Order Parameter Engineering for Random Systems

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Abstract

The chemical short-range order (CSRO) in crystalline materials influences the properties, and its effect is significant in the context of multicomponent materials. We propose a scheme for the CSRO parameter or \( \Delta \)-parameter in terms of the number of like and unlike bonds in the multicomponent systems. The OPERA or Order Parameter Engineering for RAndom Systems scheme for semi-canonical and canonical ensembles is proposed. The proposed framework of \( \Delta \)-parameter with OPERA framework can generate the single-phase supercell with desired CSRO without explicit energy calculations and provides a computationally efficient scheme for exploration of the CSRO. We demonstrate the applicability of the \( \Delta \)-parameter as a scalar quantity for describing the CSRO in multicomponent alloys and oxides (FCC-CoCrNi, BCC-MoNbTaW, and (CoCuMgNiZn)O).

Keywords

High-entropy alloys · Chemical short-range order · Order parameter · Thermodynamics

Introduction

The chemical short-range order (CSRO) has recently garnered significant attention due to its direct influence on properties. Such interest has been particularly prominent in the high-entropy materials community. Initially, high-entropy alloys were assumed to be perfectly chemically disordered, with elements residing randomly on the lattice sites. However, such a view was changed with both the experimental [1, 2] and theoretical investigations [3–5], which pointed out that CSRO is critical structural information that needs to be considered to develop the understanding of structure–property correlation in high-entropy materials. The CSRO can influence the mechanical properties of high-entropy alloys [6–9]. It has been demonstrated that local-chemical ordering can influence the dislocation activity in high-entropy alloys [10]. The CSRO can not only affect the Frank-Read source activation [11], but it also influences the cross-slip of the screw dislocations by increasing the activation barrier for dislocation movement leading to the reduction in the dynamic recovery [12]. It has been documented that CSRO is influenced by lattice distortion [13]. The CSRO also tunes the melting behaviour of HEA [14], localises lattice diffusion [15] and influences defect evolution in HEA [16]. In CoCrNi, the CSRO has been reported to be magnetically driven with repulsion between Co–Cr and Cr–Cr bond pairs [17]. CSRO influences properties and can act as nucleation sites for BCC to HCP phase transformation in refractory high-entropy alloys [18]. The presence of the multihyperuniform long-range order in high and medium entropy semiconductor alloys leads to the emergence of CSRO, which further decreases the configurational energy of the configurations compared to the structures without CSRO. It has been shown that such CSRO may be the reason behind the successful application of the rule-of-mixture approach for predicting properties in multicomponent semiconductor alloys [19]. The CSRO has been shown to influence the structural properties in the context of alloys and play a crucial role in tuning the functional properties of other high-entropy materials, such as disordered rocksalt-structured materials [20] and high-entropy rare-earth niobates and tantalates [21].

The CSRO is a local atomic property, and it is not straightforward to determine such property through experimental approaches, such as high-resolution transmission electron microscopy studies [2, 22–24], neutron total
scattering with extended X-ray absorption fine structure [9, 25] technique, etc. To deal with such a challenge, computational approaches involving Monte Carlo simulation with ab initio calculations [26, 27], cluster-expansion formalism [4, 28, 29] or with interatomic potential (classical [30–32] or machine-learned [33] interatomic potentials) has been carried out. Hybrid Monte Carlo Molecular Dynamics approach, in which the molecular dynamics can mimic the finite temperature oscillations of atoms at their lattice sites, while Monte Carlo swaps of atomic species between lattice sites are carried out. Such an approach could predict the CSRO in MoNbTaW high-entropy alloy [3, 7]. Another method involves the application of the linear response theory for the prediction of CSRO in HEA [5]. In such an approach, electronic structure calculations are employed to explain CSRO at high temperatures and incipient long-range order in high-entropy alloys. In the above-stated approaches, the emphasis is on the identification of CSRO through tedious experimental approaches or through computationally expensive methods. However, we aim to address the issue of CSRO through the inverse methodology. In the present approach, we aim to develop a method for generating CSRO in the atomic configuration without explicit energy calculations and studying the effect of CSRO on the properties in contrast to the traditional approaches, where the CSRO needs to be determined first, and the correlation between CSRO and properties are ultimately developed. In the present approach, CSRO for any crystalline material can be tuned in the supercell approach, which may be later used for simulating the variation in the properties.

It should be noted that Yu et al. have also developed a random structure generator with short-range order, which employs the Markov-Chain Monte Carlo method [34] and more recently, Fey et al. has developed a CSRO generation mechanism through the technique known as the order through informed swapping (OTIS) [35]. In addition to the above, we aim to develop the CSRO generation scheme, which does not involve the energy calculation step, and hence, numerous supercells with desired CSRO can be generated, aiding the high-throughput computational exploration of CSRO in chemically disordered crystalline lattice. In addition to the above, it should be noted that the proposed approach can also be employed to generate the structures, which are far-from equilibrium. Such configurations can be beneficial for studying CSRO phenomena through irradiation [9, 36] or deformation-induced CSRO [37], which might not be accessible through the traditional approaches, which can only generate the equilibrium-ordered structure. The present approach can also be employed for the development of multipoint ordering in complex multicomponent materials [38]. This approach can also be used for generating supercell with desired CSRO, which at this stage needs to be determined through computationally expensive approaches, as discussed earlier.

### Defining the Δ-Parameter

The concept of order parameter stems from Landau’s critical transition theory [39]. The objective of defining order parameter was to quantify any phase transition. Landau predicted that order parameter should attain a zero value in the disordered phase, while it should have a non-zero value in the ordered low-temperature phase. In addition to the above, such order parameter should have different values in different phases. The theory of order parameters was also generalised to determine the critical point in phase transition, which is quantified in terms of divergence of susceptibility of the order parameter. However, for the configurational-order parameter, such susceptibility is undefined. Hence, the configurational-order parameter should have zero value at complete disorder and non-zero value due to ordering, and it should have different values for different crystal structures. An initial attempt to describe the ordering and order–disorder transition conceptually addresses the problem as disorder arising due to thermal agitation. In such cases, the long-range order parameter (S) is defined as a fraction, which is $0 \leq S \leq 1$, where the value of 0 quantifies complete disorder, while 1 implies the complete order. Note that in such a framework, $S$ is defined as $S = \frac{r - 1}{r}$, where $p$ is the probability of finding the atom in its ‘right’ position. Note that by an atom in its ‘right’ position, it is implied that in the ordered state, a particular atom is residing in its sub-lattice, while $r$ denotes the fraction of sites occupied by this particular atom.

In Bragg-Williams (BW) approximation [40], the energy change due to the movement of the system from the perfect order (which is assumed to be of minimum) to the perfect disorder involves the change in the energy. Such change in energy arises due to the interchange of atoms from their ‘right’ to ‘wrong’ positions. In this approach, the drop of order parameter to zero value has been rationalised in terms of energy required for interchanging the atomic position in the course of disordering. It has been considered that the major interaction between atoms arises due to the nearest-neighbour interaction, and hence, the concept of short-range order was introduced, which in this approach could be calculated using nearest-neighbour pair interaction energy. Formally, short-range order in BW approach is defined in the term of difference in the probability of finding unlike and like atoms. As the disorder increases, the number of ‘wrong’ pairs (like atoms) increases and at the complete disorder, the number of ‘right’ and ‘wrong’ pairs are equal. In the BW approach, two opposing tendency of ordering, i.e.
superlattice formation and clustering, are being considered to yield a scalar value to quantify the short-range order. In such a scenario, when the temperature is lower than the order–disorder transformation temperature, the short-range order is an intermediate stage of the long-range order.

The Warren-Cowley (WC) order parameter [41] has been extensively applied for describing the ordering behaviour. Here, the order parameter for the species i and j may be expressed in term of \( \alpha_{ij} \), which is,

\[
\alpha_{ij} = 1 - \frac{P(j|i)}{c_j}
\]  

where \( P(j|i) \) is the probability of finding j atom near i atom and \( c_j \) is the concentration of j atom. The WC order parameter can have value between –1 and 1, with value of –1 implying complete superlattice formation, while at 1 complete clustering exists, and zero value describing complete disorder. The WC order parameter needs to be defined for each pair. This order parameter provides a way to correlate the chemical ordering with the peak of autocorrelation or Patterson function. Note that the peak positions of the autocorrelation function are dependent on the interatomic distances. Hence, WC order parameter provides the information about the average environment of the atom. It should be noted that \( \alpha_{ij} \) can describe the intensity of diffuse scattering in the reciprocal lattice, and therefore, these order parameters have direct experimental validity [41].

Warren-Cowley order parameter were originally developed for binary alloys with Bethe’s approximation or pair approximation to deal with ordering. The Warren-Cowley approach has been extended to multiple-component high-entropy alloys. However, high-entropy or multiple-component materials pose a significant challenge in accurately describing ordering. For example, the Warren-Cowley approach cannot describe the ordering motif, where higher-point ordering than two-point ordering are possible (e.g. oxides with multiple metal atoms at cation sites) [38]. Also, instead of one scalar value representing the degree of randomness, it is represented as a matrix with an order parameter for each of the atomic pairs. To overcome these issues of the Warren-Cowley approach in describing ordering in High-Entropy materials, recent efforts have been to quantify the order parameter as a single scalar value capable of describing the ordering in a chemically complex structure [13, 42].

In view of the above, we describe an order parameter for chemical ordering in High-Entropy materials. In our approach, the degree of disorder is expressed in terms of a scalar value, capable of dealing with chemically complex materials, while keeping the merits of the Warren-Cowley order parameter. Furthermore, such a scalar-order parameter, which can distinguish between like and unlike atom ordering does not need explicit energy calculations. The short-range order parameter (SRO) is defined in terms of the \( \Delta \)-parameter, which may be expressed as follows:

\[
\Delta = \beta_{ij} + \beta_{ji} = \frac{\sum_{i\neq j}^{K_1} (1 - \frac{m_{ij}}{2n})}{K_1} + \frac{\sum_{i\neq j}^{K_2} (\frac{m_{ij}}{n} - 1)}{K_2} \tag{2}
\]

In Eq. 2, \( \beta_{ij} \) and \( \beta_{ji} \) are the components of \( \Delta \)-parameter for unlike and like bonds, respectively, \( n \) is the number of like bonds in the perfectly disordered solid solution, \( K_1 \) and \( K_2 \) represent the number of type of unlike and like bonds, respectively and \( m_{ij} \) and \( m_{ji} \) represent the number of unlike and like bonds in the supercell, respectively. It should be noted that by like bonds, we mean the bonds between same chemical species, while unlike bond corresponds to the bonding between dissimilar chemical species. We note that Eq. 2 has been derived with an understanding that \( \Delta \) parameter may vary between [−1,1] with attaining the value of 0 at the complete chemical disorder. The number of like bonds \( n \) in the perfectly disordered solid-solution can be expressed as follows:

\[
n = \frac{N}{(2K_1 + K_2)} \tag{3}
\]

Note that the probability of finding the unlike bonds is twice the like bonds in the solid solution (see Sect. 1 in the Supplementary Information (SI)) and this is the reason for the 2n as normalising factor in the \( \beta_{ij} \) and \( 2K_1 \) in the denominator of Eq. 3. The \( N \) in the above equation is the total number of bonds in the supercell. Note that there is no cut-off in the \( \Delta \)-parameter, so the determination of \( m_{ij} \) is not limited to the identity of the coordination shell; rather it is being calculated for the full supercell, making this parameter capable of dealing with multipoint ordering. The introduction of the CSRO in the supercell can be thought of as a deviation from the disorder in the supercell [43], where the positive value of \( \Delta \)-parameter can be attained by increasing instances of like bond(s) and negative value of \( \Delta \)-parameter can be attained by increasing the instances of unlike bond(s). Since there are \( K_1 \) types of unlike bonds and \( K_2 \) types of like bonds, the particular value of \( \Delta \) can be imposed by increasing the propensity of a specific bond type. So, the first step of the generation of a supercell with desired CSRO involves the generation of chemically disordered structure.
Random Structure Generation

The generation of random structure is the first step towards creating a structure with predefined short-range order. The generation of the chemically disordered or random structure, as shown in Fig. 1, is carried out in the sequential manner. The first step of the random structure generation involves the random shuffling of atomic positions. It generates the structure with random atoms at the crystal lattice sites, generating a pseudo-random structure. The generated structure is quantified in terms of the vector, $B_{\text{real}}$, which may be represented as follows:

$$B_{\text{real}} = [m_{ii} m_{ij} \ldots m_{ik}]$$  \hspace{1cm} (4)

where $m_{ii}$ represents the like-bond number or bond between similar types of chemical species (i.e. $i$), while $m_{ij}$ is an unlike-bond number or chemical bond between unlike chemical species (i.e. $i \& j$, where $i \neq j$). The $m_{ii}$ or $m_{ij}$ in the present investigation have been determined using the neighbourlist functionality of the Atomistic Simulation Environment (ASE) [44]. The difference of the pseudo-random configuration generated through random shuffling is quantified in terms of the Euclidean distance between the $B_{\text{ideal}}$ and $B_{\text{ideal}}$. The $B_{\text{ideal}}$ is the vector containing the ideal bond numbers for like and unlike bonds for the complete chemical disorder. The ideal bond number ($n$) for like bond is defined by Eq. 3, while the ideal bond number for the unlike bond is $(2 \cdot n)$. The pseudo-random structure generated through random shuffling is further randomised through the swapping of atomic positions to ensure that the swapping leads to the lower value of $\|B_{\text{ideal}} - B_{\text{real}}\|$. The simulated annealing (SA) of initially pseudo-random structure is initially carried out, where configurations are heated to $0.1 \cdot \|B_{\text{ideal}} - B_{\text{real}}\|$ and then these configurations are cooled to 0 through the linear cooling protocol in $10 \cdot \|B_{\text{ideal}} - B_{\text{real}}\|$ steps (Fig. 1). Such swapping sequentially leads towards the random structure. However, if the structure is stuck in the combinatorial bottleneck (i.e., when any swapping does not lead to decrease in $\|B_{\text{ideal}} - B_{\text{real}}\|$), then exploration of other combinatorial landscape is allowed (perturbation). Once the configuration has reached the condition of $\|B_{\text{ideal}} - B_{\text{real}}\| = 0$, the swapping process is stopped (Fig. 2a). It can be seen in Fig. 2b that the number of steps for attaining the perfectly random structure increases with the increase in the number of elements in an alloy. It is understandable as the number of elements in the alloy increases the combinatorial complexity increases. Figure 2c shows the influence of SA and perturbation on the number of steps required for generating the
chemical disordered configuration for a 5-component alloy. It should be noted that even though SA and perturbation lead to the increased number of steps for generating perfectly chemically disordered structure, it ensures that a system is not stuck in the combinatorial bottleneck indefinitely.

**Generation of Configurations with Desired CSRO**

The CSRO is imposed on the perfectly chemically disordered supercell with the compositional constraint. To keep the composition constant, swap algorithm, as shown in Figs. 3a and b, has been devised. Initially, depending upon...
Fig. 3 Algorithm for chemical short-range order generation from the random structure. a Showing the schematic of the CSRO generation algorithm. A supercell with randomly distributed chemical elements on the lattice site is encoded as a string, with each entry representing an atom. The CSRO can be generated by swapping atoms. b Showing the details of the swap process. Considering ABCD as a hypothetical material system, where AD is the preferred bond (of various bonds such as A–A, A–B, A–C, A–D, B–B, B–C, B–D, C–C, C–D, and D–D). Two groups of bonds are defined such that swaps between group-1 and group-2 bonds lead to an increase in the preferred bond. As shown in the figure, AC and BD belong to group-1 and group-2, respectively. The swap between AC and BD leads to an increase in AD and BC bonds. CA₁ and CA₂ is the central atom in group-1 and group-2, respectively. SP₁ and SP₂ is swap pair in group-1 and group-2, respectively. Note that CN₁ and CN₂ are the nearest neighbours of CA₁ and CA₂, respectively. Also, NN in the figure is the abbreviation of the nearest neighbour.
the preferred bond (whose propensity needs to be increased), two groups of bonds are determined (group-1 and group-2). For example, in an ABCD alloy, if the A–D bond is the preferred bond, then swapping between (A–A, C–D), (A–B, D–D), as well as (A–C, B–D) can increase the preferred bond propensity. In this case, A–A, A–B, and A–C can belong to group-1, while C–D, D–D, and B–D bonds constitute group-2. One atom from the group-1 bond, which forms the preferred bond and another atom from group-2, which is not part of the preferred bond, form the central pair or \([CA_1, CA_2]\), respectively. While the left atom in group-1 and group-2 bonds form a swap pair or \([SP_1, SP_2]\), respectively. Next, the nearest neighbour of \(CA_1\) (CN1) and \(CA_2\) (CN2) is determined. It should be noted that in each swap iteration, newly changed atomic positions are interred into the forbidden list or FL. The idea behind this list is to put the constraint that once an atomic swap has been carried out to generate the required preferred bond, it should not be changed in the subsequent iterations. Suppose the swap between bonds AC and BD yields AD and BC or swap(AC, BD) → AD, BC. A slightly different swap algorithm is employed depending on whether AD or BC is the preferred bond.

In the CN1, there is a possibility that some of the atoms might already be in the FL, while other atoms might include SP1 and SP2. If the preferred bond is AD, then the CA1 is A. SP2 is directly interred into FL, as CA1 and SP2 already are forming the preferred bond or AD. SP1 atoms in the CN1 are swappable atoms in CN1 (X). Similarly, CA2 is B, whose nearest neighbours are CN2. SP1 atoms in CN2 are determined, and if any of these atoms have CA1 as their nearest neighbour, those are interred into FL, while other SP1 atoms constitute the swappable atoms in CN2 (Y). The number of swaps possible is then \(|X – Y|\).

If BC is the preferred bond in the above-stated swap scenario, in that case, SP1 atoms in CN1 are checked if they have CA2 as their nearest neighbours. Such SP1 atoms are added to the FL, while the remaining SP1 atoms are swappable atoms in CN1. In CN2, SP1 atoms are added to FL, while SP1 are swappable atoms in CN2 or Y. The number of swaps possible in such a scenario is again \(|X – Y|\).

Figure 4 shows the variation of \(\Delta\)-parameter for body-centred cubic (BCC) and face-centred cubic (FCC) lattice for 180 atom supercell. 1000 runs were carried out sequentially for 1 to 3 atom ordering (i.e. number of times atomic swaps have been carried out to increase the desired preferred bond). It can be seen that statistically \(\Delta\)-parameter is different for BCC and FCC phase, which is the first condition as depicted in Landau’s theory [39]. Note that the Landau first condition for the order parameter is that the order parameter has different values for different phases. We additionally demonstrate the effect of various constraints (i.e. no constraint, atomic identity constraint, and full constraints involving the forbidden lists) on the number of swaps possible, while keeping the composition constant. Initially, we analytically study the number of atoms which may be swapped if the identity of the bonds is like bond and unlike bond, without any consideration to the identity of atoms forming these bonds (unconstrained case). As mentioned in the Sect. 2 of SI, the change in the preferred bond number required for \(\Delta > 0\) (the preferred bond is a like bond) is
While for $\Delta < 0$, the required change in the preferred unlike bonds is

$$a = \frac{2 \cdot K_2 \cdot \Delta \cdot n \cdot (2K_1 + K_2 - 1)}{(2K_1 + K_2)}$$

(5)

While for $\Delta < 0$, the required change in the preferred unlike bonds is

$$a = -\frac{2 \cdot K_1 \cdot \Delta \cdot n \cdot (2K_1 + K_2 - 1)}{(2K_1 + K_2)}$$

(6)

While, if the bond identity is introduced (atomic identity constraint), the concept of the preferred bond becomes more specific in the comparison of the above-stated case, where only like and unlike bonds were considered. The identity of the preferred bond further narrows down the bonds which may be swapped to generate the preferred bond. As shown in the Sect. 3 of SI, the number of bond swaps for $\Delta < 0$ may be given as follows:

$$a = \frac{\Delta \cdot K_1 \cdot K_2 \cdot n \cdot (-5e - 4)}{(e^2 \cdot K_1 + 7e^2 \cdot K_2 - 4e \cdot K_1)}$$

(7)

Fig. 5: Variation of the number of preferred bonds (like and unlike, depending upon the $\Delta$) for systems containing a different number of elements. The $y$-axis represents the normalised bond number, which is the value of number of bonds which need to be increased in addition to the number of bonds at the perfect chemical disorder, (i.e., $n$ for like bonds and $2n$ for unlike bonds) divided by either $n$ (for like bonds) or $2n$ (for unlike bonds) and b normalised bond number for a different number of elements, as the full compositional constraint is applied in the OPERA framework.
If \( \Delta > 0 \), then
\[
a = \frac{2 \cdot \Delta \cdot K_1 \cdot K_2 \cdot n}{(2K_1 + K_2) \cdot \left( e - \left\lfloor \frac{e}{2} \right\rfloor - 1 \right)}
\]  
(8)

where \( e \) is the number of types of atoms in the system. Note that \( \lfloor \cdot \rfloor \) in the above expression represents the floor operator.

It can be seen in Fig. 5a that as the number of elements in the unconstrained case increases, the required number of like as well as unlike bonds increases, which implies that as the number of the type of elements in the material increases, it becomes increasingly difficult to attain the complete ordering in both sides of the disorder. As the atomic identity constraint is introduced and in addition to the identity of bond (like or unlike), the atomic identity of bond-forming elements becomes crucial, and the number of bonds, which may be swapped for desired ordering is also reduced (beyond 3 elements). Note that in case of a binary system, \( \Delta > 0 \) is not possible if the composition of the supercell needs to be constant, as the only bonds available except like bonds is an unlike bonds. The swap between this bond cannot lead to the desired like bond. So, normalised bond number (value of a bond number of a preferred bond divided by the \( n \) or \( 2n \), if the preferred bond is like and unlike bond, respectively) is zero for \( \Delta > 0 \). For the ternary system, it should be noted that for \( \Delta < 0 \), the normalised bond number for the atomic identity constraint is lower than that of unconstrained case. However, for \( \Delta > 0 \), it can be seen that normalised bond number for the unconstrained case is lower than the atomic identity constraint. Such observation can be rationalised in terms of value of unlike bonds (\( K_1 \)) and like bonds (\( K_2 \)). Ternary systems are the only case, where \( K_1 = K_2 \). Figure 5b shows the normalised bond number for binary, ternary, quaternary, and quinary systems as determined by carrying out 1000 runs for each case to determine the maximum bond change possible using OPERA code.

Both of the above-stated analytical schemes (unconstrained and atomic identity constraint) provide the upper bounds for the number of bonds desired to attain the particular \( \Delta \) value. But in reality, as we introduce the constraints in the OPERA scheme, where the composition of the supercell needs to be constant, the bond numbers which can be altered is 2 order of magnitude lower than the upper bounds as discussed earlier (Fig. 5b). Note that the variation of normalised bond number for \( \Delta > 0 \) and \( \Delta < 0 \) represents the variation when unlike and like bonds is generated through OPERA, respectively. It should also be noted that the normalised bond number is not the monotonic function of the number of types of elements in the system. Rather, it is determined by the combinatoric landscape of the multicomponent system.

\section*{Comparison of the \( \Delta \)-Parameter with the Warren-Cowley CSRO Parameter (\( \alpha_{ij} \))}

Figure 6 shows the variation of \( \alpha_{ij} \) parameters for a configuration of a CoCrNi alloy, where the propensity of Cr–Cr bonds was sequentially increased from the chemically increased number of Cr–Cr bonds sequentially. In this case, with an increase in Cr–Cr bond number, Co–Cr and Cr–Ni bond numbers decrease, and Co–Ni and Ni–Ni bonds increase, while the Co–Co bond number remains constant during the iteration.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6}
\caption{Comparison of Warren-Cowley order parameter (\( \alpha_{ij} \)) calculated for a configuration of FCC-CoCrNi alloy with \( \Delta \)-parameter calculated for the same configuration. Note that the x-axis of each plot corresponds to the iteration number, which corresponds to the increased number of Cr–Cr bonds sequentially. In this case, with an increase in Cr–Cr bond number, Co–Cr and Cr–Ni bond numbers decrease, and Co–Ni and Ni–Ni bonds increase, while the Co–Co bond number remains constant during the iteration.}
\end{figure}
disordered value (i.e., \( n \) as given by Eq. (3)) to the maximum value of Cr–Cr bonds possible in the 5 steps. Since we would like to maintain the composition of the supercell to generate desired CSRO, there are associated changes in the bond numbers. In the above-stated case of CoCrNi, with the increase in Cr–Cr bond, there is a decrease in the Co–Cr and Cr–Ni bonds, while there is increase in Co–Ni and Ni–Ni bonds. The Co–Co bond numbers remain constant. For such a scenario, it can be seen that \( \Delta \) parameter increases linearly with increase in the number of Cr–Cr bonds. However, it should be noted that even the Cr–Cr bonds are increasing, the value of \( \alpha_{\text{CrCr}} \) is decreasing, which is counterintuitive. However, as it can be seen in Eq. (1) that the Warren-Cowley CSRO parameter calculation for like bond would involve the expression \( 1 - \frac{P_{ii}}{c_i} \), where the \( P_{ii} \) is the probability of \( c_i \) finding atom \( i \) in the required coordination shell of \( i \), while \( c_i \) is the concentration of the same atom. Note that, in the present discussion, we are keeping the concentration of the ensemble of atom constant and due to the increase in Cr–Cr bonds, the \( P_{ii} \) term is increasing, but the \( c_i \) is constant. So, the value of \( \alpha_{\text{CrCr}} \) bond is decreasing; even the Cr–Cr bond propensity is increasing. Such observation points towards the fundamental limitation of Warren-Cowley CSRO for dealing with constant composition configurations, as it requires the semi-grand canonical ensemble in this scenario. But it can be seen that \( \Delta \) parameter is monotonically increasing with the increase in the Cr–Cr bond propensity in canonical ensemble (while the composition is constant), and \( \sum \alpha_{ij} \) is decreasing monotonically. Hence, the \( \Delta \) parameter can quantify the like ordering in the above-stated scenario.

**Validation of Proposed \( \Delta \)-Parameter**

We validate the proposed order parameter or \( \Delta \)-parameter with respect to the energetic change associated with the occurrence of the order in FCC medium entropy alloy (CoCrNi) and BCC high-entropy alloy (MoNbTaW) (Fig. 7a and b). We use first-principles-based linear scaling Density Functional Theory code, Locally Self-consistent Multiple Scattering (LSMS) \([45, 46]\) to calculate the energies, magnetic moments, and charges in these systems. Within LSMS, we use all parameters such that the energies are converged to within tolerances of \( 10^{-6} \) Ry/atom. We introduced the order in CoCrNi system by increasing the propensity of Cr–Cr bonds (or causing the increase in the \( \Delta \)-parameter) and studied the energy difference due to such variation. It can be seen that increased Cr–Cr interactions lead to a greater energy value, which has been reported in the literature \([47]\), while for BCC high-entropy alloy, we order the Mo–Ta bond, and it can be seen that with an increase in the number of Mo–Ta bond and hence decrease in the \( \Delta \) value, the energy of the alloy decreases, which again agrees with the reported results \([3]\). We also studied the effect of the ordering on the charge disproportion (i.e., the difference in the charge on the atom before and after the electronic minimisation. The negative value implies the gain in charge and vice versa), atomic magnetic moments, and site energies of atoms. It can be seen that

Fig. 7  
\( a \) Variation in energy with increase in \( \Delta \) due to greater Cr–Cr bonds and \( b \) Decrease in the energy of MoNbTaW HEA due to increase in Mo–Ta bonds, leading to decrease in \( \Delta \) parameter
the statistically charge disproportion and site energies for the Co and Ni atoms show the decreasing trend, while for the Cr atoms, the opposite trend can be seen (Fig. 8a and b). The magnetic moment for Co and Ni show weakly increasing trend, while the opposite can be seen for Cr (Fig. 8c). In the case of Mo–Ta bond ordering in MoNbTaW alloy, it can be seen that with an increase in the ordering, the charge disproportion and site energies show decrement for Mo atoms, while increment for Nb and Ta atoms. It is interesting to see that W atoms do not show any clear trend (Fig. 9). It should additionally be noted that with simply variation in the order parameter by $10^{-2}$, we can observe noticeable effect on the charge transfer characteristics, which points towards the long-ranged effect in charge transfer in high-entropy alloys [48].

Case of Ordering in High-Entropy Oxide

We additionally employ the OPERA framework to generate the cation ordering in (CoCuMgNiZn)O, high-entropy oxide. In such cases, the ordering can take place on multiple sub-lattices. Figure 10 shows the variation in the energy with the $\Delta$ order parameter for two cases. In the first case (constant composition), the composition of the supercell is kept constant and Cu$^{2+}$–Cu$^{2+}$ instances are increased, as carried out for alloys in the earlier section. In this case, the ordering was being carried out only on the cation sub-lattice (i.e. second nearest-neighbour ordering). It can be seen that an increase in the ordering does not lead to a trend in the energy. Such observation can be rationalised in terms of the observation that, since anion sub-lattice has only O$^{2-}$ anion,
the effect of first nearest-neighbour bond energetics do not influence the total energy of the system. But when we vary the composition of the supercell to increase the number of Cu$^{2+}$–O$^{2-}$ bonds by decreasing the Co$^{2+}$–O$^{2-}$ bond, the energy of the system decreases with a trend, as observed earlier for such oxides [49]. Through this approach, we demonstrate that OPERA approach can be employed for varying composition of the supercell in desired manner.

It should also be added that in the present investigation, the applicability of the OPERA framework for the single site ordering with ordering taking place in the cation sub-lattice has been demonstrated. However, the OPERA framework can be applied to study the complex ordering at multiple sub-lattices, which can take place in other high-entropy systems such as perovskites [50, 51], carbonitrides [52, 53], boronitrides [54], and other complex ceramics [55, 56].

**Conclusions**

The proposed work provides a high-throughput framework or OPERA (Order Parameter Engineering of RAndom Systems) scheme for studying the chemical short-range order in high-entropy materials. Instead of generating the CSRO configurations through a computationally expensive scheme, which requires either *ab initio* calculations or interatomic force fields, the OPERA method generates the desired configurations through combinatoric sampling without explicit energy calculations. Such a method allows for the exploration of both equilibrium and non-equilibrium structures. The proposed approach has been demonstrated for single-phase alloys, but it may be employed for multiphase systems, which will be explored in future investigations. This framework inherits the merit of the Warren-Cowley order parameter (i.e. different order parameters for clustering of like atoms and superstructure formation due to the unlike atoms). But it does not suffer from the fundamental limitation of the Warren-Cowley parameter, where the composition of the configuration needs to be changed (where a system needs to be in contact with an infinite reservoir of atoms), and the order parameter for each pair of atoms needs to be defined. In contrast to the above, the proposed Δ-parameter in the OPERA scheme can generate the desired CSRO trend and be quantified as a single scalar value or Δ-value.

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Data Availability The data associated with the publication can be generated using the code provided with the manuscript. Additional data can be provided on the reasonable request.

Code Availability The OPERA code and representative input files can be assessed at https://github.com/ganand1990/OPERA.

Declarations

Conflict of interest None to declare.

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