Interdependence of Magnetic and Chemical Short-Range Order in the CrCoNi Multi-Principal Element Alloy

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The presence, nature, and impact of chemical short-range order in the multi-principal element alloy CrCoNi are all topics of current interest and debate. On the basis of first-principles calculations, we present a theory of exchange interaction-driven atomic ordering in this system centered on the elimination of like-spin Cr-Cr neighbors, with significant contributions from certain magnetically aligned Co-Cr and Cr-Cr atoms. Together, these effects can explain anomalous magnetic measurements across a range of compositions and provide implications for related high-entropy alloys.

Keywords: short-range order, magnetism, frustration, NiCoCr, high-entropy alloys

Multi-principal element alloys (MPEAs), often referred to as high-entropy alloys, have become intensely investigated in recent years as they offer a practically limitless design space that, in the small portion thus far explored, has already yielded several promising materials [1–4]. In particular, a large body of research has been devoted to face-centered cubic (fcc) systems composed of 3d transition metals, namely the equimolar (Cantor) alloy CrMnFeCoNi [5] and its derivatives. These ostensibly disordered fcc MPEAs display highly desirable combinations of mechanical properties that are attributable to deformation mechanisms [3,4] that can be tuned through careful control of alloy parameters such as chemistry [6] and even magnetic structure [7]. Another potentially important, if enigmatic, factor in the engineering of this class of materials is the presence of atomic-scale short-range order (SRO). In this regard, particular attention has been given to the equiatomic CrCoNi alloy, a representative system that is noteworthy for its cryogenic damage tolerance and general mechanical superiority to the five-component CrMnFeCoNi [8–10]. Several computational [11,12] and experimental [13,14] studies have provided evidence for both the presence and possibly significant impact of SRO in this material; however, its microscopic origin has largely escaped scrutiny.

In the present work, we employ density-functional theory (DFT) calculations to explain the large energetic driving force (∼ 40 meV/atom) for SRO that has been found in this system by previous first-principles investigations [11,12]. Our results reveal the fundamental importance of exchange interactions among Cr-Cr and Cr-Co neighbors and the role of SRO in reducing magnetic frustration inherent in random solid solutions of these elements. While previous studies have identified, in various terms, the importance of Cr antiferromagnetism in the ordering of a related CrFeCoNi alloy [11,13], the role of magnetism in the chemical SRO of CrCoNi has not, to the best of our knowledge, been carefully examined. Newly identified ordering principles are extended to non-stoichiometric Cr-Co-Ni compositions, offering an explanation for previously noted discrepancies between experimental measurements of low-temperature magnetization and DFT calculations assuming complete compositional disorder [17,18].

SRO in CrCoNi was theoretically first examined by Tamm et al. [11] through Monte Carlo (MC) optimization of on-lattice density functional theory (DFT) calculations. Their results are summarized in Table I in terms of nearest neighbor Warren-Cowley (WC) SRO parameters that are also summarized in Table I. Both

| Neighbor  | Tamm et al. [11] | Ding et al. [12] | Simple structural model |
|-----------|-----------------|-----------------|------------------------|
| Pair      | DFT-MC          | DFT-MC          |                        |
| Cr-Cr     | 0.42            | 0.40            | α_{Cr-Cr}              |
| Co-Cr     | -0.16           | -0.25           | -α_{Co-Cr}/2           |
| Ni-Cr     | -0.27           | -0.15           | -α_{Ni-Cr}/2           |
| Ni-Co     | 0.15            | 0.19            | α_{Ni-Co}              |
| Co-Co     | 0.01            | 0.06            | 0.0                    |
| Ni-Ni     | 0.12            | -0.04           | 0.0                    |

TABLE I: WC SRO parameters (see Eq. (1)) reported by two previous DFT-MC studies (columns two and three), compared to our simple structural model (column four) that is intended to relieve frustration of magnetic interactions by eliminating Cr-Cr bonds.

\[
\alpha_{ij} = 1 - \frac{P(j \mid i)}{c_j} = 1 - \frac{P(j \cap i)}{P(j)P(i)}. \tag{1}
\]

Negative values indicate more \(ij\)-type neighbors than in a random alloy (corresponding to \(\alpha_{ij} = 0\) for all neighbor types) and positive the inverse. Ding et al. [12] later performed similar simulations, finding comparable order parameters that are also summarized in Table I. Both...
FIG. 1: For (a) quasirandom, (b) Cr-Cr neighbor-minimized (αCrCr = 0.5 in the simple structural model), and (c) “spin-ordered” CrCoNi: (i) example simulation cell with (ii) WC values for chemical (αCrCr), opposite-spin (αCr↑↓), and same-spin (αCr↑↑) Cr pairs and (iii) Cr atoms plus their nearest neighbor bonds colored by magnetic moment.

computational datasets are supported by analysis of x-ray absorption fine structure from Ref. [14] and share a pronounced positive value of αCrCr that, despite very short simulation times, approaches the maximum of 0.5 for $x_{Cr} = \frac{1}{3}$ on an fcc lattice.

We build upon these prior computational studies by investigating in detail the link between magnetic exchange interactions and bonding preferences in CrCoNi solid solutions. To begin, we note that a random distribution of Cr atoms on a third of the sites of an fcc lattice will average four Cr nearest neighbors per Cr atom. Given the expected antiferromagnetic interactions between Cr atoms, this configuration will give rise to frustration among neighboring Cr moments [11, 17, 20, 21]. We examine the precise nature of this frustration—and later the energetics of the system—by employing collinearly spin-polarized DFT calculations, using the Vienna Ab initio Simulation Package (VASP) [22–24] with Perdew, Burke, and Ernzerhof’s (PBE) parametrization of the generalized gradient approximation (GGA) [25] in tandem with projector-augmented wave (PAW) potentials [26]. All simulation cells contained 108 atoms and were structurally relaxed, while electronic states were sampled in reciprocal space with a $3 \times 3 \times 3$ Monkhorst-Pack grid and 420 eV plane wave cutoff.

For the quasirandom supercell depicted in Fig. [1]a(i), the calculated local moments of Cr atoms are shown in Fig. [1]a(iii) with nearest neighbor Cr-Cr bonds identified. Even by inspection, it is clear that Cr atoms bonded to several other Cr display suppressed local moments, while those with fewer Cr bonds resolve into a network of alternating polarizations. Simplistically assigning Cr atoms “up” and “down” states from the sign of their local moment enables the calculation of a WC value for same-spin Cr (denoted $\alpha_{Cr↑↑}$) as 0.65 ± 0.04, while alternate spin pairs are commensurately more likely with $\alpha_{Cr↑↓} = -0.37 \pm 0.08$, as graphed in Fig. [1](a)(ii). Although not accounting for moment magnitudes, the importance of which is emphasized below, these numbers highlight the unfavorability of same-spin nearest neighbors. In principle, noncollinear arrangements of moments could offer a pathway to resolving magnetic frustration, but this behavior is rarely observed in Cr clusters [28] and, consistent with Niu et al. [20], we could only converge our DFT calculations to collinear solutions.

Alternatively, we find local chemical ordering can reduce the mean number of same-species nearest neighbors in the solution to as low as two ($\alpha_{CrCr} = 0.5$), which should offer significant relief for frustration. To investigate this effect further, we develop supercells following a simple structural model in which $\alpha_{CrCr}$ is the dominant ordering term and other values are non-zero only by conservation of probability. Order parameters corresponding to this picture are presented in the last column of Table I for arbitrary values of $\alpha_{CrCr}$. For $\alpha_{CrCr} = 0.3, 0.4, 0.45, 0.5$ (plus the quasirandom case of $\alpha_{CrCr} = 0$), twenty 108 atom supercells were configured according to the model. Energies and net moments for these configurations, calculated as previously described, are plotted in Fig. [2] alongside those of supercells matching the nearest neighbor WC parameters of Tamm et al. and Ding et al. reproduced in Table I. It should be em-
emphasized that these are not exact replicas of those studies’ configurations. Indeed, Tamm et al. report a formation energy of 43.7 meV/atom, lower than the 62.2 ± 2.7 meV/atom recalculated presently—the discrepancy between these values suggests the importance of additional correlations, which we will address shortly.

Nevertheless, the results displayed in Fig. 2 indicate, within the margin of error (standard deviation of twenty supercells), the energy and magnetization of all configurations linearly follow \( \alpha_{CrCr} \). In the extreme case of \( \alpha_{CrCr} = 0.5 \), formation energy and net moment are 52.0 ± 3.5 meV/atom and 0.054 ± 0.04 \( \mu_B \)/atom, respectively, reduced from 88.0 ± 3.3 meV/atom and 0.28 ± 0.04 \( \mu_B \)/atom for a quasirandom solution. As reflected in parts (ii) and (iii) of Fig. 1(b), we can attribute reduction in net moments and energies to the minimization of Cr nearest neighbors with aligned local moments; indeed, \( \alpha_{CrCr} \) approaches unity (i.e., zero like-spin bonds). Identification of Cr-Cr bonds as the dominant neighbor interaction fulfills the purpose of the simple structural model. However, the large variation in atomic moments obtained from supercells with the same value of \( \alpha_{CrCr} \) implies that other types of interactions are also relevant. Indeed, for configurations with the same \( \alpha_{CrCr} \) there exists a strong correlation between moment and energy: those with lower net magnetizations, which arise from local moments closer to integer \( \mu_B \) values (±2 for Cr, 1 for Co), are also more energetically favorable.

After analyzing many aspects of these configurations, we have identified two additional ordering factors clearly affecting energy and magnetization. First, Co is found to favor moments that are antiparallel to those of neighboring Cr atoms, as shown in Fig. 3 considering the \( \alpha_{CrCr} = 0.5 \) configurations. While Ni atoms possess negligible local moments under all degrees of order, most Co align ferromagnetically, the direction of which will define a reference spin “up” state to which Cr atoms are either aligned (Cr↑) or opposed (Cr↓). The preferred anti-alignment of Cr and Co moments is reflected in Figs. 1 and 3 (as well as Tamm et al.), where Cr↓ outnumber Cr↑ 3:1. There exists a simple explanation for this ratio: \( x_{Cr↓} = \frac{1}{4} \) is maximum possible concentration that can exist on an fcc lattice with no nearest neighbors, while \( x_{Cr↑} = \frac{1}{12} \) represent the remaining Cr. The antiferromagnetic alignment of Cr-Cr and Cr-Co pairs is consistent with Anderson-type theory of magnetic interactions, as is the suppression of Ni moment in the vicinity of these elements.

The second ordering principle is that the magnitude of a Cr↓ atom’s moment correlates strongly with the sum of the local moments of its Cr second-nearest neighbors, as also shown in Fig. 3. In particular, these data indicate that second-nearest neighbor sublattices of Cr↓ (i.e., Cr↓ with six Cr↓ second-nearest neighbors) consistently display -2 \( \mu_B \) local moments. Furthermore, configurations containing the most Cr↓-Cr↓ second-nearest neighbors possess the lowest Cr↓ moments, overall magneti-
FIG. 4: Zero-field and temperature magnetization predictions for CrCoNi calculated with several different approaches, compared to 5K experimental measurements [17] for a range of Cr concentrations where \( x_{\text{Co}} = x_{\text{Ni}} = (1 - x_{\text{Cr}})/2 \). Supercell data represent the average of five distinct configurations.
(DFT) ground state via a martensitic mechanism, perhaps buoying the alloy’s metastability. We further postulate that the ability of SRO to minimize frustration among Cr atoms could be determining the fcc CrCoNi solution’s compositional range of stability. Indeed, the above results raise many questions; e.g., can the energetics of stacking faults in CrCoNi be connected to the presence of like-spin Cr bonds to the same degree as we showed for bulk energy? As a potential corollary, will Cr spins reorient as their local environment is changed by the transmission of dislocations—and how will the dynamics of this process affect slip properties? Given the more prevalent role of magnetism at low temperatures, we wonder if it could be connected to the material’s superior mechanical performance at cryogenic temperatures.

Nonetheless, we believe we have identified the magnetic interactions dictating chemical ordering behavior in fcc CrCoNi. In summary, this is primarily the unfavorability of like-spin Cr-Cr bonds, leading to frustration in a random solid solution. Complementarily, Co preferring to maximize their second-nearest neighbor alignment, which increases their local moments to negate those of opposite-spin Cr and Co, matching experimental measurements of minimal net magnetization. Together with a reduction in magnetically aligned Co-Cr pairs, these principles lead to a “spin-ordered” state we predict to further reduce energy while remaining largely disordered in chemical terms. This investigation highlights not only the dominant role of magnetism in the SRO of a representative MPEA, but also the need to analyze the ordering of these materials in spin-polarized rather than purely chemical terms.

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