Magnetic properties of CrFeCoNi based high entropy alloy

Junqi Yin and Markus Eisenbach
National Center for Computational Sciences
Oak Ridge National Laboratory, Oak Ridge, TN, USA

Makrus Daene and G. Malcolm Stocks
Materials Science and Technology Division
Oak Ridge National Laboratory, Oak Ridge, TN, USA

Abstract. Monte Carlo simulations are performed on three high entropy alloys: Cr_{0.25}Fe_{0.25}Co_{0.25}Ni_{0.25}, Cr_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Pd_{0.2}, and Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}, with exchange interactions extracted from The ab initio Korringa-Kohn-Rostoker method combined with the coherent potential approximation calculations. Using finite size scaling analyses, we estimate the magnetic phase transition temperature for the four component alloy to be 108(2) K, and although the individual critical exponents are different from 3D Heisenberg universality class, the reduced exponent follows Suzuki weak universality. With the additional Palladium component, the transition temperature elevates to about 200 K. In contrast, we find no magnetic order for the five component alloy with Manganese at any finite temperatures.

1. Introduction
The high entropy alloy (HEA) [1, 2] has increasingly drawn interests in materials science, since it opens opportunities to create novel alloys with better properties than traditional ones. However, our understanding of HEAs is still limited, especially about magnetic properties, which is important for applications requiring magnetic materials at elevated temperatures. Recent experimental studies [3, 4] measured Curie temperatures of several HEAs using CrFeCoNi as base ingredients. It is reported that CrFeCoNi is paramagnetic at finite temperatures and CrFeCoNiPd exhibits a transition temperature at about 200 K [4]. A recent study [5] also shows a transition from the paramagnetic state for CrFeCoNi to the ferromagnetic state for CrFeCoNiAl at room temperature.

In this paper, we perform Monte Carlo simulations to study magnetic properties of three different CrFeCoNi based HEAs with interaction parameters calculated from The ab initio Korringa-Kohn-Rostoker method combined with the coherent potential approximation (KKR-CPA) calculations. In contrast to Ref.[4] and [5], we observe a magnetic phase transition at a low temperature and find that the critical behavior obeys the Suzuki weak universality class.

In Sec. 2, the model, relevant methods and analysis techniques are reviewed. Our results are presented in Sec. 3 ~ 5, and we conclude in Sec.6.
2. Model and methods

2.1. Model
For all three HEAs: CrFeCoNi, CrFeCoNiPd, and CrMnFeCoNi, we only consider the case that each species has the same concentration and is randomly distributed on a FCC lattice. With exchange interactions extracted from KKR-CPA calculations, a Heisenberg model with site-dependent interactions is employed to describe the alloy systems, which is justified by the fact that no significant longitudinal spin fluctuation is observed [6] for similar systems. The Hamiltonian is defined as follows,

\[ H = \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j, \]  

(1)

where \( S_i \) is a unit vector and \( J_{ij} \) is the exchange interaction between the spin \( i \) and the spin \( j \), the value of which is determined by the species of atoms at corresponding sites and the shell (distance) with respect to each other, as shown in Fig. 1. For the first shell (i.e. the nearest-neighbor) interactions, any pairs involving Cr or Mn are antiferromagnetic except for Mn-Ni, while other components interact ferromagnetically. As the shell number increases, the \( J \) value oscillates around zero and its magnitude rapidly decreases.

2.2. Wang-Landau method
Since there are competing interactions for different shells, the more shells included, the more "glassy" the behavior becomes (i.e. the more barriers in the free energy landscape). To study the ground state structures, Wang-Landau method [7] is applied to drive the system randomly through the energy space. It is realized by updating the system according to the probability inversely proportional to the density of states.

\[ W(X|X') = \min[1, g(E(X'))/g(E(X))], \]  

(2)

where \( X \) is the system configuration.

Given an initial guess (e.g. constant), the density of states is updated iteratively. Once it converges, we will have a flat energy histogram which indicates a random walk in energy sampling. In practice, many random walkers [8] are used to speed up the ground state searching. Each walker has its own replica of the system, and they update simultaneously. Information is exchanged only by sharing a common density of state, therefore it is straightforward for the parallel implementation.

2.3. Parallel tempering and cluster update methods
Parallel tempering Monte Carlo simulations [9, 10] are employed to obtain the thermodynamics of the systems. A swap trial is performed with a Metropolis-like probability which satisfies the detailed balance condition. The transition probability from a configuration \( X_m \) simulated at temperature \( T_m \) to a configuration \( X_n \) simulated at temperature \( T_n \) would be

\[ W(X_m, T_m|X_n, T_n) = \min[1, \exp(-\Delta)], \]  

(3)

\[ \Delta = (1/k_B T_n - 1/k_B T_m)(\mathcal{H}_m - \mathcal{H}_n). \]  

(4)

Since for all three HEAs we considered the specific heat turns out to be non-divergent at the transition point, a simulation temperature set in geometric series works optimally [11].
Figure 1. Pair exchange parameters calculated from KKR-CPA method for CrFeCoNi, CrFeCoNiPd, and CrMnFeCoNi.
To counter the effect of the critical slowing down near the phase transition, we also apply the Wolff cluster update algorithm [12]. Given a randomly chosen direction $\hat{n}$, spins are iteratively added to the flipping cluster with probability

$$p = 1 - \exp \left\{ \min \left[ 0, \frac{2J_{ij}}{k_B T} (\hat{n} \cdot S_i)(\hat{n} \cdot S_j) \right] \right\},$$

and then the cluster of spins is flipped with respect to the hyperplane orthogonal to $\hat{n}$.

Therefore, a typical Monte Carlo step consists of a single spin flip trial for every spin, a cluster update for the whole system, and a replica swapping trial between neighboring temperatures.

For the data shown below, error bars are estimated from 100 different initial configurations of each alloy.

### 2.4. Finite size scaling

To study the critical behavior, we perform finite-size scaling analyses [13] near the transition point. The observable of interest are specific heat $c$, magnetization $M$, susceptibility $\chi$, and fourth order cumulant $U$, which are defined as follows,

$$c = \frac{1}{N k_B T^2} \left[ < (E)^2 > - < E >^2 \right], \; N = L^3$$

$$M = \frac{1}{N} \left[ \left( \sum_i S_i^x \right)^2 + \left( \sum_i S_i^y \right)^2 + \left( \sum_i S_i^z \right)^2 \right]$$

$$\chi = \frac{N}{T} \left[ < (M)^2 > - < M >^2 \right]$$

$$U = 1 - \frac{< (M)^4 >}{3 < (M)^2 >^2}$$

We also investigate the magnetization for each component specie with the similar definition as Eq. 7. The difference is that the summation runs over one specified type of atoms. The component $\chi$ and $U$ are defined accordingly.

Since the maximum slope of the fourth-order cumulant $U$ follows

$$\left( \frac{dU}{dK} \right)_{max} = a' L^{\frac{1}{\nu}} \left( 1 + b' L^{-\omega} \right),$$

where $K = \frac{1}{T}$, the correlation length exponent $\nu$ can be estimated directly.

With the exponent $\nu$ and critical temperature $T_c$ at hand, the critical exponent $\beta$ and $\gamma$ can be extracted from the data collapsing of the finite-size scaling forms,

$$M = L^{-\frac{\beta}{\nu}} X(t L^{\frac{1}{\nu}})$$

$$\chi T = L^{\frac{\gamma}{\nu}} \chi(t L^{\frac{1}{\nu}})$$

where $t = |1 - \frac{T}{T_c}|$, $t' = |1 - \frac{T}{T_c}'|$ and $X$ and $\chi$ are universal functions whose analytical forms are not known.
Figure 2. Snapshot of the ground state configuration for CrFeCoNi with $N = 1000$ and up to 8 shells. Red arrows denote Co; yellow arrows denote Fe; light blue arrows denote Ni; dark blue arrows denote Cr.

3. Results: $\text{Cr}_{0.25}\text{Fe}_{0.25}\text{Co}_{0.25}\text{Ni}_{0.25}$

The ground state searched by the Wang-Landau random walk is ferromagnetic for up to 20 shells included in the model. Most of the spins are collinearly aligned with Cr spins pointing the opposite direction of the other three types of spins. But some Cr spins form locally non-collinear structures whose directions are almost perpendicular to the overall magnetic direction. A snapshot of the ground state spin configuration is plotted in Fig. 2. Therefore, a magnetic phase transition is expected at some finite temperature for this four component alloy. Due to the computational cost resulting from not only linearly increased neighbors of interactions but also the "glassy" slow dynamics, the thermodynamics data in this section are collected for the model with up to 8 shells.

In Fig. 3, we show the specific heat and susceptibility for six different system sizes. A non-diverging specific heat indicates a negative $\alpha$ exponent, which is similar to the case for the classical Heisenberg model and bulk BCC Iron. A clear signal for the continuous transition is seen from the susceptibility data. The transition temperature is estimated to be $108(2)$ K according to the fourth order cumulant of the magnetization. Considering the susceptibility for each component, we find that they show more or less the same peak position. While $M_{\text{Co}}$ and $M_{\text{Ni}}$ has the largest and smallest variance, respectively, the overall susceptibility behaves like that of Iron.

As for the critical behavior, we evaluate the exponent $\beta$ and $\gamma$ following the Eq. 11 and Eq. 12,
Figure 3. Specific heat and susceptibility plots for CrFeCoNi.

Figure 4. Finite size scaling of the magnetization and its susceptibility, respectively.

respectively. The corresponding data collapsing plots are shown in Fig. 4. Both exponents are larger than those of 3D Heisenberg Universality class, but the reduced exponent $\gamma/\nu = 2.1\pm2$ is close to the Universality value 1.96(1). Many systems with competing interactions [14] or quenched disorder [15] present similar behavior which is an indication of Suzuki weak Universality.

4. Results: $\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Pd}_{0.2}$

To obtain a similar alloy but with a higher transition temperature, one can add another component that strengthens the ferromagnetic interaction. Pd-Pd has a weak ferromagnetic coupling. See Fig. 1. The ground state of CrFeCoNiPd is similar to CrFeCoNi with Pd spins pointing to the same direction as other ferromagnetic components and Cr spins partially non-collinearly aligned, as shown in Fig. 5.

In Fig. 6, The magnetization and its fourth order cumulant are plotted for the individual component and different lattice sizes, respectively. The critical temperature is estimated to be 339(2) K which is over 200 degree higher than that of the corresponding four component alloy. For the original four components, each shows similar behavior as before, i.e., similar shape of
Figure 5. Snapshot of the ground state configuration for CrFeCoNiPd with $N = 1000$ and up to 8 shells. Red arrows denote Co; yellow arrows denote Fe; light blue arrows denote Ni; dark blue arrows denote Cr; silver arrows denote Pd.

Figure 6. Magnetization and its 4th order cumulant for CrFeCoNiPd.
magnetization curve and similar individual "$T_c$". But spins on Pd becomes disorder at finite temperatures.

From the finite size scaling of susceptibility (Eq. 12) and fourth order cumulant (Eq. 10), we estimate $\nu = 0.85(2)$ and $\gamma = 1.68(4)$ which is significantly larger than that of the 3D classical Heisenberg Universality, respectively. However, $\gamma/\nu = 1.98(3)$ agrees with Universality value 1.96(1) within the error bar. It seems Suzuki week Universality holds.

5. Results: $\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}$

Another interesting topic is to investigate the effect of adding an antiferromagnetic component to CrFeCoNi. As shown in Fig. 1, Mn-Mn interaction is strongly antiferromagnetic. With the additional Manganese atom, the resulting properties change dramatically. There exists no overall magnetization at finite temperatures if enough shells (more than 3) are included in the model. With only the first three shells, we find a non-collinear ground state. In Fig. 7(a), the susceptibility for models with different numbers of interaction shells are plotted. Peaks at finite temperatures can be seen for up to 3 shells. By examining the magnetization for the individual component, the contribution to the variance mostly comes from Fe and Co. See Fig. 7(b). This behavior is different from the four component alloy where they all present similar shapes. Essentially, the spins on Cr and Ni atoms become disorder with respect to its specie at finite temperatures. As more shells included, even $M_{Fe}$ and $M_{Co}$ disappear when the temperature is higher than zero.

6. Conclusion

With exchange interactions calculated from KKR-CPA method, We have studied thermodynamic properties of three different high entropy alloys: CrFeCoNi, CrFeCoNiPd, and CrMnFeCoNi. There exists a magnetic phase transition for CrFeCoNi at 108(2) K and the critical behavior follows Suzuki weak universality. By adding Palladium to the four component alloy, we obtain a much higher transition temperature at 339(2) K. The critical behaviors of both alloys seem to follow Suzuki weak Universality. On the other hand, CrMnFeCoNi shows no magnetization at finite temperatures.
Acknowledgments

This work was sponsored by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. This research used resources of Oak Ridge National Laboratory’s Compute and Data Environment for Science (CADES) and the Oak Ridge Leadership Computing Facility, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

[1] J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsai, and S. Y. Chang, Adv. Eng. Mater. 6, 299 (2004).
[2] J. W. Yeh, Y. L. Chen, S. J. Lin, S. K. Chen, Mater. Sci. Forum 560, 1 (2007).
[3] K. B. Zhang, Z. Y. Fu, J. Y. Zhang, J. Shi, W. M. Wang, H. Wang, Y. C. Wang, and Q. J. Zhang, J. Alloys Compd. 502, 295 (2010).
[4] M. S. Lucas, L. Mauger, J. A. Muñoz, Y. Xiao, A. O. Sheets, S. L. Semiathin, J. Horwath, and Z. Turgut, J. Appl. Phys. 109, 07E307 (2011).
[5] S. Huang, W. Li, X. Li, and S. Schönecker, Materials design 103, 71 (2016).
[6] S. Mu, J. Yin, G. D. Samolyuk, S. Wimmer, Z. Pei, M. Eisenbach, S. Mankovsky, H. Ebert, G. M. Stocks, Phys. Rev. Materials 3, 014411 (2019).
[7] F. G. Wang and D. P. Landau, Phys. Rev. Lett. 86, 2050 (2001); Phys. Rev. E 64, 056101 (2001).
[8] L. Zhan, Comp. Phys. Comm. 179 (2008) 339; M. Eisenbach, C.-G. Zhou, D. M. Nicholson, G. Brown, J. Larkin and T. C. Schulthess, SC, Portland, Oregon, USA, November 14-20. ACM, New York (2009); J. Yin and D. P. Landau, J. Chem. Phys. 134, 074501 (2011); Comp. Phys. Comm. 183, 1568 (2012).
[9] R. H. Swendsen and J. S. Wang, Phys. Rev. Lett. 57, 2607 (1986).
[10] K. Hukushima and K. Nemoto, J. Phys. Soc. Japan 65, 1604 (1996).
[11] D.A. Kofke, J. Chem. Phys. 120, 10852 (2004).
[12] U. Wolff, Phys. Rev. Lett. 62, 361 (1989).
[13] See, for example, Finite Size Scaling and Numerical Simulation of Statistical Systems, edited by V. Privman (World Scientific, Singapore, 1990); D. P. Landau and K. Binder, A Guide to Monte Carlo Simulation in Statistical Physics (Cambridge University Press, Cambridge, U.K., 2000).
[14] J. Yin and D. P. Landau, Phys. Rev. E 80, 05117 (2009); Phys. Rev. E 81, 031121 (2010).
[15] J. Yin, B. Zheng, and S. Trimper, Phys. Rev. E 70, 056134 (2004); Phys. Rev. E 72, 036122 (2005).