Interplay of Crystal Structure Preference and Magnetic Ordering in High Entropy CrCoFeNiAl Alloys

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In this work, some relations between crystal structure and magnetic ordering in CrCoFeNiAl HEAs are discussed in view of the KKR-CPA calculations. Remarkably, it is noticed that the transition between *fcc* and *bcc* phases in the analysed CrCoFeNi$_x$Al and CrCoFeNiAl$_x$ alloys is closely related to change in ordering of the local magnetic moments, namely the magnetic moment on Cr is either parallel (ferromagnetic) or antiparallel (ferrimagnetic) to the magnetic moments of other atoms (Co, Fe and Ni). On the whole, the theoretical diagram showing the *fcc-bcc* phase preference and their coexistence vs. alloy composition well corroborates with available experimental data.

1. Introduction

In the recent years high entropy alloys (HEA) [1, 2] became a subject of intense experimental and theoretical investigations, since in contrast to traditional complex alloys usually consisting of one, two or three main elements, HEAs may contain over a dozen of constitutent elements with comparable atomic contributions. Surprisingly, simple structures as *bcc*, *fcc* or *hcp*, including randomly distributed atoms on crystallographic sites, were found to be structural models well describing the atoms ordering in HEAs. The configurational entropy of such N- element system, usually expressed as $S_{conf} = -k_B \Sigma_{i=1}^{N} c_i \ln c_i$ (where c_i represents concentration of $i-$th element and k_B is Boltzmann constant) is relatively high and reaches the maximum value when the concentrations of each element are the same, i.e. $c_i = 1/N$ yielding $S_{conf} = k_B \ln N$.

TABLE I

Relations between element concentration c_M, x value and c_{Al}/c_{Ni} ratio. M stands for Al in Al$_x$ and Ni in Ni$_x$ alloy.

c_M [at%]	x	c_{Al}/c_{Ni} (Al$_x$)	c_{Al}/c_{Ni} (Ni$_x$)
10	0.44	0.44	2.27
15	0.71	0.71	1.41
20	1.00	1.00	1.00
25	1.33	1.33	0.75
30	1.71	1.71	0.58
35	2.15	2.15	0.46

At very beginning, experimental investigations concerned the crystal structures, phase formation and pref-

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erence as well as conditions of their relative stability. The fact that such complex, disordered systems crystallize in very simple lattices prompted many research groups to study more fundamental aspects of HEAs as electronic, transport or magnetic properties. Noteworthy, many magnetic HEAs are based on quaternary CrCoFeNi system, which is often considered as the simplest HEA. Accordingly, experimental and theoretical results of studies of CrCoFeNiAl$_x$ ($0 < x < 2.5$) [3–6], CrCoFeNiGe [7], CrCoFeNiGa [8], CoCrFeMnNi [9] or CoCrFeNiPd$_x$ [10] have been recently reported.
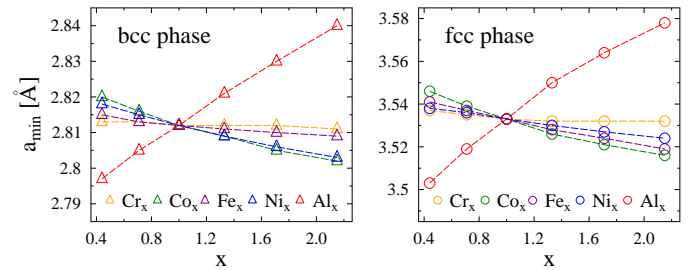

Fig. 1. Calculated lattice constants of CrCoFeNiAl systems (in *bcc* and *fcc* phases) vs. x value.

This work extends the previous theoretical studies [10, 11], focusing mostly on structural, electronic and magnetic properties in the CrCoFeNiAl HEAs. Based on results of the Korringa-Kohn-Rostoker (KKR) calculations combined with the coherent potential approximation (CPA) to account for the multi-element chemical disorder, we report some correlations between magnetic moments and their mutual ordering on transition element atoms on one hand, and the *bcc/fcc* phase preference (or coexistence) on the other one. The KKR-CPA has been already successfully applied to study the phase preference in CrCoFeNiAl$_x$ system [11] as well as to interpret the superconductivity in TaNbHfZrTi HEA [12, 13].
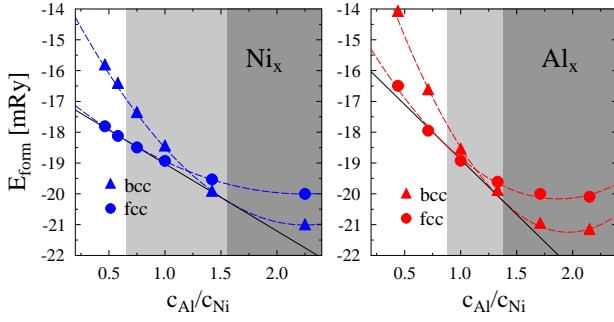
Fig. 2. Formation energies of $CrCoFeNiAl_x$ and $CrCoFeNi_xAl$ alloys from the KKR-CPA method.

Here, the crystal potential of muffin-tin form was constructed in the framework of the local spin density approximation (LSDA) and the charge- and spin-selfconsistent KKR-CPA [14] iterations were repeated until reaching the convergence of potentials and charges below 0.1 mRy and $10^{-3}e$ (e - electron charge), respectively. Total, site-decomposed and l-decomposed (with angular momentum cut-off $l_{max} = 3$) density of states, were calculated using tetrahedron $\boldsymbol{k}$-space integration technique, generating ~ 1200 tetrahedrons and $\sim 300\boldsymbol{k}$-point grid in the irreducible part of Brillouin zone. The Fermi level was precisely determined from the Lloyd formula [15].

2. Results and discussion

The KKR-CPA calculations were performed for five systems: $Cr_xCoFeNiAl$ (Cr_x), $CrCo_xFeNiAl$ (Co_x), $CrCoFe_xNiAl$ (Fe_x), $CrCoFeNi_xAl$ (Ni_x) and $CrCoFeNiAl_x$ (Al_x), where the x value was changed from 0.44 to 2.15, which is equivalent to variation of the element concentration from 10 to 35% (see Table I). The equilibrium lattice constants obtained from the total energy calculations are gathered in Fig. l. The difference between computed and available experimental values [16] does not exceed typical LDA error.

The formation energy of all considered HEA compositions (in both phases) was calculated from the well-known formula $E_{form}^{fcc/bcc} = E_{HEA}^{tot} - \Sigma_i^N c_i E_i$, where E_{HEA}^{tot} is total energy obtained at equilibrium lattice constant in bcc or fcc phases, while c_i and E_i represent concentration and total energy of i-th element bulk solid, respectively.

In the whole range of concentrations, all calculated formation energies turned out to be negative, what may tentatively support the crystal stability of the CrCoFeNiAl HEAs. Since the difference between E_{form}^{bcc} and E_{form}^{fcc} computed for Cr_x, Co_x and Fe_x systems was found to be as small as few 10^{-5} Ry, we decided to focus on Al_x and Ni_x alloys (Fig. 2), where the variation of formation energy is more pronounced. To allow for comparison of these two series, the x variable was replaced with more convenient c_{Al}/c_{Ni} ratio. In spite of quite different electronic configurations of Al and Ni atoms, the correspond-

ing differences between E_{form}^{bcc} and E_{form}^{fcc} in both alloys are very close, suggesting that c_{Al}/c_{Ni} ratio may have a strong impact on the bcc/fcc phase preference. Using the KKR-CPA x-dependent energy formation obtained in bcc and fcc phases and employing common tangent line rule, the range of phase coexistence was estimated. The regions of single fcc phase appearance (white area) or bcc (grey area) are separated by the region of their coexistence (light-grey area).

In spite of overall similarities of both HEA series, one notices that the fcc-bcc phase transition appears for $c_{Al}/c_{Ni} = 0.65$ ratio ($c_{Ni} = 14\%$) in Ni_x alloy, which is slightly smaller than the corresponding value 0.88 ($c_{Al} = 18\%$) in Al_x one. Also, in Ni_x the range of the fcc-bcc phase coexistence is broader than in Al_x. Furthermore, the phase preference changes in favor of the bcc structure for the c_{Al}/c_{Ni} ratios 1.56 ($c_{Ni} = 28\%$) and 1.38 ($c_{Al} = 26\%$) in Ni_x and Al_x, respectively. To our best knowledge, experimentally the range of the fcc-bcc phase coexistence was investigated only for Al_x HEA and both phases were detected for Al concentration between 11% and 23.8% [16], while in other work [17] the coexistence range was found to be dependent on sample preparation method, namely either $10 \div 18\%$ or $7 \div 23\%$, for as cast and homogenized alloys, respectively. Noteworthy, KKR-CPA results also remain in good agreement with previous theoretical calculations ($14 \div 24\%$) [18].

As far as the magnetic properties are concerned, KKR-CPA calculations show that total magnetic moment in bcc phase μ_{WS}^{bcc} is larger than the μ_{WS}^{fcc} value and the highest contributions arise from Fe and Co atoms, both in the Al_x and Ni_x series (Fig. 3). Besides, one can notice that except of μ_{Ni}^{bcc} in Ni_x alloy (which tends to slightly increase with x) all local magnetic moments decrease (in absolute value) with increasing c_{Al}/c_{Ni} ratio. However, some differences between two series can be notified, since in the bcc phase local magnetic moments in the Al_x series decrease more rapidly than the corresponding values in the Ni_x series. In case of the fcc phase, tendency is opposite and one observes faster change of μ_M^{fcc} (M = Cr, Co, Fe, Ni) in Ni_x systems with respect to the Al_x ones. In both systems the computed magnetic moments of Fe, Co and Ni atoms are coupled parallel (bcc and fcc) in the whole range of c_{Al}/c_{Ni} ratio, while the variation of Cr magnetic moment with HEA composition is more complex: for large c_{Al}/c_{Ni} ratio the moment was found to be oriented antiparallel to moments on other $3d$ atoms, whereas it changes the polarisation when the c_{Al}/c_{Ni} ratio is decreasing. Looking closer at shadowed backgrounds (Fig. 3) one may conclude that in Al_x and Ni_x HEA series the critical c_{Al}/c_{Ni} ratio for which the μ_{Cr}^{bcc} changes sign, almost coincides with the border composition of the single fcc phase occurence. In view of the KKR-CPA predictions of the phase preference, it seems that the Cr magnetic moment shows a strong propensity to be aligned antiparallel to moments on other transition metal atoms, both in bcc and fcc phases.
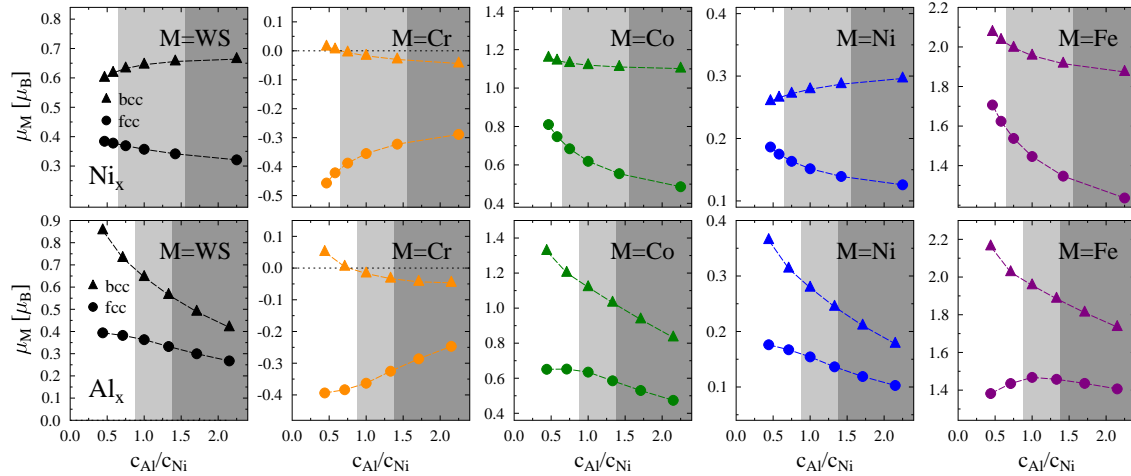
Fig. 2. Variation of average magnetic moment per Wigner-Seitz cell and local magnetic moments on consistuent atoms in $CrCoFeNiAl_x$ and $CrCoFeNi_xAl$ alloys from KKR-CPA calculations.

3. Conclusions

The results of the spin-polarised KKR-CPA calculations of the CrCoFeNiAl HEAs are presented for compositions in wide range of all element concentrations. The *fcc-bcc* phase preference as well as the phase coexistence were discussed in view of the formation energy analysis. A special attention was paid to Al_x and Ni_x series, where formation energy was found to be particularly sensitive to x. The theoretical phase diagram as well as critical composition of phase transitions quite well corroborate with available experimental data. The variation of magnetic properties with composition (c_{Al}/c_{Ni} ratio) in the $CrCoFeNi_xAl$ and $CrCoFeNiAl_x$ HEA series is rather complex, since total magnetic moment slightly decreases in both cases in *fcc* phase, while it changes in opposite way (increases in Ni_x and decreases in Al_x) in *bcc* phase. Noteworthy, in view of the KKR-CPA results, the composition limit of the single *fcc* phase occurence, both in $CrCoFeNi_xAl$ and $CrCoFeNiAl_x$ series is found to be quite close to the c_{Al}/c_{Ni} ratio when Cr magnetic moment changes its orientation with respect to the moments on Fe, Co and Ni atoms. However, Cr moment tends to be aligned antiparallel to other $3d$ moments in the energetically prefered phases.

Acknowledgments

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