

Atomic-scale properties of Ni-based FCC ternary, and quaternary alloys

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Abstract

The aim of this study is to characterize atomic-scale properties of Ni-based FCC high entropy alloys. For this purpose, we use Monte Carlo method combined with density functional theory calculations to study short-range order (SRO), atomic displacements, electronic structure, and magnetic moments in ternary NiCrCo, and quaternary NiCrCoFe alloys. According to our study, for the ternary alloy we predict negative SRO parameter between Ni-Cr and Cr-Co, and positive for Ni-Co and Cr-Cr pairs, as well as a weakly magnetic state. For the quaternary alloy we predict positive SRO parameter for Ni-Ni, Cr-Cr, Co-Co, and Fe-Fe pairs and negative for Ni-Cr, Ni-Fe, Cr-Co, and Co-Fe pairs. Atomic displacements for both ternary and quaternary alloys are negligible. In contrast to the ternary, the alloy shows a complex magnetic state. Electronic structure of the ternary and quaternary alloys shows significant changes near the Fermi energy between a random solid solution and the predicted structure with SRO. Despite that, calculated EXAFS spectra does not show enough contrast to discriminate between random and ordered structures. The predicted structures with SRO have an impact on point-defect energetics, electron-phonon coupling and thermodynamics and thus, should be used to study these properties for

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these two alloys.

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1. Introduction

In search of better materials, needed in many different industries, such as energy production, scientists have started to explore unconventional concepts of material design. Some examples of these are engineered nanostructures and alloys with many different elements. Instead of consisting of two or three principal elements, as is the case with traditional alloys, high entropy alloys (HEA) [1] have five or more elements in close to equimolar ratios that form simple solid solution phases in FCC, HCP, or BCC structures. Recent studies have shown that HEA's have many improved properties compared to conventional alloys or pure elements that they are made of [2]. For example, high strength, high ductility, better resistance to wear and corrosion.

The core effects that are considered to affect the microstructure and properties of HEA's are [3]: high entropy, sluggish diffusion, severe lattice distortion, and cocktail effect. The high number of principal elements increases the contribution to the free energy from the configurational entropy term, which stabilizes the random solid solution phase with respect to competing phases. The large fluctuations of the lattice potential between different lattice sites hinders the diffusion of atoms by creating a distribution of activation energies. Also, many low potential lattice sites act as traps and further decrease diffusivity. This has been observed in NiCrCoFeMn HEA [4] where the activation energies were higher than in pure elements and ternary alloys consisting of same elements. Due to differences in atomic sizes and bonding the lattice becomes distorted, increasing hardness and strength and making these properties insensitive to temperature. Lastly, the cocktail effect provides guidelines for manipulating material properties by adding or removing elements, which stabilize BCC or FCC phases, or improve hardness.

When creating ternary and higher element phase diagrams it is often assumed that the solid solution phases are random. This is due to the lack of experimental data as is the case for NiCrCo ternary [5] or NiCrCoFe quaternary alloys. Experimental phase diagram determinations show that the equimolar NiCrCo alloy is a solid solution in FCC phase [6, 7, 8], but no information on the detailed ordering of atoms is available. In fact, short-range order (SRO) has been observed in the binary NiCr alloy at various compositions and temperatures [9, 10, 11], which suggests that ordering between Ni-Cr pairs might also occur in the ternary and quaternary alloy. This kind of ordering could lower the configurational entropy from its maximum value, which is for a random alloy, and change the expressions for the free energy and the low-T phase diagram. SRO also decreases the enthalpy of the system, affecting defect energetics.

Computer simulation is a powerful technique to study structure and properties of a material with such an accuracy that for many systems prior experimental knowledge is not needed. It allows screening different structures and studying stability and other properties, without costly experiments. Finally, the predicted materials with required properties can be synthesized and tested. Recently, a hybrid Monte Carlo (MC) and molecular dynamics method combined with density functional theory calculations (DFT) [12] was used to study refractory HEA [13]. It was shown that the method could be used to study the ordering in an alloy at temperatures as low as 300K.

In this work we explore the short-range order of ternary and quaternary Ni based high entropy alloys using lattice MC combined with *ab initio* calculations. First we use lattice MC to find the equilibrium structure of the alloys and then, we study the atomic displacements, formation energy, electronic density of states, magnetic moments and configurational entropy for both random alloy and the structure with the SRO for which no experimental results are available.

2. Methodology

The study of SRO in Ni alloys was conducted using lattice Metropolis MC, which was combined with *ab initio* calculations to find the energetics of the input structures and to evolve the system towards a minimum of free energy at the specified temperature. The systems studied were equimolar $Ni_{0.33}Cr_{0.33}Co_{0.33}$ ternary, and $Ni_{0.25}Cr_{0.25}Co_{0.25}Fe_{0.25}$ quaternary alloys in FCC phase. The temperatures investigated were 500, 800 and 1200K.

Energy calculations were conducted using DFT with VASP software package [14, 15, 16, 17]. The supercell used consisted of 108 atoms. The plane wave cut-off energy in all calculations was 269 eV which is the value recommended for Ni by software manual and is the highest recommended cut-off for the elements under consideration. Methfessel-Paxton smearing method of the first order [18] with a smearing width of 0.1 eV was used, and integration in the Brillouin zone was performed with a mesh created using Monkhort-Pack [19] method with 2x2x2 density. Core electrons were described with projector augmented-wave pseudopotentials [20, 21] provided by VASP package. The number of valence electrons were 10, 6, 9, and 8 for Ni, Cr, Co, and Fe respectively. Generalized gradient approximation as described by Perdew-Burke-Ernzerhof (PBE) [22] was used for describing exchange-correlation of electrons. All calculations done were spin-polarized.

Additionally, calculations to investigate formation energy, structure relaxations, electronic densities of state, were conducted with higher number of k-points (3x3x3) and smaller smearing width of 0.01 eV to increase the accuracy of forces and energy. Convergence studies were made to determine calculation parameters needed for accurate results. The X-ray absorption fine structure spectrum for the NiCrCoFe HEA was calculated using ab-initio real space multiple scattering calculations (feff) as described in [23, 24, 25].

Lattice MC simulations included only trials of atomic type swaps with the acceptance probability based on the Metropolis-Hastings sampling [26]. A special quasi-random structure (SQS) [27] was selected as an initial starting point

in all calculations.

The Warren-Cowley SRO parameter [28] was used to quantify the chemical ordering around the atomic species. The SRO α_{ij}^ν was calculated using equation 1, where p_{ij}^ν is the probability of finding atomic species j around an atom of type i in the ν 's neighboring shell and c_j is the atomic concentration of type j . The SRO $\alpha = 0.0$ corresponds to a random solution. Positive values show a tendency to decrease the number of i, j pairs, while negative values correspond to the opposite.

$$\alpha_{ij}^\nu = 1 - \frac{p_{ij}^\nu}{c_j} \quad (1)$$

The SQS structures were created by swapping element species randomly in an initial randomly generated sample until a SRO of a random alloy up to the third nearest neighbor would be found. In this approach the sum of SRO squares was minimized to find a structure that would be reasonably close to an ideal random solution.

The configuration entropy of a system with non-zero SRO can be estimated using the cluster variation method (CVM) in the pair approximation [29] using the following equation:

$$S = k_B((2z - 1) \sum_i (c_i \ln c_i - c_i) - z \sum_{ij} (y_{ij} \ln y_{ij} - y_{ij}) + (z - 1)), \quad (2)$$

where $2z$ is the number of nearest-neighbors, c_i is the concentration of type i and y_{ij} is the probability of finding an i, j pair.

Formation energy was calculated using equation 3, where E_{tot} is the total energy per atom of the mixed system, c_i is the concentration of element i and $E_{i,ref}$ is the energy per atom of the reference phase of element i . Summation goes over all the elements in the alloy. The reference energies were calculated in the ground state phases of Ni, Cr, Co, and Fe, which are FCC, BCC, HCP, and BCC respectively. The lattice constants used for pure element reference energies are equation of state minimas as predicted by DFT. The calculated magnetic moments of pure element ground states agree well with similar calculations from

the literature.

$$\Delta E_f = E_{tot} - \sum_i^N c_i E_{i,ref} \quad (3)$$

3. Results and discussion

3.1. Ternary NiCrCo

Lattice MC simulations for the NiCrCo equimolar alloy at three temperatures 500K, 800K, and 1200K were performed. The simulations started from a SQS structure using 3.56Å experimental lattice parameter [30] and simulations lasted for 400 steps, which results in 4 swap trials per atom. The resulting final structure with SRO at 500K and initial SQS structure were later relaxed keeping the volume constant at 0K and analysed.

At 500K the most significant trends in the development of SRO's are shown on Figure 1. Our finding is that major deviations from a random solid solution appear for the Ni-Co, Cr-Cr, and Cr-Co pairs. The average number of Ni-Co and Cr-Cr neighbors is reduced from 4 for the random case to about 3 and the number of Ni-Cr and Cr-Co pairs is increased to 5. All the other pairs are close to the values of the random solution. With the increase of temperature the SRO parameter remains closer to the value of random solid solution with the exception of Cr-Cr pairs, which still remains significantly high, but somewhat lower than for the 500K case. The final averaged SRO parameter values are shown in Table 1.

The development of the SRO reduces the free energy mainly by lowering the formation energy, which changes from 0.093 to 0.068 *eV/atom*. Furthermore, atomic relaxation reduces the energy by no more than 6.0 meV/atom. Positive formation energy implies to a tendency to phase separate at some lower temperature, but MC at this sample size is not an adequate technique to explore this phase boundary. The experimental phase diagram at 800°C for the ternary NiCrCo alloy suggests that at the equimolar ratio the system should form a FCC solid solution [5]. We suggest that the presence of SRO may influence

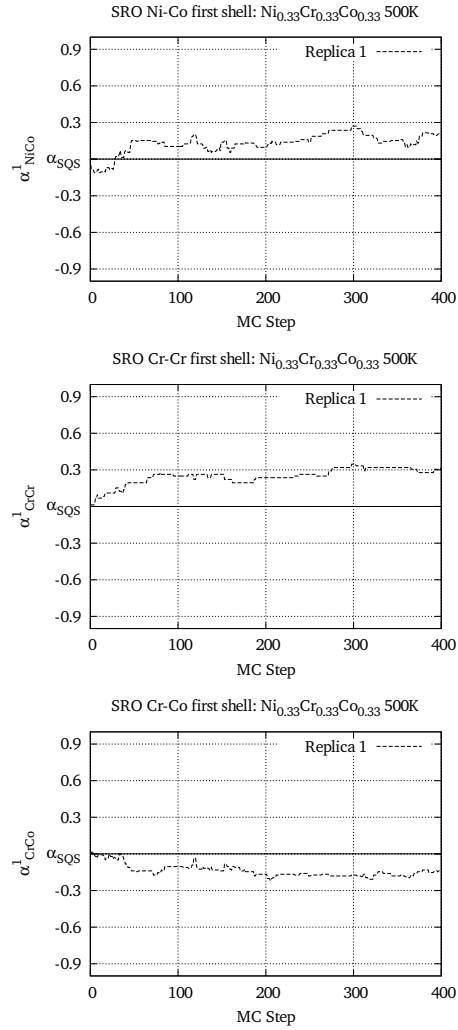


Figure 1: Development of SRO in the lattice MC simulation of NiCrCo ternary alloy at 500K. Plotted is the SRO parameter in the first neighbor shell for following pairs starting from top: Ni-Co, Cr-Cr, and Cr-Co.

the location of phase boundaries, because of the lower formation energy and configurational entropy.

The atomic displacements with respect to perfect lattice positions are found to be in the range of 0.04\AA which is comparable to the thermal fluctuations and thus is negligible for both the SQS and SRO structures. The largest displacements were mostly related to Cr atoms. This justifies the use of lattice MC for the ternary system. The electronic density of states, DOS, for the random alloy and the predicted SRO structure are shown on Figure 2. The DOS is not significantly affected by the SRO, the largest difference being near the Fermi energy, which has implications for both electric and thermal transport properties, and on the electron-phonon interaction. The system with SRO has a slightly lower mean magnetic moment than in the case of SQS which is shown in Table 2. The mean magnetic moments of both Ni and Co are lower and mean magnetic moment of Cr is higher compared to SQS. In the analysis of individual magnetic moments, which are shown in Figure 3, it can be seen that the main change occurs in the amplitude of the magnetic moments of Cr atoms. In the case of SQS, the values are closer to a random distribution than in the case of the structure with SRO. Also, magnetic moments of Cr atoms are not in the same direction, whereas the moments of Ni and Co are all pointing in the same directions. Finally, our finding is that the configurational entropy of the alloy with SRO is relatively close to the value of a random solid solution.

3.2. Quaternary NiCrCoFe

Same lattice MC simulations were done with the quaternary NiCrCoFe alloy. the simulations started from SQS structure with an experimental lattice parameter of 3.57\AA [30] and lasted for 600 steps resulting in 6 swap trials per atom. The final SRO parameters at three temperatures are provided in Table 3. The final structure from 500K simulations was relaxed at 0K without changing the volume and analysed.

Similar trends as in the case of ternary alloy are clearly present. The number of Ni-Co and Cr-Cr pairs is reduced and the number of Cr-Co is increased, when

Pair	500K	800K	1200K
Ni-Ni	0.03	0.01	0.04
Ni-Cr	-0.15	-0.14	-0.08
Ni-Co	0.18	0.10	0.12
Cr-Cr	0.31	0.26	0.12
Cr-Co	-0.17	-0.12	-0.04
Co-Co	-0.01	0.02	-0.08

Table 1: Short-range order parameter of the NiCrCo ternary FCC system averaged over last steps of the lattice MC simulation at three temperatures.

System	Ordering	E_f [$\frac{meV}{atom}$]	S_{conf} [$\frac{k_B}{atom}$]	Δr_{rms} [\AA]	$\langle \mu \rangle$ [μ_B]	$\langle \mu_{Ni} \rangle$ [μ_B]	$\langle \mu_{Cr} \rangle$ [μ_B]	$\langle \mu_{Co} \rangle$ [μ_B]	$\langle \mu_{Fe} \rangle$ [μ_B]
NiCrCo	SQS	93.01	1.099	0.045	0.305	0.172	-0.289	1.031	
	SRO	67.54	1.014	0.041	0.203	0.113	-0.402	0.899	
NiCrCoFe	SQS	76.00	1.386	0.060	0.667	0.292	-0.996	1.147	2.223
	SRO	37.08	1.217	0.042	0.587	0.311	-1.275	1.034	2.279

Table 2: Properties of NiCrCo ternary and NiCrCoFe quaternary systems for the special quasirandom structure (SQS) and structure with ordering (SRO) as predicted by lattice MC simulations at 500K. The values are obtained for 0K relaxed structures at constant volume.

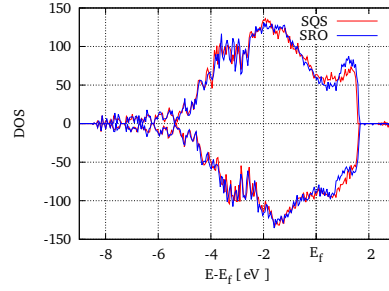


Figure 2: Electronic density of states for the initial quasi-random structure (SQS) and the structure predicted by lattice MC simulation (SRO) of NiCrCo ternary system relaxed at 0K.

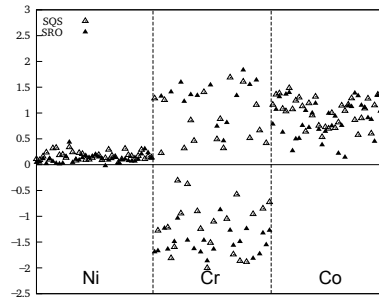


Figure 3: Magnetic moments of individual atoms in quasi-random structure (SQS) and structure with short-range order (SRO) as predicted by lattice MC at 500K.

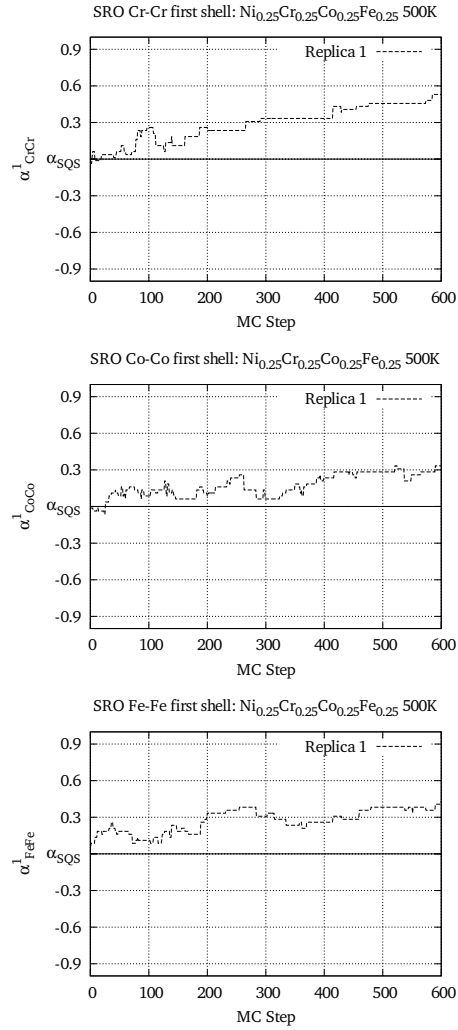


Figure 4: Development of SRO in the lattice MC simulation of NiCrCoFe quaternary alloy at 500K. Plotted is the SRO parameter in the first neighbor shell for following pairs starting from top: Cr-Cr, Co-Co, and Fe-Fe.

compared to a random alloy. Additionally, the number of Ni-Ni, Co-Co and Fe-Fe pairs is significantly reduced and the number of Ni-Cr, Ni-Fe, Cr-Co, and Co-Fe pairs is increased. Again, the increase in temperature changes the SRO parameter of all pairs towards zero, while number Cr-Cr pairs remains still significantly reduced.

As in the case of ternary alloy, the development of SRO involves a lowering of formation energy by about 40 meV/atom, from 76 to 37. Atomic relaxation further decreases this value by 9meV/atom. In contrast to the ternary alloy, the DOS at the Fermi level differs significantly from the random alloy, as seen in Figure 5. The lower density of states near the Fermi energy would decrease the electron-phonon coupling as it can be considered to be proportional to DOS. The magnetic moments of the structure with SRO have a much smaller spread and, as in the ternary alloy, the magnetic moments of Cr atoms are mostly anti-ferromagnetically aligned with respect to all other elements. SRO also increases the absolute value of mean magnetic moments. Contrary to the ternary alloy, SRO results a sizable change in relation to random solution of about 10% in the configurational entropy as calculated from the CVM model. Also, during the atomic relaxation at 0K the atoms move only slightly and the mean atomic displacement is around 0.06 Å. As with the ternary alloy the largest displacements are for Cr atoms.

Finally, the EXAFS spectra was calculated for the quaternary case for both SQS and SRO structures. The results are shown in Figure 7. The results agree quite well with experimental results, but there is no significant difference between the SQS and SRO spectras, which suggests that X-ray methods do not show enough contrast between these elements to detect the changes in SRO that we predict from lattice MC simulations.

4. Conclusions

In summary, lattice MC simulations were conducted to study SRO in Ni based ternary and quaternary alloys, as a preliminary study aiming at Ni-based

Pair	500K	800K	1200K
Ni-Ni	0.20	0.18	0.04
Ni-Cr	-0.15	-0.12	-0.13
Ni-Co	0.10	0.05	0.14
Ni-Fe	-0.15	-0.11	-0.05
Cr-Cr	0.44	0.21	0.39
Cr-Co	-0.24	-0.08	-0.19
Cr-Fe	-0.06	-0.01	-0.08
Co-Co	0.28	0.13	0.02
Co-Fe	-0.14	-0.10	0.01
Fe-Fe	0.35	0.22	0.11

Table 3: Short-range order parameter of the NiCrCoFe quaternary FCC system averaged over last steps of the lattice MC simulation at three temperatures.

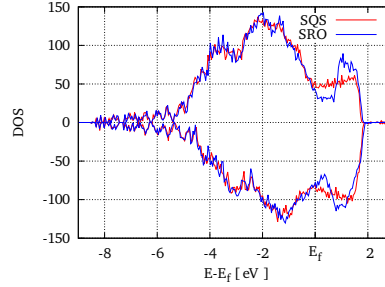


Figure 5: Electronic density of states for the initial quasi-random structure (SQS) and the structure predicted by lattice MC simulation (SRO) of NiCrCoFe quaternary system relaxed at 0K.

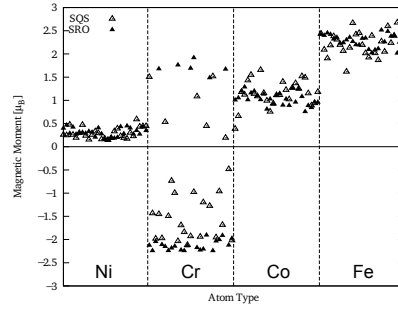


Figure 6: Magnetic moments of individual atoms in quasi-random structure (SQS) and structure with short-range order (SRO) as predicted by lattice MC at 500K.

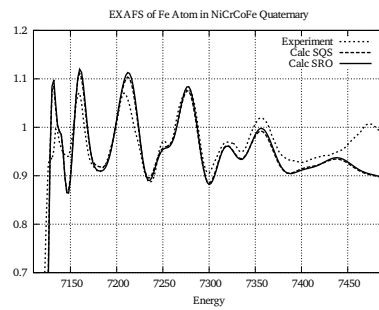


Figure 7: Calculated EXAFS of quasi-random (SQS) and structure predicted by lattice MC simulation (SRO) in comparison with experimental data.

HEA's. First, despite the common assumption that HEA's are random solid solutions, simulations for equimolar NiCrCo HEA alloy showed that the systems studied showed a degree of short range order. In which, a significant decrease in the number of Cr-Cr and increase in Ni-Cr and Cr-Co pairs was observed. Next, for the NiCrCoFe quaternary alloy a similar behavior was found. Such as a large decrease in the number of Ni-Ni, Cr-Cr, Co-Co, and Fe-Fe pairs and a moderate increase in Ni-Cr, Ni-Fe, Cr-Co, and Co-Fe pairs. Finally, to investigate formation energy, mean square displacements, electronic density of states, and configurational entropy, calculations were done with the SRO structures predicted by the lattice MC. From this data, we conclude that ordering lowers the formation energy in several tenths of meV/atom. This is enough to change the location of phase boundaries by significant amounts. Additionally, SRO defines the energy landscape for defects in both their formation and migration energies. Lastly, the change in DOS near the Fermi energy, because of the SRO, will change the electro-phonon coupling.

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- [1] J. W. Yeh, Y. L. Chen, S. J. Lin, S. K. Chen, High-Entropy Alloys - A New Era of Exploitation, *Mater. Sci. Forum* 560 (2007) 1–9. doi:10.4028/www.scientific.net/MSF.560.1.
- [2] Y. Zhang, T. T. Zuo, Z. Tang, M. C. Gao, K. a. Dahmen, P. K. Liaw, Z. P. Lu, Microstructures and properties of high-entropy alloys, *Prog. Mater. Sci.* 61 (October 2013) (2014) 1–93. doi:10.1016/j.pmatsci.2013.10.001.

- [3] J.-W. Yeh, Alloy Design Strategies and Future Trends in High-Entropy Alloys, *Jom* 65 (12) (2013) 1759–1771. doi:10.1007/s11837-013-0761-6.
- [4] K.-Y. Tsai, M.-H. Tsai, J.-W. Yeh, Sluggish diffusion in Co-Cr-Fe-Mn-Ni high-entropy alloys, *Acta Mater.* 61 (13) (2013) 4887–4897. doi:10.1016/j.actamat.2013.04.058.
- [5] S. Yang, M. Jiang, H. Li, Y. Liu, L. Wang, Assessment of Co-Cr-Ni ternary system by CALPHAD technique, *Rare Met.* 31 (1) (2012) 75–80. doi:10.1007/s12598-012-0466-y.
- [6] S. Rideout, W. D. Manly, E. L. Kamen, B. S. Lement, P. A. Beck, Intermediate Phases in Ternary Alloy Systems of Transition Elements, *Trans AIME* 191 (1951) 872–876.
- [7] G. P. Zhmurko, E. G. Kabanova, V. N. Kuznetsov, a. V. Leonov, Phase equilibria in the Co-Cr-Ni system, *Moscow Univ. Chem. Bull.* 63 (4) (2008) 234–235. doi:10.3103/S0027131408040135.
- [8] T. Omori, J. Sato, K. Shinagawa, I. Ohnuma, K. Oikawa, R. Kainuma, K. Ishida, Experimental determination of phase equilibria in the Co-Cr-Ni system, *J. Phase Equilibria Diffus.* 35 (2) (2014) 178–185. doi:10.1007/s11669-014-0292-z.
- [9] W. Schweika, H. Haubold, Neutron-scattering and Monte Carlo study of short-range order and atomic interaction in Ni 0.89 Cr 0.11, *Phys. Rev. B* 37 (16) (1988) 9240–9248.
- [10] B. Schönfeld, L. Reinhard, Short-Range Order and Atomic Displacements in Ni-20 at% Cr Single Crystals, *Phys. status solidi* 148 (1988) 457–471.
- [11] R. Caudron, M. Sarfati, In situ diffuse scattering of neutrons in alloys and application to phase diagram determination, *J. Phys. I Fr.* 2.
- [12] W. Kohn, L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.* 140 (1965) A1133. doi:10.1103/PhysRev.140.A1133.

- [13] M. Widom, W. P. Huhn, S. Maiti, W. Steurer, Hybrid Monte Carlo/Molecular Dynamics Simulation of a Refractory Metal High Entropy Alloy, *Metall. Mater. Trans. A* 45 (1) (2013) 196–200. doi:10.1007/s11661-013-2000-8.
- [14] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B* 47 (1).
- [15] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, *Phys. Rev. B* 49 (1994) 14251.
- [16] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comp. Mater. Sci.* 6 (1996) 15.
- [17] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set., *Phys. Rev. B. Condens. Matter* 54 (16) (1996) 11169–11186.
- [18] M. Methfessel, A. T. Paxton, High-precision sampling for Brillouin-zone integration in metals, *Phys. Rev. B* 40 (6) (1989) 3616–3621.
- [19] H. Monkhorst, J. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* 13 (1976) 5188–5192.
- [20] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953. doi:10.1103/PhysRevB.50.17953.
- [21] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (1999) 1758.
- [22] J. P. J. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* 77 (18) (1996) 3865.

- [23] A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure, *Phys. Rev. B* 58 (1998) 7565–7576.
- [24] J. J. Rehr, R. C. Albers, Theoretical Approaches to X-ray Absorption Fine Structure, *Rev. Mod. Phys.* 72 (2000) 621.
- [25] J. J. Rehr, J. J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto, F. D. Vila, Ab initio theory and calculations of X-ray spectra, *Comptes Rendus Physique* 10 (6) (2009) 548–559.
- [26] W. K. Hasting, Monte Carlo sampling methods using Markov chains and their applications, *Biometrika* 57 (1970) 97.
- [27] A. Zunger, S. H. Wei, L. G. Ferreira, J. E. Bernard, Special quasirandom structures, *Phys. Rev. Lett.* 65 (3) (1990) 353–356.
- [28] J. M. Cowley, An approximate theory of order in alloys, *Phys. Rev.* 77 (5) (1950) 669–675. doi:10.1103/PhysRev.138.A1384.
- [29] R. Kikuchi, CVM Entropy Algebra, *Prog. Theor. Phys. Suppl.* 115 (1994) 1–26.
- [30] M. Stocks, private communication.