Extra electron reflections in concentrated alloys do not necessitate short-range order

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In many concentrated alloys of current interest, the observation of diffuse superlattice intensities by transmission electron microscopy has been attributed to chemical short-range order. We briefly review these findings and comment on the plausibility of widespread interpretations, noting the absence of expected peaks, conflicts with theoretical predictions, and the possibility of alternative explanations.

The nature of chemical short-range order in face-centred cubic (fcc) alloys containing several 3*d* principal elements, such as 'medium entropy' VCoNi and CrCoNi, has been intensively investigated in recent years^{1–18}. While there may be little evidence that short-range order can be controlled to tailor the bulk mechanical properties of these materials^{5,6,13,17}, it has been argued that an essentially ubiquitous degree of ångström-scale order could nonetheless play an important role in a wide range of properties^{1,7}. For example, many alloys containing Co are predicted to form hexagonal close-packed lattices at ambient conditions^{19,20}, but quenched-in, short-range order could account for the persistent metastability of the fcc phase^{1,7,11}.

This view seems to be corroborated by recent transmission electron microscopy (TEM) purporting the presence of local order in a variety of samples subject to minimal thermal processing beyond high-temperature homogenization. For example, the observation of short-range order in VCoNi was proposed⁸ on the basis of diffuse intensities at $\frac{1}{2}$ {311} superlattice sites in reciprocal space while imaging in the [Ī12] zone axis, which indicates the crystallographic direction of electron incidence. An equivalent electron diffraction pattern is shown in Fig. 1. Additional $\frac{1}{3}$ {422} intensities were later reported in the [Ī11] zone axis⁹. Similar observations have at various points been attributed to short-range order in a Cr–Ni-based alloy²¹, Mn–Fe-based alloys^{22–25}, CrCoNi (refs. 10,13), CrMnFeCoNi (ref. 15) and VFeCoNi (ref. 18). The same features have also been reported without the assumption of short-range order^{5,17,26–28}.

Some of these reflections are consistent with the partial formation of a CuPt-type (L1₁) concentration wave involving the compositional enrichment and depletion of alternating {111} (and simultaneously {311}) planes (Fig. 2a). Diffuse intensities in VCoNi and CrCoNi have been interpreted to reflect modulations of V or Cr concentrations in this manner⁸⁻¹⁰, largely on the basis of electronic-structure calculations indicating repulsive interactions between V–V and Cr–Cr neighbours, although we note that CuPt-type ordering has the same nearest-neighbour pair frequencies as a random alloy. Some efforts



Fig. 1 | **Electron diffraction of CrCoNi in the** $[\bar{1}12]$ **zone axis.** This pattern, which is based on experimental data from a previous study¹³, is representative of literature results for alloys discussed in the text. Diffuse intensities at $\frac{1}{2}$ {311} superlattice positions are marked with arrows, but there are no peaks at $\frac{1}{2}$ {111} sites, as highlighted by the dashed circles. Figure adapted from ref. 13 under a Creative Commons license (http://creativecommons.org/licenses/by/4.0/).

have been made to support this theory with atomic-scale composition mapping^{8,10,18}, but, in contrast to the diffuse intensities themselves, these measurements are noisy and susceptible to local fluctuations, making it difficult to draw statistical conclusions.

Regardless of chemical specifics, the presence of superlattice reflections should not be regarded as incontrovertible evidence for ordering. In fact, widespread interpretations of short-range order are questionable on several accounts, such as the absence of additional expected peaks. By the symmetry of the fcc lattice, a CuPt-type decoration can equivalently occur in four rotational variants, corresponding to order on the $(\bar{1}11)$, (111), $(11\bar{1})$ or $(1\bar{1}1)$ planes, with four additional antiphase structures that are redundant for purposes of diffraction. The four rotational variants are illustrated in the top row of Fig. 3 from the perspective of the $[\bar{1}12]$ zone axis, with atomic columns shaded by composition; the reciprocal-space intensities expected from each



Fig. 2 | **Schematics of CuPt- and AlNi₃-type orderings. a**, The CuPt-type (L1₁) decoration of an fcc lattice. Short-range order based on this structure has been proposed for VCoNi and CrCoNi with V- or Cr-rich sites (black circles) and complementarily depleted sites (white circles) on alternating (111) planes. **b**, Similarly, an AlNi₃-type (L1₂) unit cell. First-principles calculations suggest that this general form of ordering, in which V- or Cr-rich sites (black circles) form a sublattice that minimizes nearest neighbours, should be far more energetically favourable¹², if not the ground state^{2,3}, in these systems.

variant are shown below for the same zone axis. (Reflections were determined from the basic diffraction criterion for concentration waves²⁹, as restricted by the two-dimensional nature of TEM, and verified through simulations.)

As illustrated in Fig. 3a, the $\frac{1}{2}$ {311} peaks visible in Fig. 1 are associated only with the ($\overline{1}$ II) variant. While the variants on the (111) and ($11\overline{1}$) planes are not expected to produce additional reflections in this orientation, the ($1\overline{1}$ I)-based variant depicted in Fig. 3d should be readily visible, as it would involve composition modulation across the ($1\overline{1}$ I) planes that form the rows of the atomic columns viewed by TEM. Nonetheless, the associated $\frac{1}{2}$ ($1\overline{1}$ I) peaks are missing from all experimental characterizations of the [$\overline{1}$ I2] zone axis, from either electron diffraction or the Fourier transformation of dark-field images^{8-10,13,15,17,18,21-27}. The locations where additional reflections would be expected are circled in Fig. 1 and marked in Fig. 3d. Given the quantity of material sampled across numerous studies, the absence of a variant is not statistically conceivable.

One could attempt to construct an alternative structure giving rise to only $\frac{1}{2}$ {311} intensities, but every $\frac{1}{2}$ {311} peak is related to a $\frac{1}{2}$ {111} spot by a {200} reciprocal lattice vector, for example, $\frac{1}{2}$ (131) – (020) = $\frac{1}{2}$ (111), as is the case of Fig. 3d. Since the diffraction criterion for concentration waves is independent of reciprocal lattice translations²⁹, any ordering that produces $\frac{1}{2}$ {311} peaks should also effect $\frac{1}{2}$ {111} intensities as long as all variants are present. Furthermore, $\frac{1}{3}$ {422} and $\frac{1}{2}$ {311} reflections have very recently been

Furthermore, $\frac{1}{3}$ {422} and $\frac{1}{2}$ {311} reflections have very recently been reported in pure Cu (ref. 17); $\frac{1}{3}$ {422} reflections were also previously observed in pure Ni (ref. 27). Evidently, superlattice intensities in pure elements cannot represent chemical ordering and require another explanation, of which there are in fact several.

One is the presence of nanoscale planar defects. Forbidden reflections expected from stacking faults or nanotwins in an fcc lattice³⁰ are listed in Table 1. Remarkably, these are the exact features that have been reported in the [011], [$\overline{1}12$], [$\overline{1}11$] and [013] zone axes of concentrated alloys, offering an alternative explanation for the experimental findings described above. As structural defects break the symmetry of the reciprocal lattice, it is possible for $\frac{1}{2}$ {31} peaks to appear without $\frac{1}{2}$ {111} counterparts. Of course, the obvious objection

to this hypothesis is that most imaged samples appeared to contain no such imperfections in the examined regions. Considering that stacking faults and related structures are usually quite visible under TEM, some explanation of how presumably nanoscale planar defects could otherwise escape detection would be required to prove their generation of the discussed features.

While clearly visible stacking faults produce sharp superlattice reflections³⁰, the diffuseness of the discussed intensities could imply the presence of smaller, less resolvable defects, just as short-range order causes faint reflections compared with the sharp superlattice peaks resulting from long-range order. Both faulted (Frank) loops and stacking-fault tetrahedra should produce the extra reflections listed in Table 1 and, if small enough, could plausibly escape direct recognition. In many recent studies, superlattice intensities have been associated with tiny localized features, which could correspond to defect structures. Moreover, two recent investigations have connected the enhancement of diffuse intensities to mechanical deformation²⁵ and irradiation¹⁵, while brighter superlattice reflections have been found near a crack tip²¹. Both deformation and irradiation are well known to induce planar defects at the expense of chemical order, supporting this hypothesis - in fact, the intensity of some peaks has been directly correlated to the density of planar defects²⁵.

Most observations in the [011] zone axis support the absence of detectable short-range order – CuPt-type ordering should produce additional superlattice reflections in this zone axis, which are generally not observed^{4,8,10}. (Faint intensities at $\frac{1}{2}$ {111} positions have been suggested⁹, but the signal in this region seems comparable to the background noise level. Clearer $\frac{1}{2}$ {111} intensities in the [011] zone axis have been proposed following the application of a novel post-processing algorithm¹⁴, although we believe this technique may require further discussion of a technical nature beyond the scope of this Comment.) Several studies have instead reported streaking in this zone axis^{4,21,25,26}, which would also be consistent with planar defects³⁰. Others have found no extra features, but the absence of observation in specific instances would hardly be surprising given variation in sample preparation and the inherently local nature of the proposed defects.

Another theory is that the extra reflections are merely artefacts caused by 'relrod spiking' from higher-order Laue zone diffraction¹⁷, which could account for the locations of most reported peaks, although the higher-order Laue zone intensities predicted by kinematical theory are negligible²⁷. While dynamical scattering could theoretically contribute to forbidden reflections, it is not immediately clear how this would occur in the sample geometries used in the literature, which were too thin to even produce Kikuchi diffraction. Streaking in the [011] zone axis^{4,21,25,26} and the specific peaks observed in the [013] zone axis^{24,27} may also be more consistent with faulting³⁰.

It has been additionally suggested that surface steps could produce the extra reflections^{17,27}, as has been demonstrated for $\frac{1}{3}$ {422} intensities in the [I11] zone axis³¹. However, it is less clear if this mechanism is consistent with observations in other zone axes. Additionally, surface-step reflections have been primarily observed in deposited thin films with clear step contours, which are not apparent in recent observations of differently processed samples.

Somewhat before recent interest, $\frac{1}{2}$ {311} reflections in the [$\overline{1}$ 12] zone axis of an Al_{0.5}CrFeCoNiCu alloy were suggested to possibly originate from thermal diffuse scattering²⁶. However, it has also been shown that at least $\frac{1}{3}$ {422} reflections remain essentially unchanged at liquid-nitrogen temperatures²⁷. Alternatively, scattering from static lattice displacements has been proposed as another potential source of extra

a (111)	b (1	11)	C	(111)		d (1	11)	
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Fig. 3 | **Diffraction of CuPt-type ordering in the** $[\bar{1}12]$ **zone axis. a**-**d**, The four rotational variants of a CuPt-type structure, consisting of ordering on the denoted planes. In the top row, structures are drawn from the perspective of the $[\bar{1}12]$ zone axis, with columns of atoms shaded according to the average composition. (In CuPt, types 1 and 2 would represent Cu and Pt; in recently proposed short-range order, they correspond to Cr or V enrichment and depletion as in Fig. 2.) The reciprocal-space signatures of the four variants are shown below for the same zone axis. Only reflections associated with variant **a** have been reported in the discussed alloys, questioning the existence of this form of order.

intensities^{5,28}. We note that this phenomenon can break the symmetry of the reciprocal lattice³², although a specific mechanism by which it could produce the discussed observations has not been established. Like short-range order, static displacement scattering also could not explain the intensities observed in pure elements.

While the connection between the extra reflections and short-range order is questionable on a purely experimental basis, we further note that the proposed structures are largely inconsistent with the bonding principles predicted by standard density-functional theory, either directly or through parameterized interatomic potentials. As previously noted^{10,12}, CuPt-type ordering is clearly energetically unfavourable in otherwise similar V–Ni and Cr–Ni alloys. In these systems, experimental short-range order has been primarily interpreted in terms of AlNi₃type (L1₂) (Fig. 2) or Al₃Ti-type (DO₂₂) concentration waves^{33–36}, both of which minimize nearest neighbours among the ordering solute.

First-principles calculations consistently indicate that VCoNi and CrCoNi should order similarly to the aforementioned binaries, with VCoNi clearly favouring an AlNi₃-type V sublattice³ and similar, although not identical, preferences noted for CrCoNi (refs. 7,12,16). While short-range order may differ from the long-range ordered ground state²⁹, the underlying interactions are expected to be comparable and there is essentially no indication of any energetic driving force for the formation of CuPt-type ordering.

In practice, the basic predictions of electronic-structure calculations are largely supported by diffuse X-ray scattering in CrFeCoNi, which reveals an incipient AlNi₃-type Cr sublattice² after long-term ageing below the order–disorder transition temperature. Moreover, VCoNi alloys readily form fully ordered AlNi₃-type domains (Fig. 2), which were observed alongside the nominally disordered regions characterized in ref. 8. It would be unexpected for this material to host shortrange order corresponding to an unrelated structure immediately adjacent to the theoretically predicted long-range order.

A few studies have nonetheless tried to reconcile experimental observations with theoretical predictions. In particular, local instances of ordering on $\frac{1}{2}$ {311} planes were identified in high-temperature

Table 1 | Extra reflections from fcc planar defects

Zone axis	Extra reflections	Observations (reference)
[011]	Streaking	4,21,25,26
[Ī11]	$\frac{1}{3}$ {422}	5,9,17,21,24,26-28
[112]	$\frac{1}{2}$ {311}	8–10,13,15,17,18,21–27
[013]	$\frac{1}{2}$ {311}	24,27

The reciprocal-space features expected from planar defects³⁰ match recent experimental observations in concentrated alloys, as noted for each zone axis. In most cases, the intensities were originally attributed to short-range order.

thermodynamic simulations of CrCoNi parameterized by a carefully developed 'neural network' interatomic potential¹². However, the CuPt-type structure was noted to be energetically unfavourable and it is unclear if these regions represent anything beyond random fluctuations. Their equilibrium frequency does not vary with temperature above the order–disorder phase transition and equivalent instances of theoretically favourable {100}- and {110}-based motifs are consistently more prevalent, even though their associated peaks are not found experimentally.

Clearer agreement has been found between experimental diffraction patterns and simulations¹⁴ for certain previously generated theoretical structures⁷. These, however, were selected from a large collection of tiny configurations that were created to statistically explore highly speculative ordering principles rather than represent realistic chemical environments. Consequently, individual structures probably contained configurational fluctuations that, given the small cell size, could lead to various extra reflections.

Altogether, there seems to be little theoretical basis for any form of short-range order consistent with the electron diffraction of VCoNi, CrCoNi and other similar alloys, while reported features consistently match those expected from symmetry-breaking effects such as changes in the stacking sequence. On the weight of the circumstantial evidence, we believe that assumptions of ordering should be revisited, and the possibility that other phenomena produced the observed diffuse intensities deserves further investigation. This is not to say that any experimental sample necessarily lacked short-range order, simply that it may not be definitively detected by the employed techniques.

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Competing interests

The authors declare no competing interests.