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A critical analysis of the X-ray diffraction intensities in concentrated multicomponent alloys

The decrease in the X-ray diffraction Bragg peak intensity from concentrated multicomponent alloys (CMA), has been modeled in literature akin to the effect of temperature. In the current work, experiments and computations are used to comprehend the effect of atomic disorder in CMA on the Bragg peaks of powder diffraction patterns. Ni–Co–Fe–Cr–Mn and Cu–Ni–Co–Fe–V have been used as model systems for the study. It is proved that the intensity decrease is not insignificant, but is not anomalous either. A recipe is evolved to compare the Bragg peak intensities across the alloys of a CMA. It is demonstrated that it is incorrect to model the effect of an increase in atomic disorder in a CMA, as a temperature effect. A ‘good measure’ of lattice distortion is identified and further it is established that full width half maximum is a good measure of the bond length distortion. It is demonstrated that the true strain due to bond length distortion is of significantly lower magnitude than that given by a priori measures of lattice strain. In the scheme of categorization of defects in crystals, it is argued that CMA is a separate class (as distinct from type-I and type-II defects); which should be construed as a defected solid, rather than a defect in a solid.

Keywords: X-ray diffraction; Lattice strain; Concentrated multicomponent alloys.

1. Introduction

The current work pertains to X-ray diffraction (XRD) study of concentrated multicomponent alloys (CMA). Excellent texts have summarized the progress in XRD techniques, which span more than half a century [1–2]. The concept of CMA, though of comparatively recent origin, has also been covered in comprehensive textbooks [4, 5].

In the last decade, intense studies have been carried out on CMA [4, 6]. In many of these alloys, one or more disordered solid solutions (DSS) typically with a bcc or fcc structure, are entropically stabilized in competition with possible intermetallic compounds and hence these alloys have been termed high entropy alloys (HEA) [5]. This is typically achieved by the mixing of five or more elements in equimolar proportions in the alloy [7–9]. The strain in the lattice, arising from atomic size differences between the elements is usually characterized by $\Delta R_{\text{max}}$ or $\delta$ (or $\delta r$) parameters [10, 11]:

$$\Delta R_{\text{max}} = \frac{\text{Max}(r_i - \bar{r})}{\bar{r}} \quad (1)$$

$$\delta = \left[ \sum_{i=1}^{n} C_i \left( 1 - \frac{r_i}{\bar{r}} \right)^2 \right]^{1/2} \quad (2)$$

where, $\bar{r} = \frac{1}{n} \sum_{i=1}^{n} C_i r_i$, $r_i$ is the radius of $i^{th}$ element in the alloy, $n$ is the total number of elements in the alloy, $C_i$ is the atomic fraction of the $i^{th}$ element in the alloy. Owen et al. [12] have used a product of $\delta$ and $\bar{r}$ i.e. $(\delta d_{\text{Yeh}} = \delta \times \bar{r})$ as a measure of the lattice distortion. The ‘intrinsic lattice distortion’ ($\bar{d}_{\text{Yeh}}$) is an important parameter, which has been used in conjunction with the Debye–Waller factor, for the computation of the intensity of the Bragg peaks [13]:

$$\bar{d}_{\text{Yeh}} = \left[ \sum_{i=1}^{n} (d_i \text{eff} - \bar{d})^2 \right]^{1/2} \quad (3)$$

where, $\bar{d}$ is the average lattice parameter and $d_i \text{eff} = \frac{n}{C_i}(1 + \Delta V_i / V) ^ {1/3}$ $d_i$. The parameters $C_i$, $d_i$, $V_i$ and $\Delta V_i$ are: the atomic fraction, the lattice constant of the $i^{th}$ element, the unit cell volume of the $i^{th}$ element and the difference in the unit cell volumes between the $i^{th}$ and the $j^{th}$ elements, respectively. It is to be noted that the intensity referred to above is the area under the Bragg peak (integrated intensity) above the baseline [14].

Feng and Widom [15] have used variance as a measure of lattice distortion given by the following formula.

$$\sigma_D = \left( \frac{1}{n} \sum_{i=1}^{n} (r_i^2) - \left( \frac{1}{n} \sum_{i=1}^{n} r_i \right)^2 \right) \quad (4)$$

On closer inspection, this parameter ($\sigma_D$) is found identical to $\bar{d}_{\text{Yeh}}$. Another parameter of recent origin, which has
been used as a measure of the lattice distortion, is the interatomic spacing matrix \( S^b \) [16].

X-ray scattering from solid solutions have been studied for more than sixty years [1, 17]. One of the important contributions is due to Huang [18], wherein the effect of the formation of dilute solid solutions on the XRD intensities was computed. The assertions made in the work of Huang [18], which include the “weakening of the maxima” and the “presence of diffuse maxima”, have subsequently been experimentally confirmed [19–21]. The effect of temperature, atomic disorder, strain, crystallite size and crystalline defects on the XRD pattern has been comprehensively described [2, 3, 22]. Considerable attention has been given to the effect of these factors on the diffuse scattering present between the Bragg peaks [23–25]. Defects have been categorized into two classes, based on the displacement they create [2]: (I) having \( r^{-2} \) (or faster) decay and (II) \( r^{-\frac{1}{2}} \) (or slower) decay. Only defects of type-II show broadening of the Bragg peaks [2]. For example, isolated point defects belong to the first class, while dislocations belong to the second class.

Yeh et al. [13] have considered the effect of an increase in the number of elements (in the Cu–Ni–Al–Co–Cr–Fe–Si system) on the XRD powder pattern intensities. They have modeled the effect of atomic disorder, with concomitant increase in lattice strain, akin to a thermal effect according to the equation [3, 26]:

\[
M^T = 8\pi^2 (u^2)^T \left( \frac{\sin \theta}{\lambda} \right)^2 = \frac{6h^2}{mk\Theta_M} \left( \varphi(x) + \frac{x}{4} \right) \left( \frac{\sin \theta}{\lambda} \right)^2
\]  

(5)

where, \((u^2)^T\) is mean square displacement of atoms, \( h \) is Planck’s constant, \( T \) is the temperature at which the experiment has been conducted, \( m \) is the atomic mass, \( k \) is the Boltzmann constant, \( \varphi \) is the Debye function, \( \Theta_M \) is the characteristic temperature and \( x \) is \( \Theta_M / T \) (\( \theta \) & \( \lambda \) have their usual meaning according to Bragg’s equation). This leads to a decrease in the intensity of the peaks by the factor \( e^{-2M^T} \) (the Debye–Waller temperature factor, \( \Gamma_T \)). It is to be noted that, \( \Theta_M \) is technically different from the Debye temperature (\( \Theta_D \)), which is used in the context of the Debye theory of specific heat; however, the difference between the values of \( \Theta_M \) and \( \Theta_D \) is not usually large [3]. Additionally, Calamitou et al. [27] have used the following equation to account for the contributions to lattice distortion arising from thermal and non-thermal effects.

\[
8\pi^2 U_{iso} = \frac{6h^2}{mk\Theta_M} \left( \varphi(x) + \frac{x}{4} \right) + d^2
\]  

(6)

where, \( 8\pi^2 U_{iso} \) is the isotropic atomic displacement parameter (ADP). The first term in Eq. (6) is due to thermal effects and the second term can be considered to arise from static displacements. In a subsequent work of rather recent origin, Yeh [28] has attributed the diminished intensity of the Bragg peaks in the Ni–Co–Fe–Cr–Mn system to lattice distortion, which supposedly results in a high magnitude of diffuse scattering.

The intensities observed in the powder diffraction patterns obtained from CMA arise from two contributions [29]: (i) from the Bragg peaks and (ii) diffuse scattering between the peaks. An important work of recent origin in the context of diffraction from CMA is due to Owen et al. [12]. Using neutron diffraction and allied computations, they addressed the question: “are the lattices in high entropy alloys severely distorted?”. They used total scattering data to understand the local atomic environments, via pair distribution functions (PDF). It is to be noted that their work did not focus on the broadening of Bragg peaks. Important observations/conclusions from their work include: (i) Bragg peaks did not show “pronounced dampening”, (ii) the widths of the PDF peaks of HEA were not “disproportionately larger” than that of simpler alloys, (iii) thermal vibrations in HEA were the highest amongst the alloys studied, (iv) there is no indication of anomalously large local lattice strain in HEA and (v) the breadth of the PDF peak is dominated by thermal effects rather than static displacements due to atomic disorder. It is important to note that Owen et al. [12] envisaged atomic disorder within the \( U_{iso} \) term in the Rietveld refinement process (i.e. akin to the effect of temperature and as considered by Yeh et al. [13]). Further, it is not clear if the computations performed using an “average atom” [12] can capture the essential features of an actual alloy. The problem of anomalous decrease in the intensities of Bragg peaks has also been addressed by Guo et al. [30]. They have highlighted the issue of fluorescence and further have stated that: “Nevertheless, the reason why the (111) peak, and this peak alone showed an intensity decrease with an increasing \( N \), remains unknown and needs further study” [30]. The recent works of Oh et al. [31], Okamoto et al. [32] and Song et al. [33] are also noteworthy. Using density functional theory (DFT) and extended X-ray absorption fine structure (EXAFS), Oh et al. [31] have shown that the magnitude of the average distortions is small, but the mean deviation of the distribution of distortion values is large. Okamoto et al. [32] have used XRD and first principle calculations to arrive at the atomic displacements in a CMA. Using ‘supercells’ for computations, Song et al. [33] have shown that the “local lattice distortion of the refractory HEAs is much more significant than that of the 3d HEAs” [31]. They highlighted the limitations of using empirical atomic radii.

The addition of alloying element(s), leading to the formation of a CMA, has the following major effects [26]: (i) change in lattice parameter leading to a shift in peak position; (ii) change in the average atomic scattering factor leading to a change in the intensity of peaks; (iii) change in the solidus temperature; (iv) change in the level of absorption. Point (iv) is of importance, as for a given radiation some elements may cause fluorescence, thus leading to a reduced Bragg peak intensity along with a concomitant increase in background intensity. Additionally, the elastic constants will change on increasing the number of elements in an alloy.

In general, an increase in the temperature causes four important effects on the XRD powder patterns [1, 26]: (i) peak shift due to lattice parameter increase, (ii) decrease in the intensity of the Bragg peaks (given by the Debye–Waller temperature factor), (iii) increase in the diffuse background with increase in \( \sin(\theta)/\lambda \) and (iv) diffuse scattering ‘tail’ around the Bragg peaks. Standard formulations found in textbooks [1, 26] consider the effect of thermal vibrations as a decrease in the intensity of the Bragg peaks, via a decrease in peak height, without an increase in peak width (usually characterized by the full width half maximum (FWHM)). Advanced theoretical treatments of the subject can also be found in the literature [3, 34]. The difference in the nature of the diff-

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fuse scattering between static (due to atomic disorder) and dynamic (due to thermal vibrations) disorder has been clearly delineated in the literature [23, 24].

The atomic ‘disorder’ in CMA/DSS arises because of three reasons: (i) probabilistic occupation of lattice sites according to the stoichiometry (henceforth referred to as ‘elemental disorder’ [35]), (ii) displacement of atoms from lattice sites due to atomic size differences (henceforth referred to as positional disorder), and (iii) thermal atomic vibrations. Point (i) increases the configurational entropy of the system and hence is expected to play a role in the stabilization of a DSS. The static and dynamic aspects of disorder are best understood by considering two scenarios: the heating of pure Ni from 0 K (case-a) versus alloying it with Co at 0 K (case-b). In case-a, the atoms vibrate about their mean positions (i.e., the reference lattice is still intact and a time averaged picture will reveal ‘smear out’ atoms in lattice sites), while in case-b the ‘lattice’ is permanently distorted. The atomic size effect in an alloy on the XRD pattern has been investigated for a considerable length of time [3, 36–38]. Guinier [39] has arrived at an analytical expression, wherein terms related to positional disorder, Laue scattering and peak asymmetry have been delineated. Using an illustrative example in one dimension, Guinier showed that peak broadening occurs due to the formation of a disordered alloy. Important literature exists on the effect of alloying on the diffuse scattering intensity between the Bragg peaks [24, 25, 36]. It is important to note at this juncture that the size difference between the elements constituting a CMA is usually small.

The current work aims at the following tasks with regard to (powder) XRD patterns from CMA:

(1) Comprehend the effect of atomic disorder on the FWHM and intensity of the Bragg peaks.
(2) Show that it is incorrect to model the effect of atomic disorder as a change in temperature.
(3) Establish that the primary reasons for the decrease in intensity, on the formation of the Cu–Ni–Al–Co–Cr–Fe–Si multicomponent alloys ([13]), are due to a decrease in the average atomic scattering factor and change in the average absorption factor and not due to atomic disorder.
(4) Show that the decrease in intensity of the Bragg peaks cannot be correlated with the number of elements.
(5) Study the effect of change in solubility temperature across alloys on the Bragg intensities.
(6) Evolve a methodology to compare XRD peaks across alloys and to isolate the effects of lattice strain.
(7) Identify an a priori parameter for lattice strain, which correlates with the broadening of Bragg peaks.
(8) Demonstrate that such a priori parameters are not good measures of bond length distortion and that the bond distortion in single phase CMA is of significantly lower magnitude than that hitherto anticipated.
(9) Prove that FWHM of the Bragg peak is a good measure of strain arising due to bond length distortion.
(10) Establish that the atomic disorder in CMA constitutes a defect forming a separate class; wherein, the defect is of non-local nature and permeates the whole crystal.

It is to be noted that much of the literature has focused on the emphasis of the current work is on the Bragg peaks and concentrated alloys. Another point to be noted is that, even equimolar binary solid solutions at room temperature are rare and hence the occurrence of disordered equimolar solid solutions with two to five elements is extremely rare.

To achieve the abovementioned tasks, model computations are performed in addition to experimental investigations. The Ni–Co–Fe–Cr–Mn (labelled as system-SA) and Cu–Ni–Co–Fe–V (system-SB) alloy systems are chosen as model systems for the current study, as these alloys form a single phase fcc solid solution [40, 41]. In other respects the SA and SB systems are of diverse nature, as will become evident in the discussion of the results. Additionally, the alloys investigated by Yeh et al. [13] (Cu–Ni–Al–Co–Cr–Fe–Si, system-SY) are also synthesized to perform a comparative study and to unequivocally answer the question: ‘is there an anomalous decrease in XRD peak intensities on the formation of CMA?’ The atomic radius difference between the elements is small in both the systems (SA & SB), which is typical for most of the single phase HEA systems. This implies that the positional disorder in the CMAs is small and so is expected to be its effect on the XRD peak profile.

In the context of the formation of CMA, the atomic radii listed in the literature are often used for the computation of a priori measures of ‘lattice strain’. In this context the following important points are to be noted:

(1) The atomic radius of an element in an alloy is expected to be dependent on the local environment, although this effect is not significant [32, 42].
(2) Multiple listings of atomic radii exist in the literature (e.g., the Goldschmidt radius [43, 44], radii based on empirical formulations [45, 46]).

The issue of the type of atomic radii listing to be used in alloys for the computation of distortion, has also been addressed [32, 33]. In metallic systems, the Goldschmidt’s listing of radii seems to serve well [47]. In the current work the Goldschmidt radius (for 12-coordination) has been used for computations, which is expected to be the logical choice for alloys with the fcc structure. The terms ‘lattice strain’ and ‘lattice distortion’ have been interchangeably used to essentially depict atomic displacements from a perfect lattice. It is important to note that the strain computed using a priori parameters (e.g., $\delta$ & $\Delta_R_{max}$), may not be a good measure of the bond length distortion in CMA [33]. This implies that, the bond length distortion has to be compared with the a priori measures of lattice strain. The lattice strain as measured by parameters such as $\delta$ & $\Delta_R_{max}$ is dimensionless, while lattice distortion as measured by parameters such as $\delta_u$ & $\delta$ has dimensions of length. The terms CMA and DSS [6] have been used as synonyms in some places in the current work; however, it should be noted that the acronym DSS refers to the formation of a single phase disordered solid solution in the present context.

It is expected that this work will suitably augment the classic works of Huang, Guinier, Krivoglaz and Warren and the contemporary works of Owen et al. [12], Oh et al. [31], Okamoto et al. [32] and Song et al. [33]. In this context, it is important to note that XRD facilities are easily accessible as compared to that for neutron diffraction. The following effects are not included in the current work and form the scope for future work:

(i) multiple scattering effects,
(ii) effect of short range order (SRO),
(iii) dependence of the atomic radii on the environment, and (iv) atomic disorder on the diffuse scattering.

To keep the contents of the manuscript ‘tangible’, only important parts of the formalism and results are presented in the main document and ‘subsidiary’ information has been moved to the supplemental material section [the hyperlink to the electronic supplemental material (ESM) is given in the data accessibility statement]. Subsequent to a critical analysis of the results from the literature, a systematic attempt is made via computations and experiments to establish that CMA warrant special consideration and need to be contrasted with dilute solid solutions.

2. Experimental details

Equimolar alloys belonging to SA, SB and SY systems were synthesized by vacuum arc melting, followed by annealing for 24 hrs at 800 °C for achieving good compositional homogeneity. The number of element(s) in the alloys is designated by a numeral after the system (e.g. SA1 is pure Ni, SA2 is the Ni–Co binary, SA3 is Ni–Co–Fe ternary, SA4 is Ni–Co–Fe–Cr quaternary, etc.). To minimize texture and microsegregation which could be present in the as-cast samples, the specimens were: (i) filed to micron sized particles and (ii) the filed particles/powder was annealed at 800 °C for 48 hrs under vacuum (in quartz tube with Ti getter). The importance of removal of texture has been highlighted by Guo et al. [30]. This is to remove microstrain induced in the material because of the filing operation. In some of the literature pertaining to HEA, it is not clear if texture effects have been adequately accounted for (e.g. [113, 28]). The heat treatment process additionally avoids peak broadening effects due to dislocations and grain size. The as-cast bulk samples were characterized for microstructure in a scanning electron microscope (SEM) and the compositions were determined using energy dispersive X-ray analysis (EDX). A Bruker D8 Focus (dwell time of 250 s step⁻¹, step size 0.02°, Cr-Kα radiation) and PANalytical Empyrean (dwell time of 250 s step⁻¹, step size 0.02°, Cu-Kα radiation) were used for the XRD studies. The soludus temperatures of the samples were determined by performing differential scanning calorimetry (DSC) using a Perkin Elmer (STA 8000) instrument (heating rate of 10 K min⁻¹, temperature range of 1200–1600 °C).

Multiple parameters and methods have been used to quantify/analyze peak broadening in XRD. These include: FWHM, variance, integral breadth (fb) methods, Fourier methods and double Voigt methods [2, 14, 48–50]. The book by Mittemeijer and Welzel [14] gives an excellent summary of the methods. In the current work, FWHM is used as a measure of peak broadening given its simplicity, albeit the fact that integral breadth has been recommended by some investigators [51]. The experimental peak broadening (FWHM_experimental) is determined from a Gaussian profile fit. Other functions have been used in the literature [49] and functions like the Lorentzian and the pseudo-Voigt differ essentially in the ‘tail region’ of the profile. The Gaussian profile has been used in the current work to maintain consistency with the computational peak profile fitting, wherein it is a natural choice [52]. A comparison of the different methods of peak fitting for the cases in the current study can be found in the supplementary material. The readers may consult Chapter 4 of Ref. [14] for an illustrative description of the peak fitting methods. The Kα2 peak is subtracted before ‘peak fitting’ using Match software [53]. This standard method is based on Rachinger’s algorithm [54], which uses Fourier transform of the XRD peak profile with the Stokes’s deconvolution procedure [55], to distribute the statistical error and to isolate the Kα1 peak. The FWHM of the first elements in the respective systems (FWHM_element) has been used as reference to isolate the broadening purely due to atomic level strain (FWHM_atomic_strain). This is achieved by using: FWHM.atomic_strain = FWHM.experimental − FWHM.element.

This procedure effectively ‘subtracts’ the broadening from instrumental and other sources, which are not due to atomic disorder/strain. Despite the fact that extreme care was taken to minimize the effect of experimental variables including the level of the sample surface, its flatness, etc., it should be noted that the intensities obtained are subject to errors inherent in the method. This further emphasizes the use of FWHM as a definitive parameter in the context of CMA. To make a comparison of Bragg data, not only across systems, but between experimental and computational routes, the most intense 111 peak has been used.

3. Computational methodology

Computations were performed to understand the effect of the following on the XRD Bragg peak: pure positional disorder (case-i), pure elemental disorder (case-ii) and combined positional and elemental disorder (case-iii).

A c × c × c cubic cluster with fcc structure was generated by placing elements on perfect lattice sites. The cluster was built of ‘c’ fcc unit cells in each orthogonal direction (within the supercell approximation). Models of equimolar multi-component alloys were constructed by progressively increasing the number of elements from one to five in this cluster. As the cluster size was increased (by increasing ‘c’), the broadening due to system size (also known as crystal truncation rods, CTR [56]) decreased. The largest cluster size used in the current computations was with $c = 11$. In the disordered fcc alloys the 100 peak is absent, while the 111 and 200 peaks are present ($h, k, l$ unmixed). An important point to be noted is that exact stoichiometry cannot be achieved for all compositions for the clusters considered. However, the deviation from the desired composition is negligible, especially in a large sized $11 \times 11 \times 11$ cluster. For example in the $5 \times 5 \times 5$ cluster there are 500 atoms ($N = 500$) and for the $ABC$ ternary alloy the closest to equi-stoichiometry which can be obtained is $A_{167}B_{167}C_{167}$. In the abovementioned approach, a comparison across systems is made between clusters of the same size, which is advantageous as compared to an approach where supercell size is varied with stoichiometry (e.g. [33]).

To evaluate the effect of ‘pure’ positional disorder on the XRD peak intensities (case-i), a model system was created with Ni atoms on a perfect lattice. Further, the atoms were displaced with respect to their mean positions by a magnitude $u$. The direction of $u$ was randomly chosen, while the magnitude was kept fixed for a particular computation. In this approach the magnitude of $u$ gives a direct control on the degree of distortion, as will become evident in the discussion of the results. The intensity and FWHM of a Bragg peak (111 peak) was tracked as a function of the
magnitude of the displacement ($u$). To emphasize, in this hypothetical construct there exists pure positional disorder, without the influence of the atomic scattering factor of alloying elements added.

To study the effect of atomic scattering factor of the elements on the intensities of the Bragg peaks (case-ii), atoms of different elements were introduced on a perfect lattice. This was achieved by randomly placing elements on an average lattice (i.e. the lattice parameter was computed using the radius of an ‘average atom’). This is a case of pure elemental disorder without positional disorder. The number of elements was increased from two to five.

To generate clusters with both positional and elemental disorder (case-iii), atoms according to a prescribed composition were first introduced into a perfect average lattice (as in case-ii) and they were further allowed to relax to equilibrium positions using a molecular dynamics (MD) simulation as described later in this section. For each of the above-mentioned cases (i–iii), five random clusters were created and XRD patterns were computed according to the approach described below. The broadening due to crystallite size was subtracted by using the computed FWHM for the pure element of the series. This is akin to the procedure for the experimental data, wherein a Gaussian profile was assumed for the Bragg peaks (additional details can be found in the supplemental material). The scatter in the computed FWHM for the five random configurations is shown as an ‘error bar’ in the results presented.

For the clusters considered above (cases-i, ii & iii), intensity-2θ plots were computed using the equation [3]:

$$I = \sum_{p} \sum_{q} f_p f_q \exp \left[ \frac{2 \pi i}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{r}_{pq} \right]$$  \hspace{1cm} (7)

where, $f_p$ & $f_q$ are the atomic scattering factors of the $p^{th}$ and $q^{th}$ atoms; $\mathbf{s}$ & $\mathbf{s}_0$ are unit vectors in the direction of diffracted and primary beams respectively and $\mathbf{r}_{pq}$ is the displacement vector between the $p^{th}$ and $q^{th}$ atoms. It is noteworthy that: (i) for crystallites in random orientations this equation simplifies to the Debye scattering equation [57] and (ii) this is the fundamental equation used for the derivation of other formulae, wherein the intensity is split into those arising from fundamental reflections, short range order (diffuse intensity), size effect modulation, etc. The splitting process typically involves approximations and is necessitated by the computational effort involved for large crystallites. In the current work, Eq. (7) was used without simplifications and hence no approximations are involved.

A Matlab [58] code is written to evaluate Eq. (7) for the $c \times c \times c$ cluster. It is to be noted that this methodology has the advantage that each type of atom is treated explicitly, unlike the ‘average atom models’, which are sometimes used in the literature. As mentioned earlier, a Gaussian profile fit for the intensity was assumed, though other functions may arise due to the use of ‘$d$’ in Bragg’s equation. In the specific case of pure positional disorder (case-i discussed earlier), $I_{AC}$ is the same as ‘$u$’. To reduce the effect of a finite cluster size, the values of FWHM and $I_{AC}$ computed for various cluster sizes, are extrapolated to an ‘infinite’ size.

4. Lessons from a critical analysis of powder diffraction patterns in the Cu–Ni–Al–Co–Cr–Fe–Si system

The Cu–Ni–Al–Co–Cr–Fe–Si alloy system (SY) investigated by Yeh et al. [13] has the following inherent complexities: (i) the presence of more than one phase for alloys beyond SY2; (ii) the formation of a compound in alloys SY5, SY6 and SY7 (with a total of three phases); (iii) the mass absorption coefficient ($\mu/p$) for the elements used in the alloy varies drastically for Cu-Kα radiation, and (iv) change in the average atomic scattering factor ($f_{avg} = \sum_{i} C_i f_i$, where $C_i$ is the mole fraction & $f_i$ is the atomic scattering factor of the $i^{th}$ element) across the alloys in the system. The difference in mass absorption coefficients for the elements leads to a variation of $\mu/p$ (SY1 to SY7). The mass absorption coefficient for the alloys is computed as:

$$\left( \frac{\mu}{p} \right)_{\text{alloy}} = n \sum_{i=1}^{n} \left( \frac{\mu}{p} \right)_i w_i$$ \hspace{1cm} (8)

where, for the $i^{th}$ element, $w_i$ is the weight fraction, $\mu_i$ is the linear absorption coefficient and $p_i$ is the density. The solids temperature will change across the alloys in the system with concomitant effects on the thermal diffuse scattering and the intensity of the Bragg peaks. Formation of multiple phases in alloys beyond SY2 implies that the volume (or weight) fraction of material giving rise to a peak (say the (111) peak from the fcc phase) decreases, thus making a direct comparison of intensities across alloys difficult. The above-mentioned aspects render a fruitful comparison of
The intensity of a given peak across alloys is: (i) directly proportional to the square of the average atomic scattering factor \(f_{\text{avg}}^2\), and (ii) inversely proportional to the absorption factor \(1/2\mu_{\text{alloy}}\) for the alloy. This integrated factor \(I_{\text{111}} = f_{\text{avg}}^2/(2\mu_{\text{alloy}})\) (designated as \(I_{\text{SA}}\)) represents the intensity variation due to scattering factors and absorption coefficients across the alloys. As stated before, the melting point \(T_m\) or the solidus temperature \(T_s\) of the system changes across the alloys of the SY system. If the intensity of a given peak (say the 111 peak) is compared across samples, this aspect has to be accounted for. Other factors being equal, the amplitude of the vibrations scale with the homologous temperature \((T/T_m)\) and hence change in solidus temperature due to the change in composition, is akin to heating or cooling the sample (depending on the decrease or increase in the solidus temperature, respectively). There exists no precise way of incorporating this effect on the intensity of the Bragg peaks (as material properties, especially the elastic properties change across systems) and further integrating this term with that resulting from the inclusion of the atomic scattering factor and absorption factor \(I_{\text{SA}}\). However, the change in solidus temperature can be approximately accounted for as follows: (i) a pure element is considered as the starting material, (ii) the change in solidus temperature is tracked with an increase in the number of elements, (iii) this is treated as heating or cooling of the elemental metal (depending on decrease or increase in solidus temperature), (iv) this effect on the intensity of the Bragg peaks is modeled as a change in \(T\) in Eq. (4) (resulting in a new factor \(I_T\)), and (v) \(I_{\text{SA}}\) and \(I_T\) are multiplied to obtain a new integrated factor \(I_{\text{SAT}}\). It is important to note that this factor \(I_T\) should be conceived akin to the ‘real’ temperature factor, unlike the atomic disorder modeled as a temperature factor. In an alloy series with increasing \(n\), the alloy with \(n\)-1 elements can be considered as the reference for the alloy with \(n\) elements; but, in the current work the pure element \((n = 1)\) is considered as the reference. This is necessitated by the fact that \(\Theta_M\) data is not available for most of the multi-component alloys in the literature.

The various parameters related to the SY system ((i) atomic scattering factor \(f\), (ii) mass absorption coefficient \((\mu/\rho)\), (iii) solidus temperature \(T_s\), and (iv) atomic radius are listed in Table 2 of ESM. The following points can be noted from the table: (i) the average atomic scattering factor \(f_{\text{avg}}\) changes across the alloys with a drastic decrease from SY2 to SY3; (ii) the mass absorption coefficient is a function of the radiation used (Cu-K\(_\alpha\), Cr-K\(_\alpha\), etc.); (iii) the solidus temperature \(T_s\) has a bandwidth of more than 200 °C. These variations result in a variation in the intensity of 111 Bragg peak across the alloys (Fig. 1a). The percentage variations in intensity (minimum to maximum) due to these factors are: (i) 66% in \(I_s\), (ii) 307% in \(I_A\) and (iii) 0.13% in \(I_T\). Hence, the variation in \(T_s\) across the alloys has the least effect, while the absorption factor plays the biggest role (using Cu-K\(_\alpha\) radiation).

A comparison of the mass absorption coefficients for three different radiations (Cu-K\(_\alpha\), Cr-K\(_\alpha\), Mo-K\(_\alpha\)), across the alloys in the SY system is shown in Fig. 1b. It can be seen from the plots that the effect of the variation of \((\mu/\rho)\) across alloys could have been avoided by using Cr-K\(_\alpha\) or even Mo-K\(_\alpha\) radiation. Finally, to compare intensities across multiple radiations, the value of \(I_{\text{SAT}}\) obtained is multiplied by another factor (designated \(I_p\)) to obtain \(I_{\text{net}}\) [63]. Details regarding the same can be found in the ESM. The factor \(I_p\) is dependent on two parameters: (i) the wavelength \((\lambda)\) of the radiation used, and (ii) the critical excitation voltage \((V_c)\). Figure 2a shows the plot of \(I_{\text{net}}\) across the alloys in the SY system for Cu-K\(_\alpha\), Mo-K\(_\alpha\) and Cr-K\(_\alpha\) radiations, assuming that a single phase fcc alloy is obtained; which is clearly not the actual case. It is seen from the figure that, the variation in the intensity of the 111 peak across the alloys in the SY system is small for Mo-K\(_\alpha\) and Cr-K\(_\alpha\) radiations, as compared to Cu-K\(_\alpha\) radiation. Given that a low intensity is obtained with Mo K\(_\alpha\) radiation, it is preferable to use Cr-K\(_\alpha\) for investigations involving the comparison of the intensities across systems. The experimental results of the current investigation (SY system) for Cu and Cr-K\(_\alpha\) radiations are shown in Fig. 2b ((i) & (ii)). The intensities of the 111 peaks have been normalized with respect to the in-
tensity for the pure element. The data extracted from the work of Yeh et al. (Figure 2 in [13]) has been overlaid on the figure for comparison (Fig. 2b (iii)). To address the issue of the change in phase fraction of the fcc phase as we traverse across the alloys in the system, the intensity has been (approximately) corrected taking into account this aspect (Fig. 2b (iv) for Cu-K$_a$ & Fig. 2b (v) for Cr-K$_a$). The trends observed in Fig. 2a, corroborate well with the experimental investigations for the SY system after the correction for the phase fraction, using Cu and Cr-K$_a$ radiations (Fig. 2b). This further strengthens the argument in favour of the use of Cr-K$_a$ radiation for the investigation of alloys across the SY system. Corresponding results and other details for the SY system can be found in Section 5.1 of the ESM. It is curious to note that the variation in $I_{111}$ with $n$ using Cu-K$_a$ radiation, displays a visual trend similar to that resulting from treating lattice distortion as a thermal effect (as in Fig. 5, Yeh et al. [13]).

It is important to note that, the distortion factor used by Yeh et al. [13] ($\bar{\mu}_{Yeh}$) is different from that used by Owen et al. [12]. The use of $\bar{\mu}_{Yeh}$ as a measure of lattice distortion results in a severe ‘damping’ of the Bragg peaks on the formation of CMA. Further, the temperature corresponding to the value of $\bar{\mu}_{Yeh}$ used by Yeh et al. is 5985 K for the SY7 alloy (using Eq. (4)), which ‘seems rather unreasonable’. The corresponding temperature using $\bar{\mu}_{Owen}$ is 520 K. The validity of the method of averaging of the intensity obtained from the bcc and fcc structures used by Yeh et al. [13], is also not clear.

The remaining important factor for comparison of intensities across alloys is that arising from atomic disorder, which leads to a decrease in the intensity of the Bragg peaks. This aspect is considered in the next section for the single phase alloys systems SA and SB.

In summary, the above analyses lead us to the following ‘recipe’ for a fruitful and meaningful comparison of peak intensities across alloys (in CMA). (1) an alloy system which forms a single phase CMA must be chosen. (2) a radiation that shows minimum fluorescence (absorption) for...
the elements in the alloy system (e. g. Mo-Kα for the SY system) is preferred and if this is not possible, a radiation must be chosen, wherein the variation in absorption factor is small across the alloys (e. g. Cr-Kα). (3) The results must be corrected/normalized for variation of: (a) average atomic scattering factor, (b) absorption factor and (c) solidus temperature across alloys. Once the above-mentioned factors are taken into account, any remaining variation in the intensity of the Bragg peaks across the alloys is purely due to the effect of the strain arising from atomic disorder. Needless to point out, the sinθ/λ dependence of the atomic scattering factor, temperature factor and the Lorentz-polarization factor have to be considered.

5. Results and discussion (SA and SB systems)

The results obtained from computations performed for the case of pure positional and pure elemental disorder are considered briefly first. Additional details regarding the same can be found later in the manuscript and in Section 4 of ESM. The results for the case of pure positional disorder (in the absence of elemental disorder) are shown in Fig. 3, which shows the plot of FWHM and intensity as a function of ωAC. The following important conclusions can be drawn from the figure. (i) Pure positional disorder which permeates the entire crystal, leads to a broadening of the Bragg peaks. (ii) The magnitude of broadening is approximately linear with the distortion (ωAC); (iii) The intensity monotonically decreases with distortion. Pure elemental disorder (without positional disorder) does not lead to peak broadening; however, there is an intensity change due to change in the average atomic scattering factor (Iavg). These model computations form the reference point for easy analyses of the other results in the current work.

Figure 4 shows the experimental XRD patterns obtained from the alloys of the SA system using Cr-Kα radiation. It is clearly seen that there is no anomalous decrease in the intensity of the peaks, on increasing the number of elements in the alloy. XRD patterns obtained using Cu-Kα radiation for the SA system and from the SB system (Cu & Cr-Kα radiations) can be found in Section 5.2 of the ESM. The inset to Fig. 4 shows the computed XRD pattern in the vicinity of the 111 Bragg peak. The peak shifts are due to a change in the average lattice parameter. The intensity of the peaks depends on many factors as discussed before and is considered again later in the manuscript. It is to be noted that the peaks are symmetric, within the resolution of the experiments and computations; which is in contrast to that observed for defects such as edge dislocations and stacking faults [64].

The results related to the 111 peak from SA and SB systems are presented in this section, while those for the 200 peak can be found in ESM (Sections 5 & 6). The FWHM for the pure elements of the two series (i.e. SA1 and SB1) for the 111 peak are: 0.049° (SA1, Cr-Kα) and 0.053° (SB1, Cr-Kα). The variation of the experimentally (using Cr-Kα) and computationally determined FWHM for the 111 peak, with ∆Rmax and ωAC for the SA system, is shown in Fig. 5. The inset to Fig. 5a shows the variation in FWHM with the number of elements in the SA system. As mentioned in Section 2, the value of the FWHM of the Bragg peaks is representative of the lattice distortion. For a measure of lattice distortion, the use of FWHM of the Bragg peaks is preferred over the use of FWHM of the PDF (as measured from total scattering [12]). This helps in the decoupling of the contributions from static (due to atomic disorder) and dynamic disorder (due to temperature), as the Bragg peak width is not affected by thermal effects. However, it should be noted that the Bragg data is related to the average structure, unlike the total scattering data [12]. The error bar associated with the computational plot corresponds to five different configurations used in the study. Two important points can be noted from the figure: (i) the peak broadening observed (FWHM) is significant (in the range of ~0.07°–0.09°), especially in contrast to that expected due to purely elemental disorder (Fig. 3) and (ii) a reasonable match exists between the experimental and computational plots, which include the trendlines. The broadening of the Bragg peaks was envisaged by Guinier [1] for the case of a linear equiatomic disordered binary alloy. The value of broadening observed is comparable to that obtained for cold worked metals (e. g. peak broadening of ~0.08° is reported for the 111 peak in cold worked Al [63]). The correspondence between the experimental and computational results can be considered as good, as with an increase in the number of elements, the computational
result is expected to yield poorer approximation. This is due to the number of binaries involved and the methodology used to obtain the binary potentials.

The corresponding plots for the SB system and plots of FWHM with other measures of distortion (like \( \delta \) & \( R_{\text{avg}} \)) are shown in the ESM. A monotonic increase in FWHM with \( \bar{\Omega}_{\text{Owen}}^D \) is observed in both SA and SB systems. The variation of FWHM with \( \Delta R_{\text{max}} \) is monotonic for the SA system, but not for the SB system. It is to be noted that the computed values capture the combined effect of elemental and positional disorder. The parameter \( \bar{\Omega}_{\text{Owen}}^D \) is a measure of the distortion with reference to an ‘average lattice’, represented as a ‘root mean square quantity’ and seems to be the best amongst the a priori measures of lattice distortion (with \( \delta \) as the second best).

The inset to Fig. 5b, shows a plot of the variation of the FWHM in the SA alloy series with \( \bar{\Omega}_{\text{AC}} \), which shows a good correspondence with the plots in the main figure. This reveals that, an a priori computed parameter like \( \bar{\Omega}_{\text{Owen}}^D \) correlates well with FWHM. It is to be noted that, \( \bar{\Omega}_{\text{AC}} \) is a parameter from the computations and experimental data points corresponding to this parameter have been overlaid in the inset to Fig. 5b. The computational model slightly overestimates the values FWHM and the distortions. The term ‘correlates’ in the current context implies a monotonic increase. Important aspects regarding the use of parameters of lattice strain like \( \bar{\Omega}_{\text{Owen}}^D \) and \( \bar{\Omega}_{\text{AC}} \) are discussed later in the manuscript.

The variation in the intensity of the 111 peak with the number of elements in the SA system (experimental), using Cu-K_α and Cr-K_α radiations, is shown in Fig. 6a (i) and (ii). The variation in \( I_{\text{max}} \) with the number of elements in the system is shown in Fig. 6b. Figure 6a (iii) and (iv) shows the plots of (i) and (ii) corrected for the variation in \( I_{\text{max}} \). Thus, the intensity variation seen in the plots (iii) and (iv) arises purely due to lattice strain. It can be concluded that the intensity decrease due to the formation of CMA, which is about 10–20%, is not insignificant. However, this cannot be considered as anomalous either. The plot of intensities, which have been corrected for the variation in \( I_{\text{net}} \), with \( \bar{\Omega}_{\text{Owen}}^D \) and \( \Delta R_{\text{max}} \) are shown in Fig. 6c and d. A monotonic decrease in the intensities with these parameters is observed. The corresponding plots for the SB system are shown in Fig. 7. Two important differences to be noted between Fig. 6 and Fig. 7 are: (i) in the SB system the lattice distortion (\( \bar{\Omega}_{\text{Owen}}^D \)) does not increase monotonically with the number of elements and (ii) the intensity variation is not a monotonic function of \( \Delta R_{\text{max}} \). An important point to be noted is the increase in the intensity of the 111 Bragg peak between SB3 and SB4 (as seen clearly in Fig. 7c). This implies that the decrease in the observed intensity cannot be correlated with the number of elements in an alloy. Another point to be emphasized is that the decrease in the intensity with \( \bar{\Omega}_{\text{Owen}}^D \) is monotonic for both the SA and SB systems, while this is not the case with \( \Delta R_{\text{max}} \) in the SB system. This reinforces the confidence placed on \( \bar{\Omega}_{\text{Owen}}^D \) as a measure of lattice distortion.

Figure 8a shows the variation in the computed 111 Bragg peak intensity, with the number of elements, in the SA system. The variation arising purely due to lattice distortion (plot (iii)) is obtained from the total magnitude (plot (ii)) by subtracting the value obtained due to elemental disorder on the perfect lattice (plot (ii)). Figure 8b shows the variation in computed intensity, due to the component arising from the lattice distortion, as a function of \( \bar{\Omega}_{\text{AC}} \). Similar to the experimental observations, a monotonic decrease in the intensity is observed with lattice distortion (\( \bar{\Omega}_{\text{AC}} \)).

A study of the plots of FWHM of 111 peaks with \( \bar{\Omega}_{\text{Owen}}^D \) or \( \bar{\Omega}_{\text{AC}} \) reveals that the lattice strain as measured by these parameters, has a progressively diminishing effect on the Bragg peak broadening. This, on the one hand, effectively ‘avoids’ the occurrence of ‘anomalous effects’ with an increasing strain; but, on the other hand, raises the question: “Are these measures of lattice strain truly representative of the bond length distortion?” A true measure of lattice strain, which is responsible for the strain energy in the crystal, should be computed from the actual bond length distortion. Bond length distortion in an fcc crystal can be defined as:

\[
\Delta D = \frac{1}{2N} \sum_{i=1}^{N} \sum_{j=1}^{N} \left| D_{ij} - D_{ij}^0 \right| \]

where, \( D_{ij} \) is the bond length distortion of the bond ‘ij’.
length between the \(i\)th atom and its nearest neighbour the \(j\)th atom, \(D_{ij}\) is the equilibrium bond length \((r_i + r_j)\) between the atoms and \(N\) is the number of atoms. The corresponding strain can be computed as: 
\[
e_{ij} = \frac{1}{62} \sum_{i=1}^{N} \left( \frac{D_i - D_{ij}}{D_{ij}} \right).\]

Figure 9a and b pertains to the case of pure positional disorder in nickel (computed), which was considered earlier. The main plot shows the variation of FWHM with \(\Delta D\) and the inset shows the plot of \(\Delta D\) with \(\bar{u}_{AC}\). Figure 9c–e pertains to the computed results from the SA system. Figure 9c shows the variation of FWHM with bond distortion (\(\Delta D\)). Insets to the figure show the variation of \(\Delta D\) with \(\bar{u}_{Owen}\) (Fig. 9d) and \(\Delta D\) with \(\bar{u}_{AC}\) (Fig. 9e). As didactically utilized before, experimentally obtained FWHM data are studied as a variation of computationally obtained \(\Delta D\). The following observations and conclusions can be drawn from this figure, analyzed in conjunction with Fig. 3. (i) For both Ni and the SA system; the computed FWHM scales approximately linearly with \(\Delta D\) and the ‘saturation’ observed in the FWHM–\(\bar{u}_{Owen}\) plot is absent. This unambiguously establishes the fact that FWHM is the true measure of bond distortion. (ii) The value of \(\Delta D\) ‘saturates’ with increasing \(\bar{u}_{Owen}\) and explains the reason behind the nature of the FWHM–\(\bar{u}_{Owen}\) plots. The \(\Delta D\)–\(\bar{u}_{AC}\) plot does not show this saturation behaviour; but is not linear either. This further demonstrates that, a priori measures like \(\bar{u}_{Owen}\) or \(\bar{u}\), or even an a posteriori measure like \(\bar{u}_{AC}\) of the strain, do not accurately represent the bond distortion in CMA. (iii) In the ‘special case’ of pure unreliaxed positional disorder, \(\bar{u}_{AC}\) is commensurate with true lattice distortion (Fig. 9c), as observed from the approximately linear trendline. Thus, the approximately linear nature of the variation of FWHM with \(\bar{u}_{AC}\) (Fig. 3), is explained. The corresponding plots for the SB system, highlighting the importance of \(\Delta D\), can be found in the ESM (Section 6.1).

The percentage increase in the lattice distortion between SA2 and SA5, as computed by various measures is as follows (the value of these parameters for SA5 is included in the brackets) (i) 100 % for \(\bar{u}_{Owen}\) (0.018 Å), (ii) 226 % for \(\Delta R_{max}\) (0.026 Å), (iii) 114 % for \(\bar{d}\) (0.015 Å), (iv) 39 % for \(\bar{u}_{AC}\) (0.021 Å) and (v) 33 % for \(\Delta D\) (0.012 Å). The corresponding values for the SB system can be found in Section 6.1 of the ESM. This calculation, in conjunction with the results presented earlier, implies that the increase in bond length distortions on increasing the number of elements in a CMA is of significantly lower magnitude than that measured by a priori measures of lattice strain. The bond distortion, which is a true measure of strain in the alloy and which contributes to the strain energy, is not large as previously anticipated in the standard literature. This implies that the strain energy penalty to the crystal is lower and explains the relative ease of the formation of DSS in the presence of multiple elements. To emphasize, entropy has to overcome the effects of a lower magnitude of ‘true strain’ in the crystal and hence it is not surprising that DSS form in CMA. The availability of atoms of multiple sizes helps in this regard (as illustrated in the ESM Section 7.1). In this context it is important to note that large lattice strains will lead to the formation of a compound [11].
The importance of the source of atomic radii, used for the calculation of lattice strain parameters, was highlighted in the introduction (Section 1). A few points are worthy of discussion here. Owen et al. [12] have concluded that the increase in the PDF peak width cannot be correlated with the value of \( \delta \). In our analysis, this stems from the use of bcc CN-8 radii for Cr (& perhaps hcp radius for Co). Using the fcc CN-12 listing of Goldschmidt radii [43, 44], the value of \( \delta \) increases in the following order for the alloys investigated by Owen et al. [12]: Ni-20Cr (\( \delta = 0.00322 \)) < Ni-25Cr (\( \delta = 0.00348 \)) < Ni-33Cr (\( \delta = 0.00378 \)) < Ni-37.5Co-25Cr (\( \delta = 0.00992 \)) < NiCoFeCrMn (\( \delta = 0.01181 \)). These values of \( \delta \) have been calculated from Pearson’s listing and if Goldschmidt’s listing of radii [43, 44], the value of \( \delta \) seems to best correlate with the values of FWHM, as compared to parameters like \( \Delta R_{\text{max}} \), \( \delta \) & \( R_{\text{avg}} \).

1) The intensity variation observed in the SY alloy system is primarily due to the variation in the atomic scattering factor and the absorption coefficient and not due to atomic disorder. Based on the lessons learnt from the alloy system, a ‘recipe’ is developed to compare XRD intensities across alloy systems; such that the effect of lattice strains on the XRD peaks can be isolated. In the analysis the effect of change in the solidus temperature across alloys is included. This is a temperature factor in the ‘true’ sense, unlike lattice distortion modeled as a thermal effect.

2) (i) Pure positional disorder (in the absence of elemental disorder) leads to an increase in the peak width (FWHM), along with a decrease in the intensity. (ii) Pure elemental disorder (without positional disorder) does not lead to peak broadening; however, there is an intensity change due to a change in the average atomic scattering factor (\( f_{\text{avg}} \)).

3) (i) The FWHM of a given XRD peak increases with the strain in the lattice, which arises due to the formation of a CMA. The lattice distortion parameter (\( \eta_{\text{Owen}} \)) seems to best correlate with the values of FWHM, as compared to parameters like \( \Delta R_{\text{max}} \), \( \delta \) & \( R_{\text{avg}} \).

(ii) The atomic diameter as listed by Goldschmidt (for 12-coordination) gives the best results for the computation of \( \eta_{\text{Owen}} \).

(iii) Given that the peak broadening observed is an important signature of CMA, it is incorrect to model the effect of lattice distortion as a ‘temperature factor’.

4) (i) On the formation of a CMA, the intensity of the Bragg peaks decreases with lattice strain; but this aspect cannot be correlated with the number of elements, which decides the configurational entropy.

(ii) The decrease in intensity is not insignificant; however, this cannot be termed as anomalous either. In fact, for some combinations of alloys and radiation used (e.g. with Cr-K\(_\alpha\) radiation for alloys SB3 & SB4), the intensity observed may actually increase with an increase in number of elements in a CMA, which essentially implies the predominance of other factors over strain.

5) (i) If a priori measures such as \( \eta_{\text{Owen}} \) or \( \Delta R_{\text{max}} \) or a posteriori measures like \( \eta_{\text{AC}} \), are used as parameters of lattice strain, it may be construed that the lattice strain has a progressively diminishing effect on the FWHM and the intensities of the Bragg peaks.

(ii) The bond length distortion, which can be directly related to the strain energy cost to the crystal, can be perceived as a ‘true measure’ of lattice strain. It is established that FWHM, which is an experimentally and computationally accessible quantity, is a measure of true lattice strain arising from bond length distortion. This can thus be used to separate the static and dynamic components of disorder.

(iii) It is demonstrated that the bond length distortion in CMA is of significantly lower magnitude than that given by a priori measures of strain; which effectively ‘avoids’ the occurrence of ‘anomalous effects’ with an increasing number of elements.

6) In CMA the entire crystal can be construed as a deformed solid, rather than a defect in a solid (i.e. the atomic disorder permeates the whole crystal and is of non-local nature). The disorder in CMA should be categorized as a separate class; as distinct from type-I (decay \( r^{-2} \)) and type-II (decay \( r^{-1/2} \)) defects.

6. Summary and conclusions

Two systems (Ni–Co–Fe–Cr–Mn (SA) & Cu–Ni–Co–Fe–V (SB)) were computationally and experimentally investigated to evaluate the effect of atomic disorder on the Bragg peak, in a powder XRD pattern from CMA. The formation of DSS is observed in the SA and SB systems. The Cu–Ni–Al–Co–Cr–Fe–Si (SY) system was used as a reference for the studies. Computations were performed using the fundamental equation for diffraction, to understand the effect of lattice distortion on the FWHM of the XRD peaks. The following conclusions can be drawn from the study.
It is expected that the lessons learnt and conclusions drawn can be considered as general, which are applicable to other concentrated single phase systems. However, further investigations on diverse systems, especially with non-equimolar compositions, are needed to confirm the assertions.

Ethics statement
The consent of all the authors was sought before submission of the manuscript.

Data Accessibility Statement
The data related to the article are contained in the figures in the main document and in the Electronic Supplemental Material (ESM) [http://home.iitk.ac.in/~ananth/Archive/ESM_X-Ray_Diffraction_Intensities_in_Concentrated_Multicomponent_Alloys.pdf].

Competing Interests Statement
The authors declare no competing interests.

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Author Contributions
Rameshwar Naorem and Sukriti Mantri performed the computations and prepared the manuscript. The current affiliations of the authors lani and Anandh Subramaniam designed the Scheme of investigations and computed the relaxed coordinates using MD simulations. Kantesh Ba-

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