tatarenko (1989)).

The results obtained are presented in § 4.

## § 2. CONFIGURATIONAL DESCRIPTION

In the case of the disordered interstitial $NiH_c$ alloy, the nickel atoms are distributed at the sites of the fcc crystal lattice, and the H atoms are within the corresponding octahedral interstices. Such interstices form their own fcc crystal lattice. In the framework of the lattice gas model, neglecting the non-pair atomic interactions, the Hamiltonian H of the alloy in question can be written in the following form (for example Bugaev and Chepulskii (1995a,b))

$$H = N\nu_0 + \Phi \sum_{\mathbf{R}} C_{\mathbf{R}} + 1/2 \sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2}, \tag{1}$$

where $\nu_0$ is the energy per site of pure nickel, $\Phi$ is the potential of the injection of a H atom into an octahedral interstice, $V_{\mathbf{R}_1-\mathbf{R}_2}$ is the H–H (pair) mixing potential,

$$C_{\mathbf{R}} = \begin{cases} 1, & \text{if the octahedral interstice } \mathbf{R} \text{ is occupied by a H atom,} \\ 0, & \text{otherwise,} \end{cases} \tag{2}$$

and the summations on the radius-vectors $\mathbf{R}$, $\mathbf{R}_1$ and $\mathbf{R}_2$ are carried over all N octahedral interstices. It should be emphasized that equation (1) is valid only under the assumption that all crystal lattice octahedral interstices are symmetry equivalent, because only in this case is the injection potential independent on $\mathbf{R}$ and the mixing potential is a function of $\mathbf{R}_1 - \mathbf{R}_2$ (Bugaev and Chepulskii 1995a, b). Such a situation takes place in the disordered state of alloy, which is under investigation in the present paper.

In this work, we investigate the behaviour of the Warren (1969)–Cowley (1950) SRO parameters $\alpha_{\mathbf{R}}$:

$$\alpha_{\mathbf{R}_1-\mathbf{R}_2} = (\langle C_{\mathbf{R}_1} C_{\mathbf{R}_2} \rangle - c^2)[c(1-c)]^{-1}, \tag{3}$$

where $\langle \cdots \rangle$ means the statistical average,

$$c = \langle C_{\mathbf{R}} \rangle = \frac{N_H}{N} \tag{4}$$

is the concentration of the H atoms and $N_H$ is the total number of H atoms. In fact, $\alpha_{\mathbf{R}}$ is a normalized pair correlation function. The positive or negative values of $\alpha_{\mathbf{R}}$ correspond to the correlative attraction or repulsion respectively of impurity atoms separated by the vector $\mathbf{R}$.

Also, we study the behaviour of the Fourier transform $\alpha_{\mathbf{k}}$ of the SRO parameters:

$$\alpha_{\mathbf{k}} = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \exp(-i\mathbf{k}\cdot\mathbf{R}), \quad \alpha_{\mathbf{R}} = N^{-1} \sum_{\mathbf{q}} \alpha_{\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{R}). \tag{5}$$

In equation (5) and below, the summation on $\mathbf{q}$ is carried over all N points specified by the cyclic boundary conditions in the corresponding first Brillouin zone.

To calculate the SRO, we use the recently developed analytical (so-called ring) approximation (Chepulskii 1998, Chepulskii and Bugaev 1998a,b,c), in the framework of which

$$\alpha_{\mathbf{k}} = \left( I + \frac{c(1-c)}{k_B T} \tilde{W}^{\mathrm{eff}}_{\mathbf{k}} \right)^{-1}, \tag{6}$$

where

$$I = N^{-1} \sum_{\mathbf{q}} \left(1 + \frac{c(1-c)}{k_B T} \tilde{W}_{\mathbf{q}}\right)^{-1}, \tag{7}$$

$$\tilde{W}_{\mathbf{k}}^{\text{eff}} = \tilde{W}_{\mathbf{k}} - \frac{(1-2c)^2}{2k_B T} N^{-1} \sum_{\mathbf{q}} \tilde{W}_{\mathbf{q}} \tilde{W}_{\mathbf{k}-\mathbf{q}} \left(1 + \frac{c(1-c)}{k_B T} \tilde{W}_{\mathbf{q}}\right)^{-1} \times \left(1 + \frac{c(1-c)}{k_B T} \tilde{W}_{\mathbf{k}-\mathbf{q}}\right)^{-1}, \tag{8}$$

$$\tilde{W}_{\mathbf{k}} = \tilde{V}_{\mathbf{k}} + \mu, \tag{9}$$

$\tilde{V}_{\mathbf{k}}$ is the Fourier transform of the mixing potential $V_{\mathbf{R}}$ given by

$$\tilde{V}_{\mathbf{k}} = \sum_{\mathbf{R}} V_{\mathbf{R}} \exp(-i\mathbf{k}\cdot \mathbf{R}), \quad V_{\mathbf{R}} = N^{-1} \sum_{\mathbf{R}} \tilde{V}_{\mathbf{q}} \exp(i\mathbf{q}\cdot \mathbf{R}), \tag{10}$$

$\mu$ is the quantity to be found from

$$N^{-1} \sum_{\mathbf{q}} \alpha_{\mathbf{q}} = 1, \tag{11}$$

T is the absolute temperature and $k_B$ is the Boltzmann constant. The ring approximation was used in the context of a modified thermodynamic perturbation theory within the grand-canonical ensemble by means of the thermodynamic fluctuation method; the inverse effective number of atoms interacting with one fixed atom was used as a small parameter of expansion.

This choice of the ring approximation is due to the optimal combination of the high numerical accuracy of the results obtained within this approximation and its comparative analytical simplicity. For example, within the ring approximation, it is possible to describe the temperature dependence of the position in reciprocal space of the maximum of the SRO Fourier transform even for temperature-independent atomic interactions. Also, within the ring approximation, the effective radius of atomic interactions in an alloy is not limited *a priori* (in contrast with the widely used Monte Carlo and cluster variation methods), because only the Fourier transform of the mixing potential appears in the corresponding expressions (6)–(11). Moreover, it was revealed (Chepulskii and Bugaev 1998b) that the numerical accuracy of this approximation increases with increase in the effective radius. Thus, the ring approximation is suitable for a description of actual alloys with a long-range character of atomic interactions caused, for example, by strain-induced effects (see § 3.2).

The other important advantage of the ring approximation is the ability to calculate the Fourier transform of the SRO parameters directly, without neglecting the values of these parameters for coordination shells with large radii, which is done for the Monte Carlo and cluster variation methods. This is especially important in the case of alloys with long-range atomic interactions and/or of alloys whose temperature is closed to the order–disorder phase transformation temperature (owing to the corresponding increase in the effective radius of interatomic spatial correlations). Chepulskii (1999) revealed that the above-mentioned neglect may result in a wrong description of the SRO Fourier transform in the vicinity of the origin of the reciprocal space. Within the ring approximation, through the integration of the SRO Fourier transform over the first Brillouin zone, it is possible to calculate the SRO parameter for an *arbitrary* coordination shell as well.

## § 3. CALCULATION OF THE MIXING POTENTIAL

In the present work we suppose that the direct (electrochemical) and indirect (strain-induced) H–H atomic interactions give the dominating contributions $V_{\mathbf{R}}^{el}$ and $V_{\mathbf{R}}^{str}$ respectively to the total interatomic mixing potential:

$$V_{\mathbf{R}} = V_{\mathbf{R}}^{el} + V_{\mathbf{R}}^{str}. \tag{12}$$

Accordingly,

$$\tilde{V}_{\mathbf{k}} = \tilde{V}_{\mathbf{k}}^{el} + \tilde{V}_{\mathbf{k}}^{str}, \tag{13}$$

where the Fourier transforms $\tilde{V}_{\mathbf{k}}^{el}$ and $\tilde{V}_{\mathbf{k}}^{str}$ are determined in analogy with equation (10).

### 3.1. *Direct (electrochemical) contribution*

The direct (electrochemical) interactions between the impurity interstitials inside the host crystal are created by ‘direct’ interactions of their electrical charges, under conditions of not only their screening by the available non-bonded charge carriers but also of the operation of the Pauli exclusion principle in forming a distribution of identical particles over the states. For the approximate description of such interactions between H atoms inside fcc Ni, we shall assume that the H atoms on interstices interact directly between themselves almost in the same way as in the isolated molecules containing these atoms (Molodkin *et al.* 1992, Tatarenko and Tsinman 1992). The corresponding potential is chosen in the following form (Khachaturyan 1983):

$$V_{\mathbf{R}}^{el} = \begin{cases} \varphi_{r=|\mathbf{R}|} & \text{at } \mathbf{R} \neq \mathbf{0}, \\ 0 & \text{at } \mathbf{R} = \mathbf{0}, \end{cases} \tag{14}$$

where

$$\varphi_r = A \exp(-Br) - \frac{C}{r^6}, \tag{15}$$

and A, B, and C are positive parameters determined through the independent experimental data. The first term in equation (15) corresponds to the short-range forces of a ‘contact’ repulsion between ‘overlapped’ filled electronic shells around the nuclei of H atoms, and the second term to the weak fluctuation polarization forces of a dispersion attraction between the cores of H ions. It is supposed that the electrostatic (Coulomb) ionic H–H interaction screened by free charge carriers in fcc Ni is comparatively small and its contribution may be neglected.

In the present study, we use the following values of the parameters of H–H electrochemical potential (15), which have been determined by Mirskaya *et al.* (1974): $A = 212.628\,\mathrm{eV}$, $B = 4.29\,\mathrm{\AA}^{-1}$ and $C = 1.258\,41\,\mathrm{eV\,\AA}^6$ ($\varphi_r$ is determined in electronvolts, and r in ångströms).

### 3.2. *Indirect (strain-induced) contribution*

The indirect (strain-induced) contribution to the mixing potential attributed to the elastic distortion fields induced by H atoms in a Ni crystal was calculated independently within the Khachaturyan (1967) theory based on the microscopic Matsubara (1952)–Kanzaki (1957)–Krivoglaz (1958) lattice-statics method. This approach allows us to take into account the anisotropy and discrete (atomic) structure of a crystal lattice in contrast with the macroscopic continuum theory of elasticity (Khachaturyan 1978, 1983, Peisl 1978, Dietrich and Wagner 1979, Bugaev and Tatarenko 1989, Krivoglaz 1996). Within this theory, for the fcc Ni–H alloy, we have

$$\tilde{V}^{\mathrm{str}}_{\mathbf{k}\neq\mathbf{0}} = -\sum_{\mathrm{i,j=x,y,z}} \tilde{F}^{\mathrm{i}\,*}_{\mathbf{k}} G^{\mathrm{ij}}_{\mathbf{k}} \tilde{F}^{\,\mathrm{j}}_{\mathbf{k}} + Q, \tag{16}$$

$$\tilde{V}^{\mathrm{str}}_{\mathbf{k}=\mathbf{0}} = -3\nu(C_{11} + 2C_{12})L^2 + Q, \tag{17}$$

where

$$Q = N^{-1} \sum_{\mathbf{k}\neq\mathbf{0}} \sum_{\mathrm{i,j=x,y,z}} \tilde{F}^{\mathrm{i}\,*}_{\mathbf{k}} G^{\mathrm{ij}}_{\mathbf{k}} \tilde{F}^{\mathrm{j}}_{\mathbf{k}}, \tag{18}$$

$\tilde{\mathbf{F}}_{\mathbf{k}}$ is the Fourier transform of Kanzaki forces (Bugaev and Tatarenko 1989) given by

$$\tilde{\mathbf{F}}_{\mathbf{k}} = -i\,\frac{a^2}{2}\,(C_{11} + 2C_{12})L \left\| \begin{matrix} \sin\left(\dfrac{k_x a}{2}\right) \\ \sin\left(\dfrac{k_y a}{2}\right) \\ \sin\left(\dfrac{k_z a}{2}\right) \end{matrix} \right\| \exp\left[-i(k_x + k_y + k_z)\,\frac{a}{2}\right], \tag{19}$$

$$\nu = \frac{a^3}{4} \tag{20}$$

is the volume of the unit cell, a is the lattice parameter, $C_{ij}$ are the elastic moduli of fcc Ni

$$L = \frac{1}{a}\frac{\partial a}{\partial c}\bigg|_{c=0}, \tag{21}$$

$$\mathbf{G}_{\mathbf{k}} = [\tilde{\mathbf{A}}_{\mathbf{k}}]^{-1}, \tag{22}$$

and $\tilde{\mathbf{A}}_{\mathbf{k}}$ is the Fourier transform of the dynamical matrix. We use the following expressions for the elements of $\tilde{\mathbf{A}}_{\mathbf{k}}$, derived by Kushwaha and Kushwaha (1978):

$$\begin{aligned} \tilde{A}^{xx}_{\mathbf{k}} = {} & \tfrac{1}{4} M\omega_L^2 \left[2 - \cos\left(\frac{ak_x}{2}\right)\cos\left(\frac{ak_y}{2}\right) - \cos\left(\frac{ak_x}{2}\right)\cos\left(\frac{ak_z}{2}\right)\right] \\ & + \tfrac{1}{4} M(2\omega_T^2 - \omega_L^2)\left[1 - \cos\left(\frac{ak_y}{2}\right)\cos\left(\frac{ak_z}{2}\right)\right] \\ & + \tfrac{1}{8}(4aC_{11} - M\omega_L^2)[1 - \cos(ak_x)] \\ & + \tfrac{1}{8}(4aC_{44} - M\omega_T^2)[2 - \cos(ak_y) - \cos(ak_z)], \end{aligned} \tag{23}$$

$$\tilde{A}^{xy}_{\mathbf{k}} = a(C_{12} + C_{44})\sin\left(\frac{ak_x}{2}\right)\sin\left(\frac{ak_y}{2}\right), \tag{24}$$

where M is the mass of the Ni atom, $\omega_L$ and $\omega_T$ are the cyclic longitudinal and transverse frequencies respectively of the phonons. In all the above expressions $k_x$, $k_y$ and $k_z$ are the Cartesian coordinates of the wave-vector in the first Brillouin zone of the fcc lattice. The other elements of the matrix $\tilde{A}_k$ may be obtained from equations (23) and (24) by cyclic permutation of the Cartesian indices x, y and z.

For the calculations, we used the following values: $M = 9.748 \times 10^{-26}$ kg, $a = 3.52$ Å, $L = 0.0768$ (Bauer *et al.* 1968, Baranowski *et al.* 1971, Peisl 1978), $\omega_L = 53.72 \, \mathrm{Trad\,s^{-1}}, \omega_T = 39.40 \, \mathrm{Trad\,s^{-1}}$ (Birgeneau *et al.* 1964). For the values of the temperature-dependent elastic moduli of Ni, those obtained by Simmons (1965) were used. The concentration interval at issue (see below) was so chosen that the Vegard rule is fulfilled well (Bauer *et al.* 1968, Baranowski *et al.* 1971, Peisl 1978) as it is a necessary condition of applicability of the Matsubara–Kanzaki–Krivoglaz lattice-statics method (for example Krivoglaz (1958, 1969, 1996) and Khachaturyan (1967, 1983)).

## §4. RESULTS

In figures 1 and 2 as well as in table 1, the results of the performed calculations are presented. Namely, in figure 1, the values for the first 11 coordination shells of the SRO parameters obtained within the ring approximation (6)–(11) and of the total mixing potential as well as the direct (electrochemical) and indirect (strain-induced) contributions to it are shown in the case of the $NiH_{0.1}$ alloy at T = 500 K. In figure 2,

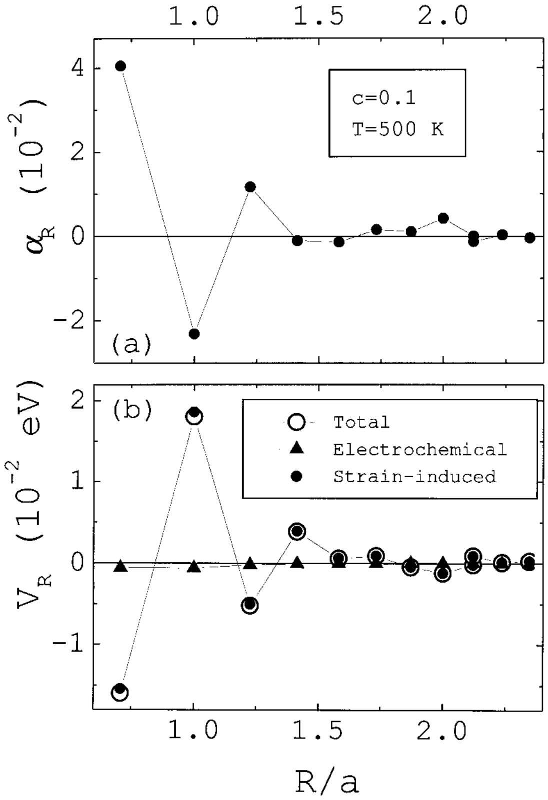

Figure 1. In the case of fcc $NiH_{0.1}$ alloy at $T = 500$ K, the values for the first 11 coordination shells (*a*) of the SRO parameters obtained within the ring approximation (6)–(11) and (*b*) of the total mixing potential as well as the direct (electrochemical) and indirect (strain-induced) contributions into it.

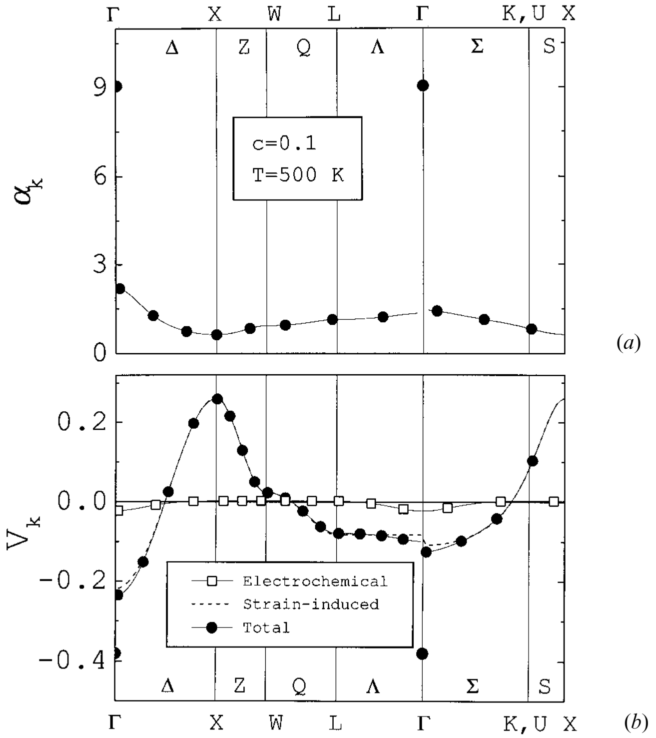

Figure 2. In the case of fcc $NiH_{0.1}$ alloy at $T = 500$ K, the dependences on the wave-vector along the high-symmetry directions (Bradley and Cracknell 1972) within the corresponding first Brillouin zone (*a*) of the Fourier transform of the SRO parameters calculated in the framework of the ring approximation (6)–(11) and (*b*) of the Fourier transforms of the total mixing potential as well as of the direct (electrochemical) and indirect (strain-induced) contributions into it.

in the same case, are presented the dependences on the wave-vector along the high-symmetry directions (Bradley and Cracknell 1972) within the corresponding first Brillouin zone of the Fourier transform of the SRO parameters calculated within the ring approximation and of the Fourier transforms of the total mixing potential as well as of the direct (electrochemical) and indirect (strain-induced) contributions to it. In table 1, the values of the critical temperature $T_c$ of the absolute loss of stability of the disordered state in the cases of three considered values of the H atom concentration ($c = 0.10$, 0.25 and 0.50) in Ni–H alloy are listed.

Table 1. The values of the critical temperature $T_c$ of the absolute loss of stability of the disordered state for three values of the H atom concentration in fcc Ni–H alloy.

| c | $T_c$ (K) |
|---|---|
| 0.10 | 450(50) |
| 0.25 | 850(50) |
| 0.50 | 1050(50) |

It should be emphasized that, in both figure 1 and figure 2, the corresponding temperature was chosen to be closed to the critical temperature of the absolute loss of stability of the disordered state, because in this case the information on the long-range order (LRO) superstructure appearing as a result of order–disorder phase transformation may be extracted through the data (in both direct space and reciprocal space) on the SRO. Namely, when the temperature approaches its critical value, the positions of the maxima of the Fourier transform of the SRO parameters correspond to the instability wave-vectors characterizing such a LRO superstructure (Khachaturyan 1978, 1983). In direct space, in the critical region, the values of the SRO parameters for the first-nearest coordination shells within the correlation radius give information about the spatial distribution of the impurity atoms in the future (i.e. for temperatures decreasing below the critical temperature) LRO superstructure.

Note that the results on the SRO corresponding to the concentrations $c = 0.25$ and $c = 0.50$ are not presented, because they are qualitatively very similar to those corresponding to the concentration $c = 0.10$ which are shown in figures 1 and 2. Note also that the concentration and temperature dependences of the direct (electrochemical) and indirect (strain-induced) contributions to the total mixing potential are rather weak.

From figures 1 and 2 and table 1, one may conclude the following. The major contribution to the total mixing potential is from the strain-induced part. Note that the obtained results concerning the H–H mixing potential are in agreement with those obtained by Blanter (1999). It should be emphasized that the non-analytical nature of $\alpha_{\mathbf{k}}$ at the origin of reciprocal space (i.e. at the $\Gamma$ point) is attributed to the same non-analytical nature of $\tilde{V}^{\text{str}}_{\mathbf{k}}$ (Molodkin *et al.* 1992, Tatarenko and Tsinman 1992, Zunger 1994).

The high-temperature behaviour of the SRO may be obtained by expanding equation (6) in a series in powers of the quantity $V_{\mathbf{R}}/(k_B T)$. As a result, we have, to first order,

$$\alpha_{\mathbf{R}} = -\frac{c(1-c)}{k_B T} V_{\mathbf{R}}. \tag{25}$$

Thus, at high temperatures, the topologies of the SRO in both real space and reciprocal space ‘mirror’ the corresponding topologies of the mixing potential. In real space, the ‘mirror’ topology means the opposite sign, whereas in reciprocal space it means the presence of a maximum instead of a minimum and vice versa. In principle (for example Chepulskii and Bugaev (1998c), Chepulskii (1999)), this ‘mirror’ topology may be violated on decrease in the temperature. However, this is not the case with the Ni–H interstitial alloy. Note that, on decrease in the temperature, $\alpha_{\mathbf{k}}$ is characterized by an increase in the intensity at the $\Gamma$ point and $\alpha_{\mathbf{R}}$ demonstrates a decrease in the correlative repulsion for the fourth coordination shell.

In view of the LRO, the maximum of $\alpha_{\mathbf{k}}$ at the $\Gamma$ point of reciprocal space corresponds to the decomposition (segregation) reaction. The strong peak of the function $\alpha_{\mathbf{k}}$ at this point in the critical region (see figure 2 (*a*)) indicates the occurrence of a decomposition reaction below the temperature of the order–disorder phase transformation. The same conclusion follows from the strong correlative attraction for the first coordination shell (see figure 1 (*a*)). However, the oscillation character of the function $\alpha_{\mathbf{R}}$ demonstrates also the possibility of an ordering reaction at the order–disorder and/or order–order phase transformations.

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