Effective interactions and atomic ordering in Ni-rich Ni-Re alloys

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Interatomic interactions and ordering in fcc Ni-rich Ni-Re alloys are studied by means of first-principles methods combined with statistical mechanics simulations based on the Ising Hamiltonian. First-principles calculations are employed to obtain effective chemical and strain-induced interactions, as well as ordering energies and enthalpies of formation of random and ordered Ni-Re alloys. Based on the nonmagnetic enthalpies of formation, we speculate that the type of ordering can be different in alloys with Re content less than 10 at.%. We demonstrate that effective chemical interactions in this system are quite sensitive to the alloy composition, atomic volume, and magnetic state. In statistical thermodynamic simulations, we have used renormalized interactions, which correctly reproduce ordering energies obtained in the direct total energy calculations. Monte Carlo simulations for Ni_{0.91}Re_{0.09} alloy show that there exists a strong ordering tendency of the $(1\frac{1}{2}0)$ type leading to precipitation of the D1_a ordered structure at about 940 K. Our results for the atomic short-range order indicate, however, that the presently applied theory overestimates the strength of the ordering tendency compared to that observed in the experiment.

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I. INTRODUCTION

Re produces an outstanding and unique strengthening effect on single-crystal Ni-based superalloys. In fact, generations of Ni-based superalloys are usually grouped by their Re content: the first generation alloys have no Re, the second and third generation alloys contain 2–3 wt.% and 5–6 wt.% Re, respectively [1]. Owing to the fundamental importance of Re to Ni-based single-crystal superalloys, intensive investigations of the effect of Re were performed [2–10]. It has been found that Re atoms strongly partition to the γ phase [4,5,10], slow down γ' precipitate coarsening kinetics [6], and modify the misfit between the γ matrix and γ' precipitates [2,3]. While the effect of Re additions on the Ni-based superalloys is well documented [7]. Its origin is still under debate. Moreover, the existing information about its distribution in the γ matrix is highly controversial [8–10].

Scanning transmission electron microscopy and energydispersive x-ray spectroscopy were utilized to investigate distribution of Re and W in the second-generation superalloy DD6 [10]. It was reported that Re and W were enriching in the γ phase close to the γ/γ' interface after creep tests which were conducted at 1100 °C under stress 140 MPa for 12 h with the stress axis parallel to the [001] orientation. Mottura *et al.* studied the local atomic structure around the solute atoms in a Ni-Re binary alloy by the extended x-ray absorption fine structure (EXAFS) technique [8] and found that Re atoms were surrounded by Ni atoms only. They also investigated the distribution of Re in binary Ni-Re alloys and the CMSX-4 superalloy using the atom probe tomography (APT) and found no evidence for Re clustering [9].

According to the recent Ni-Re phase diagram [11], there is a large miscibility gap in this system with a peritectic reaction at 1893 K and a peritectic composition of 17.4 at.% Re in the Ni-rich part. On cooling below the peritectic temperature, the solubility of Re in Ni decreases to 12.2 at.% Re at 1073 K, and the solubility of Ni in Re is 14.3 at.% Ni, changing little with temperature. Due to this large miscibility gap in the Ni-Re phase diagram, it has been suggested that Re atoms conglomerate into small clusters in the Ni matrix creating efficient obstacles against dislocation motion [12,13].

Such a clustering of Re has been reported by Blavette *et al.* [12] for Re-modified versions of CMSX-2 and PWA 1480 superalloys on the basis of the APT and by Wanderka *et al.* [4] for the second-generation alloy CMSX-4, also by Rusing *et al.* [14] for a model Ni-Al-Ta-Re superalloy. They found a possible formation of nanometer-size Re clusters in the γ matrix separated by about 20 nm [14], which acted as obstacles against dislocation motion in the γ matrix [4,12].

At the same time, the most recent theoretical and experimental investigations indicate the existence of pronounced ordering in Ni-rich alloys [15–17]. In particular, Levy et al. [15] conducted high-throughput density functional theory (DFT) calculations for Re binary alloys, and predicted that two compounds, D1_a-Ni₄Re and DO₁₉-NiRe₃, should be stable at low temperature in the Ni-Re system. Mottura et al. [16] calculated the binding energies of Re-Re pairs and the stability of small Re clusters in Ni using DFT, and found strong repulsion between the Re-Re nearest-neighbor pair while Re clusters were unstable. The repulsion between Re-Re pairs was rapidly reduced with the distance, so they suggested that solute atoms should be isolated, which was equivalent to an atomic ordering. A further investigation was done by Maisel et al. [17] theoretically and experimentally for the Ni-Re binary system up to 30 at.% Re. They also found that the $D1_a$ -Ni₄Re phase was stable in this concentration range. Combining with Monte Carlo simulations and the EXAFS experiments, they showed that the D1_a-Ni₄Re was most likely to precipitate in Ni_{96.62}Re_{3.38} at about 930 K [17].

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Unfortunately, little is known about the atomic shortrange order (SRO) in Ni-rich Ni-Re alloys. There is only one experimental investigation by Schönfeld *et al.* using a diffuse x-ray scattering technique for Ni-9.4 at.% Re alloy composition at 873 K [18]. According to their results, the α_{110} Warren-Cowley SRO parameter is negative, which indicates an ordering tendency; however, it is rather small and the authors could not establish the type of the local order [18]. Although there exist several first-principles calculations of the Ni-Re system [15–17], they do not shed light on the effective interactions governing the atomic configuration and to great extent the thermodynamics of this system. At the same time, in the two latest investigations [17,19], the ferromagnetic (FM) results were used to determine phase equilibria at temperatures much higher than the Curie temperature of Ni.

Therefore, the main aim of this work is to investigate the effective interactions in the Ni-Re system, in particular their dependence on different internal and external parameters. We consider various types of effective cluster interactions, demonstrating their nontrivial behavior, which show up in their dependence on volume, concentration, temperature, and magnetic state. At the end, we perform Monte Carlo statistical thermodynamic simulations of high-temperature ordering in Ni-Re alloys and compare our results with existing theoretical [17] and experimental data [18]. Our analysis of the phase stability is based on the consideration of the interatomic interactions, ordering energies, and enthalpies of formation of random and ordered alloys.

II. METHODOLOGY

A. Effective interactions

In this paper, we will consider two types of effective cluster interactions. First of all, we calculate fully renormalized interactions, which describe the interactions of Re atoms in Ni in the dilute limit. They can be obtained from a set of the total energies of supercells where positions in a given cluster are occupied by Ni and Re atoms in different configurations. Such an *n*-site, or *n*-atom, interaction for a given cluster *s* is determined as [20]

$$W_s^{(n)} = \sum_{t \in \text{Re-even}} E_t - \sum_{t \in \text{Re-odd}} E_t, \quad (1)$$

where the first sum is over all the configurations with an even number of Re atoms in the cluster and the other one with an odd number of Re atoms. For instance, the fully renormalized Re-Re pair interaction at the *p*th coordination shell is

$$W_p^{(2)} = E_p^{\text{ReRe}} - 2E_{\text{imp}}^{\text{Re}} + E_{\text{Ni}},$$
 (2)

where E_p^{ReRe} is the total energy of a supercell with two Re atoms at the *p*th coordination shell, $E_{\text{imp}}^{\text{Re}}$ the total energy of the supercell with one Re atom, and E_{Ni} the total energy of pure Ni.

Let us note that these interactions are truly pair interactions only in the case when either there are only two Re atoms in the whole system or multisite interactions are negligible. Neither of these cases is relevant for real Ni-Re alloys; nevertheless, these interactions can be used for a qualitative analysis of stability. This is so, since they are connected with the effective interactions of the concentration-independent (CI) Ising Hamiltonian

$$H^{\text{CI}} = \frac{1}{2^2 2} \sum_{p} \widetilde{V}_p^{(2)} \sum_{i,j \in p} \sigma_i \sigma_j + \frac{1}{2^3 3} \sum_{t} \widetilde{V}_t^{(3)} \sum_{i,j,k \in t} \sigma_i \sigma_j \sigma_k$$
$$+ \frac{1}{2^4 4} \sum_{q} \widetilde{V}_q^{(4)} \sum_{i,j,k,l \in q} \sigma_i \sigma_j \sigma_k \sigma_l + \cdots$$
(3)

in the following way:

$$W_p^{(2)} = \widetilde{V}_p^{(2)} + \sum_t D_t^{(3)} \widetilde{V}_t^{(3)} + \sum_q D_q^{(4)} \widetilde{V}_q^{(4)} + \cdots$$
(4)

or in general

$$W_p^{(n)} = \widetilde{V}_p^{(n)} + \sum_c D_c^{(n+1)} \widetilde{V}_c^{(n+1)} + \cdots,$$
 (5)

where $D_s^{(n)}$ are the coefficients, which depend on the geometry of the lattice. Thus the differences between the fully renormalized multisite interactions and the usual effective cluster interactions are given by higher-order effective cluster interactions.

In the statistical thermodynamic simulations, we will use concentration-dependent (CD) effective cluster interactions (ECIs), which are parameters of the following Hamiltonian:

$$H^{\rm CD} = \frac{1}{2} \sum_{p} V_p^{(2)} \sum_{i,j \in p} \delta c_i \delta c_j + \frac{1}{3} \sum_{t} V_t^{(3)} \sum_{i,j,k \in t} \delta c_i \delta c_j \delta c_k + \frac{1}{4} \sum_{q} V_q^{(4)} \sum_{i,j,k,l \in q} \delta c_i \delta c_j \delta c_k \delta c_l.$$
(6)

Here, $V_s^{(n)}$ is the *n*-site effective interaction for the cluster of an *s* type, which depends on the alloy composition, lattice constant, and magnetic state; δc_i are the concentration fluctuations at sites *i*: $\delta c_i = c_i - c$, where c_i is the occupation number at site *i*, taking on values 1 or 0 if the site *i* is occupied by the Re or Ni atom, respectively, and *c* is the concentration of Re. Again, there is a mathematically well-established connection between \tilde{V} and V [21,22], and in particular, $V_p^{(2)} = \tilde{V}_p^{(2)} = W_p^{(2)}$ if multisite interactions are negligible. However, in real systems, and especially in the case of the Ni-Re system, these interactions are disconnected by complicated physics of interatomic bonding.

Moreover, in Ni-Re alloys, the ECIs are implicitly temperature dependent in a quite complicated way since the magnetic state depends on the alloy configuration and composition. Another source of the temperature dependence is a thermal lattice expansion, which should also play an important role in this system as will be shown below.

The ordering energy, i.e., the difference of the energies of the ordered and random alloys for a fixed lattice constant in terms of the ECI, can be expressed as

$$\Delta E_{\rm ord} = \frac{1}{2}c(1-c)\sum_{p} z_{p}V_{p}^{(2)}\alpha_{p} + \text{h.o.t.},$$
(7)

where the first term is the contribution from effective pair interactions (EPIs) expressed using Warren-Cowley SRO parameters [23,24] $\alpha_p = (\langle c_i c_j \rangle - c^2)[c(1-c)]^{-1}$ and coordination

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number z_p for the *p*th coordination shell, and h.o.t. stands for higher-order terms due to multisite interactions.

B. First-principles methods

1. Green's function exact muffin-tin orbital method

Several *ab initio* codes have been used in this work for the total energy and effective interaction calculations. In order to get the concentration-dependent ECIs and provide a model description of random and paramagnetic alloys, the Green's function exact muffin-tin orbitals (EMTO) method [25–28] has been used. The electronic structures of chemically and magnetically random alloys were obtained in the coherent potential approximation (CPA) [29,30]. The calculations have been done by the Lyngby version of the code [31].

The screened generalized perturbation method (SGPM) [32,33] as implemented in the Lyngby version of the EMTO code has been used in the ECI calculations. The intersite screening constants for the screened Coulomb interactions [32] contributing to the pair interactions have been determined in the nonmagnetic calculations of the Ni_{0.9}Re_{0.1} random alloy using the locally self-consistent Green's function (ELSGF) method within the EMTO technique [34,35]. The ELSGF method accurately accounts for local environment effects in alloys and it has been also used to calculate the total energies of random Ni-Re alloys.

The total energies have been obtained in the generalized gradient approximation (GGA) for the exchange-correlation energy using the PBE functional [36]. All the self-consistent EMTO-CPA and ELSGF calculations were performed by using an orbital momentum cutoff of $l_{\text{max}} = 3$ for partial waves. The integration over the Brillouin zone was performed using a $28 \times 28 \times 28$ grid of k points determined according to the Monkhorst-Pack scheme [37] in all the EMTO-CPA and ELSGF self-consistent calculations except for the SGPM interactions. In the later case, the Monkhorst-Pack grid was $38 \times 38 \times 38$.

The paramagnetic state has been modeled by the disordered local moment (DLM) spin configuration [38,39] with longitudinal spin fluctuations (LSFs) [40,41]. In order to simplify calculations, we have used an approximate expression for the entropy of the LSFs, $S^{LSF} = 3 \ln(m_i)$ [41], where m_i is the local magnetic moment. This expression corresponds to the classical high-temperature limit for the quadratic form of the LSF energy, which is a reasonable approximation for Ni [40].

2. Projector augmented wave method calculations

Although the size mismatch of Ni and Re atoms is rather moderate, about 10%, local lattice relaxations play an important role in alloy energetics [42]. In order to take the local relaxation effects into account, we have also used the projector augmented wave (PAW) method [43,44] as implemented in the Vienna *ab initio* simulation package (VASP) [45,46] in the calculations of relaxation energies. All the calculations have been performed using the PBE form of the GGA [36]. The Ni pseudopotential with ten valence electrons as updated on 2 August 2007 and the Re pseudopotential updated on 17 January 2003 with seven valence electrons have been employed [44]. Fully renormalized and strain-induced interactions have been determined in the dilute limit using a $4 \times 4 \times 4$ supercell of the initial cubic 4-atom fcc unit cell in the ferromagnetic (FM) and the nonmagnetic (NM) states. In order to keep the cubic symmetry of the underlying fcc lattice, which is preserved on average in real alloys, the translation vectors of supercells have been fixed. The integration over the Brillouin zone has been done using the $4 \times 4 \times 4$ Monkhorst-Pack grid [37]. Due to the different cell sizes of random and ordered structures, we have chosen different *k*-point grids in our calculations following the Monkhorst-Pack scheme using equivalent *k*-point densities in order to avoid systematic errors.

In the calculations of the formation enthalpies of Ni-Re alloys, all the structures for ordered alloys have been fully relaxed, while in the case of random alloys, the shape of the supercell has been fixed. Other details for all of the VASP-PAW calculations are as follows. The convergence criteria for the total energy was 10^{-5} eV/cell while for forces during structural optimization was 9×10^{-3} eV/Å. Plane waves up to 350 eV were included in the PAW calculations.

The electronic structure and total energies of random Ni-Re alloys in the PAW calculations have been obtained by using supercells with different sizes. A Ni_{0.9375}Re_{0.0625} random alloy was modeled by a 144-atom supercell formed by $3 \times 3 \times 4$ translations of the 4-atom fcc cubic cell $[3 \times 3 \times 4(\times 4)]$, Ni_{0.89}Re_{0.11} by a 216-atom supercell $[6 \times 6 \times 6(\times 1)]$, Ni_{0.89}Re_{0.21} by a 240-atom supercell $[3 \times 4 \times 5(\times 4)]$, Ni_{0.75}Re_{0.25} by a 256-atom supercell $[4 \times 4 \times 4(\times 4)]$, and Ni_{0.67}Re_{0.33} by a 192-atom supercell $[3 \times 4 \times 4(\times 4)]$ with distribution of alloy components, which satisfies the randomness condition for the first eight pair correlation functions in all the cases [34,47]. The Monkhorst-Pack grids for the supercells Ni_{0.9375}Re_{0.25}, Ni_{0.89}Re_{0.11}, Ni_{0.8}Re_{0.2}, Ni_{0.75}Re_{0.25}, and Ni_{0.67}Re_{0.33} are $5 \times 5 \times 4$, $4 \times 4 \times 4$, $5 \times 4 \times 3$, $4 \times 4 \times 4$, and $5 \times 4 \times 4$, respectively.

III. GROUND-STATE PROPERTIES OF Ni-Re ALLOYS

Ni is an itinerant ferromagnet with magnetic moment of about 0.6 μ_B in the ground state [40,48,49]. The addition of Re strongly suppresses spin polarization in Ni-Re alloys at 0 K, which become nonmagnetic when Re concentration exceeds 12 at.%. [42,50]. In Fig. 1, we show the magnetic moment of Ni in Ni-Re random alloys obtained in the EMTO-CPA calculations together with the existing experimental data [50]. At finite temperatures, however, Ni can acquire a finite local magnetic moment (in a simple static one-electron picture given by the local spin-density approximation or GGA) due to the LSF, which will be discussed latter.

The lattice parameters of Ni-Re alloys have been previously obtained experimentally and theoretically in a number of investigations [11,51–54]. In Fig. 2, we show our GGA-PBE results for Ni-rich random alloys obtained in the EMTO-CPA and supercell VASP-PAW calculations. In the NM state, our calculated lattice parameters of pure Ni are 3.520 Å and 3.508 Å in the EMTO-CPA and VASP-PAW calculations, respectively, while in the FM state, the lattice parameter of Ni is 3.527 Å in the EMTO-CPA and 3.515 Å in the VASP-PAW calculations. Note that the experimental 0 K lattice parameter of Ni is about 3.515 Å [55], and the expected DFT value



FIG. 1. Magnetic moment of Ni as a function of Re concentration in Ni-Re alloys. The calculations have been done in the FM state at a lattice constant of 3.515 Å. The experimental data are taken from Ref. [50].

without a contribution from zero-point vibrations is 3.508 Å [56].

This means that the EMTO-CPA method somewhat overestimates the equilibrium lattice constant of Ni (if the VASP-PAW results are accurate in the DFT sense). The theoretical concentration dependence of the lattice parameters at 0 K in Ni-Re alloys is slightly steeper than the experimental one at room temperature (RT) [11,51,53]. The latter is most probably related to the fact that GGA noticeably overestimates the equilibrium volume of 5d metals [57–59]. As will be clear from discussion below, it can affect to some extent the concentration dependence of the formation enthalpies.



FIG. 2. Calculated 0 K lattice parameters of Ni-Re random alloys without contribution from local atomic relaxations. The EMTO-CPA calculations have been done in the FM and NM states. The VASP-PAW calculations have been done in the NM state using random Ni-Re alloys modeled by supercells of different sizes. The experimental results are also shown for comparison [11,51,53].



FIG. 3. Calculated 0 K enthalpies of formation of ordered structures and random Ni-Re alloys with respect to fcc Ni in the FM (open symbols) and NM (filled symbols) states and hcp Re. Open circles show the enthalpies of formation of random Ni-Re alloys obtained by the EMTO-CPA method in the FM state.

The calculated enthalpies of formation of random and some (presumably most stable Ni-rich) ordered Ni-Re alloys are shown in Fig. 3. In these calculations, we have taken the hcp Re and fcc Ni as the reference states. By open circles we show the formation energies of the FM random alloys and by other open symbols the formation enthalpies of the ordered alloys, obtained by the PAW method, relative to the FM fcc Ni (all the ordered structures come out nonmagnetic in our calculations except $A_{15}B$, whose magnetic energy, however, is only about 0.34 mRy/atom). They correspond to the stability at 0 K. The NM enthalpies of formation (which means that they are determined relative to the NM fcc Ni, whose energy is about 4.10 mRy higher than that of FM Ni) can be roughly associated with the stability at elevated temperatures, i.e., above the Curie temperature of Ni (630 K) [54].

It is obvious that the magnetic state produces a huge effect on stability of Ni-rich Ni-Re alloys. The slope and the curvature of the NM and FM formation energies of random alloys in the dilute limit of Re in Ni clearly show the drastic change from ordering to phase separation. This is a very important point for consideration of the phase stability in Ni-Re alloys at high temperatures, i.e., under processing and service.

The point is that the enthalpies of formation of alloys with concentration of Re less than 20 at.% exhibit quite pronounced downward shift in the NM state leading to the different phase equilibria picture. For the FM reference state, the $D1_a$ -Ni₄Re phase is the outermost Ni-rich stable phase, which is the result of previous *ab initio* calculations in the FM state [15,17]. But this is not the case for the NM reference state. In particular, a Pt₈Ti-type ordered structure [60] becomes stable for the alloy composition Ni₈Re against the phase separation to pure Ni and $D1_a$ -Ni₄Re, as one can see in Fig. 3.

A substantial shift of the energy of the NM Ni reference state means that other ordered structures, with less content



FIG. 4. $A_{15}B$ ordered structure. Positions of B atoms are shown by large (red) spheres, while positions of A atoms are shown only in one cubic fcc unit cell for clarity. The other positions of the A atoms in the cell can be obtained by translations of the cubic unit cell (without replacing B atoms shown in the figure).

of Re, which are unstable in the FM consideration, can also become stable. For instance, we have checked the stability of the $A_{15}B$ ordered structure shown in Fig. 4, and found that it is highly stable against phase separation into fcc Ni and $D1_a$ -Ni₄Re, while the Pt₈Ti-Ni₈Re phase becomes unstable if one considers its stability with respect to the $A_{15}B$ -Ni₁₅Re ordered structure and $D1_a$ -Ni₄Re.

Let us note that our VASP-PAW result for the formation enthalpy of the D1_a-Ni₄Re in the FM state, -4.53 mRy/atom, is in good agreement with existing first-principles results, which are -4.70 [15] and -4.23 [17] mRy/atom, respectively. The formation enthalpy of the D1_a-Ni₄Re is -7.80 mRy/atom for the NM Ni reference state.

We do not know whether there are some other (more) stable ordered phases in the NM case. To some extent such a simple 0 K consideration of the NM phases does not guarantee in general that the found stable ordered phases are really stable at high temperature, since the stability in this case is determined by the Gibbs free energy, which includes all the relevant thermal excitations. Unfortunately, obtaining the Gibbs free energy is a formidable task for this system, since the accurate account of thermal magnetic excitations at elevated temperatures is practically impossible at the present time. Therefore, it is a subject of speculation whether the "stable by enthalpy consideration" NM ordered structures are indeed stable at high temperatures. On the other hand, it is clear that such NM enthalpies provide a valuable qualitative insight into what may really be happening at high temperatures. At the same time, the existing assumption that the FM consideration of the enthalpies in Ni-Re alloys provides the basis for phase stability consideration at high temperatures is highly doubtful.

In Fig. 3, we also show the formation enthalpies of random Ni-Re alloys determined in the EMTO-CPA and VASP-PAW calculations. As one can see the agreement between the EMTO-CPA and VASP-PAW results, which is quite good up to about 10 at.% of Re, is worsening beyond 15 at.% of Re, similarly to the results of Ref. [54]. One of the possible reasons why the EMTO-CPA results are higher than the VASP-PAW

ones is the overestimated lattice constants in the EMTO-CPA calculations. The EMTO-CPA also produces higher values for the enthalpies of formation of the ordered structures. In particular, the EMTO-CPA enthalpy of formation of the DI_a structure is -6.5 mRy/atom. However, if the PBE-sol functional [61] is used, which produces smaller equilibrium lattice constants, the enthalpy becomes -7.5 mRy/atom, which is close to the VASP-PAW result. The reason of such sensitivity of the formation enthalpies to the equilibrium lattice constants will become clear in the following sections. The other possible reason is inaccuracy of the EMTO method due to the use of the atomic sphere approximation (ASA) for one-electron density and potential during self-consistent interactions.

IV. EFFECTIVE INTERACTIONS AND ORDERING IN Ni-Re ALLOYS

A. Fully renormalized interactions of Re atoms in Ni

In Table I, we show the first six total fully renormalized pair Re interactions as they are determined in Eq. (2). The calculations have been done in the NM and FM states using a 256-atom supercell $[4 \times 4 \times 4(\times 4)]$ for a fixed lattice constant of 3.585 Å, which corresponds to the experimental lattice parameter of Ni at 1300 K [62] or Ni_{0.9}Re_{0.1} alloy at about 1000 K. One can see that there is a huge difference between the values of the nearest-neighbor pair interaction in the FM and NM states: in the FM state, the interaction is strongly negative, while it is very large and positive in the NM state. This is reflected in the concentration dependence of the corresponding enthalpies of formation of random alloys, whose slope is roughly proportional to the value of the dominating interaction (taken with the opposite sign).

The fully renormalized total interactions have been obtained by finding the total energies of $4 \times 4 \times 4(\times 4)$ supercells whose volumes and shapes were fixed, but the local atomic positions were relaxed. If the atomic positions are fixed to the underlying fcc lattice, one obtains the chemical interactions. The difference between chemical and total interactions is the strain-induced interaction, which is associated with local atomic relaxations.

In Table I, we also show the strain-induced interactions, which have been obtained in the dilute limit. As one can see the FM and NM strain-induced interactions do not differ much in

TABLE I. Fully renormalized strain-induced (SI) and total pair interactions of Re in Ni (in mRy) obtained in the VASP-PAW calculations in the FM and NM states.

	FM		NM	
lmn	SI	Total	SI	Total
110	-2.80	-9.60	-3.01	29.55
200	-0.53	-11.75	-1.34	7.10
211	-0.13	-6.54	-0.32	3.67
220	-0.40	2.49	-1.21	8.84
310	-0.31	-3.58	-0.44	0.02
222	-0.04	-2.08	-0.14	-0.21

TABLE II. Fully renormalized strain-induced (SI) and total threeatom, $W_t^{(3)}$, and four-atom, $W_q^{(4)}$, interactions (in mRy) in the FM and NM states.

	FM		N	NM	
Interactions	SI	Total	SI	Total	
$W_{111}^{(3)}$	-2.12	12.52	-4.37	-16.86	
$W_{112}^{(3)}$	-1.60	10.28	-0.61	-5.63	
$W_{113}^{(3)}$	-2.35	11.55	-2.37	-5.56	
$W_{114}^{(3)}$	0.36	7.18	-1.99	-14.17	
$W_{1111}^{(4)}$	-1.14	-11.34	1.55	11.72	

contrast to the total interactions. They are also quite moderate in size compared to the total interactions.

What we would like to demonstrate now is that those fully renormalized pair interactions should contain substantial contributions from the multisite (or many-atom) interactions. In Table II, we show four fully renormalized three-site interactions— $W_{111}^{(3)}$, $W_{112}^{(3)}$, $W_{113}^{(3)}$, and $W_{114}^{(3)}$, which are for the triangle of the nearest neighbors and triangles formed by two nearest neighbors and one next-nearest neighbor, the third neighbor, and the fourth neighbor, respectively—and one four-site interaction, $W_{1111}^{(4)}$, for the tetrahedron of the nearest neighbors. As in the case of pair interactions, they have been obtained directly from the total energies as defined by Eq. (1).

As in the case of pair interactions, fully renormalized many-atom interactions strongly depend on the magnetic state. They are quite large and do not show substantial decreasing with increasing of the order: the four-atom interaction for the tetrahedron of the nearest neighbors is as strong as the interaction for the triangle of the nearest neighbors. Although we have not checked the higher-order interactions, it is clear that they can be quite large too.

In general, if the interactions of order n > m are negligible, the interactions of the CI Hamiltonian in Eq. (3) can be obtained in the direct calculations using Eq. (1), starting from order *m* interactions and going down with the order. However, in the case of the Ni-Re system, it is hardly possible, or extremely time consuming.

Another interesting point is that the multisite strain-induced interactions are also quite large. In the microscopic theory of elasticity [63,64], it is assumed that the strain-induced interactions of the order $n \ge 3$ are negligible. This is not the case here if we compare them with pair strain-induced interactions, although they are definitely much less than total or chemical interactions.

B. SGPM effective chemical interactions

The existence of multisite interactions in the system that are large and slowly decaying with the order means that interatomic bonding and interactions in this system depend strongly on the local and global alloy composition. In this case, the ordering behavior in a restricted concentration range can be investigated by the CD ECI. They can be easily obtained by the SGPM, which is a quite accurate computational tool for many metallic alloys. However, the SGPM interactions, especially for the first-nearest-neighbor coordination shell, can be in error due to inaccurate treatment of electrostatics in the atomic sphere (or muffin-tin) approximations, though the ASA is corrected by accounting for the multipole moment contributions in the present implementation of the SGPM and EMTO [20].

The latter is a problem in systems with large charge transfer, like Ni-Re alloys, since the electrostatic contribution due to the screened Coulomb interactions becomes very large, amplifying the error of the ASA. However, the SGPM still has its own advantages. It may not be advanced to produce very accurate ordering energetics for this system; however, it allows one to get a qualitative picture of the effective interactions in the paramagnetic state in Ni-Re alloys at high temperature, as will be discussed below.

As has been mentioned above, the disappearance of the local magnetic moment in Ni-Re alloys above the Curie temperature in the standard DFT calculations is a failure of DFT to incorporate the thermal magnetic excitations. In a simplified static approximation, the missing contribution from the LSF can be included using different techniques [40,41]. But all of them require the use of the DLM description of alloy components. This is where the CPA-based *ab initio* techniques have an advantage over the usual Hamiltonian methods, like VASP-PAW. The SGPM calculations can reveal at least on a semiquantitative level the effect of LSF on the effective interactions.

In Fig. 5, we show the dependence of the local magnetic moment of Ni on temperature in $Ni_{0.9}Re_{0.1}$ alloy at a fixed lattice constant of 3.585 Å obtained using a simplified scheme described above. As one can see, the Ni local magnetic moment at 800 K becomes as large as in pure Ni in the ground state and grows further with the temperature. This is, of course, a qualitative result. However, it makes an important point showing that a NM consideration of Ni-Re alloys at elevated temperatures can be in error.

Next, in Fig. 6, we show the SGPM interactions together with the corresponding one-electron and screened Coulomb contributions for Ni_{0.9}Re_{0.1} alloy in the NM and LSF states at 1300 K obtained for lattice constant 3.585 Å. One can see that the one-electron contribution is large and negative in both



FIG. 5. Temperature dependence of the local magnetic moment of Ni in $Ni_{0.9}Re_{0.1}$ due to LSF.



FIG. 6. SGPM interactions for $Ni_{0.9}Re_{0.1}$ alloy in the NM state (filled symbols) and in the LSF (open symbols) state at 1300 K. The one-electron contribution is shown by triangles and screened Coulomb interactions by diamonds.

cases; i.e., electronic structure "favors" clustering or phase separation in Ni-Re alloys (the LSF substantially decreases the one-electron contribution in this case). At the same time, the screened Coulomb interaction at the first coordination shell has the opposite sign and it is about twice as large as the one-electron contribution.

In other words, the screened Coulomb interaction gives the dominating contribution to the effective interaction at the first coordination shell, which, in the end, promotes strong ordering in the system. Since the screened Coulomb interaction is the result of the "charge transfer" effects originating from the size difference of Ni and Re, this contribution is quite sensitive to the lattice constant (see, for instance, the discussion in Ref. [33] of interactions in Cu-Au). One can also see that the contribution from the screened Coulomb interactions is larger in the NM state than in the LSF. The latter is again partly a size effect: the induced local magnetic moment on Ni in the LSF state makes it larger thereby decreasing the charge transfer between Ni and Re.

The concentration and lattice constant dependencies of the strongest EPI at the first coordination shell, $V_{110}^{(2)}$, obtained in the NM and LSF states are shown in Fig. 7. First of all, one can see that there is a quite strong dependence of the EPI on concentration especially in the NM case even for a fixed lattice constant. If the calculations are done for the equilibrium lattice constant (in this case we have used just Vegard's law [65] for the lattice parameters at the other concentrations), which corresponds to the given composition, the value of chemical interaction substantially decreases. This is so, since the charge transfer becomes reduced with increasing lattice spacing and therefore the screened Coulomb interactions also decrease.

The complexity of the Ni-Re system is also reflected in the pronounced concentration dependence of the multisite



FIG. 7. The nearest-neighbor EPI, $V_{110}^{(2)}$, in the NM state (squares) and in the LSF state at 1300 K (circles). Filled symbols show the interactions at a fixed lattice constant of 3.585 Å (experimental value for pure Ni at 1300 K), while open symbols for lattice parameters which correspond to the given concentrations using Vegard's law [65]. The lattice parameters of Re are taken from experimental data at 1300 K [66].

ECIs. In Fig. 8, we show the concentration dependence of the strongest three- and four-site SGPM interactions in the Ni-Re system: $V_{111}^{(3)}$ and $V_{114}^{(3)}$ are the three-site interactions for the triangles formed by three nearest neighbors and by three subsequent sites on the line in the close-packed direction [110]; $V_{1111}^{(4)}$ is the four-site interaction for tetrahedron of four nearest neighbors. One can see that $V_{1111}^{(4)}$ decreases monotonically



FIG. 8. The strongest three-site, $V_t^{(3)}$, and four-site, $V_q^{(4)}$, chemical interactions in Ni-Re alloys as a function of Re concentration. Filled symbols show the interactions in the NM state and open symbols in the LSF state at 1300 K. The lattice constant is fixed to the value of 3.585 Å.

TABLE III. Ordering energies (in mRy/atom) of Ni-Re alloys in the NM state obtained from the total energy and SGPM interactions in the EMTO calculations. The values in parentheses are obtained by the downshift of the nearest-neighbor effective pair interaction by 17 mRy (see discussion in the text).

Structure		SGPM	Contributions		
	$E_{\rm tot}$ Total	Total	$\sum V^{(2)}$	$\sum V^{(3)}$	$\sum V^{(4)}$
$\overline{A_{15}B(Ni_{15}Re)}$	-0.34	-1.31 (-0.91)	-1.15	-0.12	0.03
Pt ₈ Ti (Ni ₈ Re)	-1.85	-2.75(-1.49)	-3.25	0.42	0.08
$D1_a$ (Ni ₄ Re)	-6.83	-10.29(-6.21)	-9.93	-0.14	-0.22
H60 (Ni ₃ Re)	-7.34	-11.95 (-7.44)	-11.03	-0.90	-0.02
$L1_2$ (Ni ₃ Re)	11.97	3.93 (10.69)	-9.18	12.52	0.59
DO_{22} (Ni ₃ Re)	-2.43	-10.30 (-3.54)	-13.97	3.53	0.14

with concentration and changes sign at about 18 at.% Re in the LSF state, while it has a local maximum around 7 at.% Re in the NM state. A nonmonotonic behavior of the four-site interactions means that there should exist non-negligibly at least six-site CI ECIs in the Ni-Re system.

C. Ordering energies in Ni-Re alloys

The quality of the SGPM interactions can be checked by comparing the ordering energies calculated directly from the total energies of the ordered and random phases, and those obtained by the SGPM method at the same lattice constant and concentration. In Table III, we show the ordering energies of the A₁₅B, Pt₈Ti, D1_a, H60, L1₂, and DO₂₂ structures obtained from the strongest SGPM interactions, which include the first 40 EPIs and 77 three-site and 26 four-site ECIs, and in the corresponding total energy calculations. In all the cases, the lattice constant was 3.585 Å.

As one can see, the overall ordering trends are quite well reproduced by the SGPM interactions, although the SGPM quite substantially overestimates the strength of ordering in Ni-Re alloys. This is most probably due to the overestimated screened Coulomb interaction at the first coordination shell. It is obtained in the atomic sphere approximation and this means that the error can be simply due to the overlapping of the atomic spheres of the nearest-neighbor atoms. Taking into consideration the fact that the value of the screened Coulomb interactions at the first coordination shell is huge (see Fig. 6), the ASA error can be also relatively large.

As one can see in Table III, the reduction of this interaction by about 17 mRy brings the SGPM results for ordering energies very close to the total energy EMTO results. Of course, the other SGPM interactions, especially at the first several coordination shells, can be in error; however, the resulting interactions reproduce the quantitative picture of the ordering in the NM state quite well.

The decomposition of the ordering energy into the contributions from interactions of a different order shows the importance of many-atom or multisite interactions in Ni-Re alloys. In Table III we show the ordering energies of three different structures, L_{12} , DO_{22} , and H60, for the same alloy composition, Ni₃Re. They are very different, although, for instance, L_{12} and DO_{22} are closely related to each other. Comparing contributions from interactions of different orders, one can trace the origin of such a large difference: it stems from the three-site interactions, which produce very large positive contribution to the ordering energy of the $L1_2$ structure, although the contribution of the three-site interactions to the ordering energy of the H60 phase is small. This result shows the nontrivial character of interactions and ordering in Ni-Re alloys.

D. Short-range order

As has been pointed out, the origin of the overestimation of the ordering energy by the SGPM is mainly due to the too large screened Coulomb interaction at the first coordination shell. Therefore in order to obtain atomic SRO parameters in the $Ni_{0.91}Re_{0.09}$ alloy about 900 K, which are experimentally known [18], we have used the renormalized in this way SGPM interactions obtained in the LSF state at 900 K with additional contributions from the strain-induced interactions presented in Tables I and II in Monte Carlo statistical thermodynamic simulations.

The Monte Carlo simulations have been done in the canonical ensemble using the Metropolis algorithm [67]. The Monte Carlo simulation box contained 16384 atoms $(16 \times 16 \times 16 \times 16$ supercell of the 4-atom fcc unit cell). The EPI at the first 21 coordination shells, 17 strongest three-site, and 2 strongest four-site interactions have been used in the configurational Hamiltonian. At each temperature, the system was first equilibrated for 4000 MC steps/atom. After that, the statistical data were obtained by averaging over additional 4000 MC steps/atom.

The Warren-Cowley SRO parameters for the (200) and (211) coordination shells are shown in Fig. 9. It is clear that there is an order-disorder transition at about 940 K. The snapshot of the MC simulation box at 300 K in this figure shows that this is a phase separation transition where the $D1_a$ ordered structure precipitates in pure Ni. This makes the direct comparison of the experimental and theoretical SRO parameters at 880 K impossible, since it is obvious that according to the experimental SRO parameters the alloy is most probably in a random state [18].

Therefore, in Table IV, we show the calculated Warren-Cowley SRO parameters, α_{lmn} , for Ni-9.0 at.% Re at 880 K and 1000 K, i.e., those which are below and above the transition temperature in our MC simulations, together with the experimental data [18] of the Ni-9.4 at.% Re at 873 K. It is obvious that the calculated atomic SRO is much stronger than the experimental one even at 1000 K. The origin of the disagreement is most probably the oversimplified theoretical



FIG. 9. Calculated SRO parameters for α_{200} and α_{211} in Ni_{0.91}Re_{0.09}. A low-temperature (300 K) snapshot out of a Monte Carlo simulation box is shown for this composition. The ordered D1_a structure can be seen in this snapshot.

description of the high-temperature state of Ni-Re alloys and corresponding effective interactions, although our results are in qualitative agreement with theoretical simulations by Maisel *et al.* [17]. Clearly, a more thorough investigation of the Ni-Re system at high temperature is needed to resolve the controversy.

V. SUMMARY

Ni-rich Ni-Re alloys exhibit very pronounced ordering in the NM state, which actually becomes stronger with decreasing Re concentration and making stable ordered structures like $A_{15}B$ (at least against separation to pure Ni and $D1_a$ -Ni₄Re). This means that theoretical simulations [17] of the atomic ordering in N_{96.62}Re_{3.38} based on the FM state, which predict the phase separation into pure Ni and $D1_a$ -Ni₄Re at 930 K,

TABLE IV. Warren-Cowley SRO parameters, α_{lmn} , as determined in Monte Carlo simulations for Ni-9.0 at.% Re at 880 K and 1000 K. The experimental parameters are taken from Ref. [18] for the Ni-9.4 at.% Re at 873 K. The experimental data were obtained using two methods: Georgopoulos-Cohen (GC) and Borie-Sparks (BS).

lmn	α_{lmn}				
	Ni-9.0 at.% Re (LSF)		Ni-9.4 at.% Re (Ref. [18])		
	880 K	1000 K	GC	BS	
000	1.000	1.000	1.062(11)	1.218(5)	
110	-0.097	-0.086	-0.018(4)	-0.024(2)	
200	0.176	0.048	-0.028(4)	-0.008(2)	
211	0.166	0.061	0.011(2)	0.012(1)	
220	-0.086	-0.040	-0.025(3)	-0.036(1)	
310	0.030	-0.006	-0.004(2)	0.003(1)	
222	-0.088	-0.041			
312	0.151	0.017			
400	0.174	0.032			
411	-0.078	-0.011			
330	-0.076	-0.001			

can be just an artifact of the FM presentation of the enthalpies of formation.

On the other hand, the NM description of the phase equilibria at high temperature is also an oversimplification: Ni is an itinerant ferromagnet, whose atoms indeed lose their local magnetic moment at 0 K upon their randomization, like in the DLM model, which presents a paramagnetic state of the usual Heisenberg system. However, in reality, the local magnetic moments fluctuate at finite temperature, leading to a nonzero local magnetic moment in the DLM presentation. In this paper, we have shown that such LSFs produce a noticeable effect upon interactions in the system: they reduce strong ordering interactions at the first coordination shell (see Fig. 7) thereby affecting the stability of different ordered phases.

Unfortunately, the latter is practically impossible to predict using the usual DFT calculations. The problem is even more complex than it may appear from the standard procedure based on the cluster expansion and the consequent use of the corresponding interactions in Monte Carlo simulations. Although the enthalpies of formation are expanded for those kinds of simulations, they do not take into consideration strain effects, which should be pronounced when an ordered phase with Re precipitates in Ni due to presumably substantial size mismatch of these phases. This topic needs a further thorough investigation.

In order to quantify theoretical results for CD ECI, we have calculated the atomic SRO in Ni-9.0 at.% Re. According to the existing experimental data this is a random alloy with not so much pronounced SRO below 873 K. Our Monte Carlo simulations with CD ECIs, which have been renormalized to reproduce the ordering energy of the $D1_a$ and Pt_8Ti structures, predict a phase separation to the ordered $D1_a$ phase and pure Ni at about 940 K. The calculated SRO at 1000 K agrees qualitatively with the experimental data, although it is substantially stronger. The latter means that there is indeed substantial reduction of the ordering in real Ni-Re alloys compared to the present theoretical simulations. A further investigation of the behavior of Re in Ni under experimental conditions is needed in order to understand high-temperature phase equilibria and in the end the origin of the Re strengthening effect in Ni-based superalloys.

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