Atomic-Scale Distorted Lattice in Chemically Disordered Equimolar Complex Alloys

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Abstract

It is a longstanding notion that alloying different sized elements can cause lattice distortion and phase transition in chemically complex alloys. However, a quantitative understanding of it remains difficult for traditional alloys, and becomes even more challenging for equimolar multicomponent alloys, also known as "high entropy alloys", which recently emerged as a promising structural/functional material and have been attracting tremendous research interest due to their unique properties. In this work, we carried out extensive first-principles calculations on a series of equimolar complex alloys with a chemically disordered crystalline structure, and characterized their atomic-scale lattice distortions in terms of the local residual strains. Albeit the confounding chemical/geometric complexities, we are able to show that the average attributes of such an atomic-scale distorted lattice, such as the lattice constant and the overall magnitude of the distortion induced residual strains, can be predicted very well by a simple physical model taking into account the efficient packing of different sized atoms interacting in an effective elastic medium. The findings of our current research unveils the details of locally distorted atomic packing in chemically disordered complex alloys, which sheds quantitative insights into the unusual strengthening mechanism as recently discovered in high entropy alloys.

1. Introduction

Lattice distortion is a long-standing notion that can be dated back to the discovery of solid-solution strengthening in conventional alloys [1-3]. In principle, this strengthening effect stems from the interaction between dislocations and the elastic strain field induced by inhomogeneities, i.e. atomic size misfit and/or elastic modulus misfit, which generally result in lattice distortions[4-6]. In theory, such a strain field comprises both volumetric strain and shear strain, where the latter is usually omitted for its complexity despite its considerable strengthening effect[7]. By assuming that volumetric strains dominate lattice distortion in various solid solution models[4-6, 8], mean-field approaches, such as those based on the classic Eshelby theory [9], were widely used to calculate the local volumetric strain field. Such models are featured by picturing the solute atoms as an isolated unsheared "inclusion" embedded in an elastic "matrix" made up of the solvent atoms. The limitations of the mean-field approach, which usually neglects residual shear strains due to deformation asymmetry in a sheared elastic "matrix", has been long recognized, however, the theoretical results so obtained enabled quantitative knowledge of lattice distortion in terms of the average volumetric strains [4-6, 8]. In physical metallurgy, such knowledge was of great importance, which played an essential role in the understanding and early design of the best-performing solute-strengthened dilute alloys, such as Al alloys[10], Ti alloys[11], and Ni-based superalloys[12].

In sharp contrast to the conventional alloy design paradigm, which is usually based on one principal element, a new alloy design strategy, known as "high entropy alloy" (HEA)[13-19], was recently proposed to obtain complex multicomponent alloys with outstanding properties. Unlike

traditional alloys, HEAs are defined comprising at least five elements mixed in an equal or near-equal atomic fraction [14, 15]. In doing so, it was expected that the configurational entropy of mixing in these alloys can be maximized, thereby stabilizing a random solid solution phase against others, such as intermetallic compounds [13-17]. According to the recent works[20-23], many solid-solution HEAs display extraordinary mechanical properties unparalleled by traditional alloys, such as FeCoNiCrMn[21], $Fe_{32}Mn_{30}Ni_{30}Co_6Cr_2$[22], $Fe_{50}Mn_{30}Co_{10}Cr_{10}$[20], $Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$[23]. To rationalize these findings, it was often proposed that severe lattice distortion might be present in the HEAs due to the mixing of numerous different sized elements, which leads to the impediment of dislocation movements, sluggish diffusion kinetics and precipitation of nano-sized coherent secondary phases[16, 17, 24, 25]. Nevertheless, it still remains elusive with the nature of lattice distortion in the HEAs. Unlike traditional alloys, there lacks a clear distinction between solvent and solute elements in these alloys; therefore, the use of the traditional ways, such as the Elshelby theory, to quantify the lattice distortion in HEAs could be questionable. More importantly, there is an increasing and open debate recently [26-29] about the lattice distortion experimentally detected in HEAs. Controversial results reported from different groups have been brought into question, such as those obtained from X-ray diffraction [25, 30-32], which are either not conclusive or usually do not agree with the transmission electron microscopy observations [33, 34] or atomistic simulations [29]. Therefore, despite the fundamental importance, the issue of lattice distortion in HEAs still remains open. In this work, through first-principle calculations combined with theoretical modeling, we intend to carry out a detailed investigation of the local strain field in equiatomic HEAs. Unlike the previous works [4-6, 8, 35], we will take into account not only the volumetric strains but also the shear strains, the latter of which might play a much more important role to the dislocation strengthening mechanisms in HEAs, as suggested in

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Ref[7]. For this purpose, a series of equimolar complex alloys, ranging from binary, ternary, quaternary to quinary alloys, with a chemically disordered face centered cubic (FCC) structure were constructed using the elements of Fe, Co, Ni, Cr and Mn, which were chosen as the model systems for a systematic study of the lattice distortion in these chemically disordered equimolar complex alloys.

2. Methods: DFT Calculations

In the present study, density functional theory (DFT) calculations are performed by using the Vienna *ab initio* simulation package (VASP)[36, 37] with the projector augmented wave (PAW) method[38, 39] and generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE)[40]. The exchange-correlation functional for elements Fe, Cr, Ni, Co, and Mn includes semicore p states as valence electrons. Plane-wave energy cutoff of 600 eV and Monkhorst–Pack k-point mesh[41] density of 0.2 Å^{-1} are used, which have been tested to ensure an energy accuracy of 1 meV/atom. The convergence of energy and force is set to 1.0×10^{-7} eV and 1.0×10^{-3} eVÅ^{-1}, respectively.

To model the random solid solution and quantify the local relaxation effects, special quasi-random structures (SQSs)[42] are generated using the mcsqs tool in the alloy theoretic automated toolkit (ATAT)[43]. For binary, ternary, quaternary and quinary FCC alloys, SQSs with 32, 108, 108 and 120 atoms, respectively, are constructed. Thereafter, the structure optimization is done in a two-step way. Firstly, an initial calculation of the volume-energy relationship is performed for each alloy structure, with atomic positions and cell shape fixed. The derived volume-energy data are fitted by the third-order Birch-Murnaghan equation of state[44, 45] to obtain the equilibrium lattice constant of the pristine structure. Thereafter, a further relaxation of atomic positions, cell volume and shape was executed. Thereby, the residual stresses due to the atomic mismatch in

pristine HEAs were relieved to explore the local lattice distortion. Here, the quasi-Newton algorithm with a smearing parameter of 0.1 eV was adopted to relax the ions into their instantaneous ground state.

Various elastic constants, including bulk modulus (B), shear modulus (G) and Poisson ratio (ν), can be deduced for the HEAs from our studies. The direction dependent elastic constants of c_{11} and c_{12} were calculated from the standard energy-strain method, in line with the previous investigations on HEAs [46, 47]. After that, the bulk modulus (B) was extracted from the third-order Birch-Murnaghan equation of state and the shear modulus (G) was derived through the arithmetic Hill average of the Voigt and Reuss bounds [48]. The Poisson ratio (ν) was then computed via ν=(3B-2G)/2(3B+G). The lattice constants, elastic constants and the lattice distortion of distorted structures, as well as those for pristine structures, are summarized in Table 1. As our first attempt, non-spin polarized calculations were performed for simplicity. After that, four equiatomic complex alloys, including FeCoNiCrMn, FeCoNiCr, FeCoNi and FeCrNi, were selected to study the effect of magnetism on lattice distortion. Following Refs[35, 49], ferromagnetic structure was constructed for FeNiCo, and paramagnetic structures for FeCoNi, FeCrNi, and FeCoNiCrMn, at T = 0 K. In general, the Mn and Cr spins were set to be aligned anti-parallel to the Fe, Co and Ni spins.

3. Results of DFT Calculations

To model a random solid solution structure, the special quasi-random structure (SQS) approach, which was well established for simulating chemically disordered structures[42, 50], was employed in our first-principles calculations based on density-functional-theory (DFT). First, a pristine structure with an ideal FCC symmetry was constructed, of which the lattice constant was determined at the local energy minimum that corresponded to an ideal or un-distorted random

solid-solution configuration. Subsequently, the pristine FCC structure was energetically relaxed by allowing the atoms to stray away from their ideal positions in the pristine FCC lattice. As a result, this generated local atomic strains and a more energetically favorable but distorted random solid solution structure (see **Section 2**). During the DFT calculations, the temperature was set at 0 K to eliminate the effect of thermal fluctuation on lattice distortion. As an example, **Figs. 1 (a)-(b)** show the simulated results for the 3-D atomic configurations of the FeCoNiCr alloy before and after the local distortion. Remarkably, the local distortions are discernible at various sites, as marked in **Figs. 1(a)-(b)**, in the distorted atomic structure with comparison to the pristine lattice without local shear deformation. Furthermore, we calculated the X-ray diffraction (XRD) spectra of the pristine and distorted atomic structure. As shown in **Fig. 1(c)**, the pristine structure exhibits sharp diffraction peaks, conforming to ideal FCC structure as one expects. By comparison, the distorted structure displays similar FCC diffraction peaks; however, the peak profiles are seen widening, notable at the high diffraction angles but insignificant at the low diffraction angles. Interestingly, splitting of the (311) peak can be observed in the distorted structure. On average, the lattice constant decreases from 3.4998 Ă to 3.4984 Ă as a result of the lattice distortion. However, no peak splitting can be observed on the simulated XRD pattern of the individual element (see **Figs. 2(a)-(e)**). Similar results were also obtained for other alloys, as seen in **Supplementary Figs. S2-11**. In the HEA literatures [28, 51], a similar phenomenon of peak splitting was reported based on the experimental data obtained from apparent single phased alloys, which was then attributed to either lattice distortion or the emergence of a secondary phase. Based on our current work, in which the alloys retained the single-phase FCC structure throughout the simulations, we conclude that the peak splitting we observed is due to the lattice distortion rather than the formation of a secondary phase.

To further characterize the local lattice distortions, we calculated the density distribution of the valence electrons with the partial electron density (PED) function. In theory, PED is derived by transforming the eigenfunctions with an energy window just below the Fermi level (energy level ranging from -1 eV up to the Fermi energy)[52], which provides the detailed information about the shape of frontier orbitals in real space. A denser k point sampling (k spacing of 0.14 Å^{-1}) were used for the calculation of PED. The contour plots of PED in the (001) plane of FeCoNiCr are shown in **Fig. 3(a)-(b)**. Through the PEDs, one can see that chemical bonding is anisotropic and asymmetric in the pristine structure, the intensity of which becomes even stronger after the distortion, as highlighted in Fig. 3(b). Similar results can be found in **Supplementary Figs. S2-11** for other alloys. This is in sharp contrast to the chemical bonding in pure metals, which exhibits a perfect 4-fold symmetry in 2D (see **Supplementary Fig. S1**).

To quantitatively characterize the local lattice distortions, here we calculated the local strain tensor around each atom. Following the previous work [53], the local deformation gradient tensor for each atom can be calculated via $\mathbf{J}_i = \left(\sum_{j \in N_i^0} \mathbf{r}_{ji}^{0T} \mathbf{r}_{ji}^0 \right)^{-1} \left(\sum_{j \in N_i^0} \mathbf{r}_{ji}^{0T} \mathbf{r}_{ji} \right)$, where $\mathbf{r}_{ji}$ is the vector between atom j and i with j being one of the neighboring atom of the central atom i; N_i^0 is the total number of the nearest neighbors of atom i and superscript "0" means the reference or un-distorted configuration (see **Appendix A**). **Fig. 4(a)-(d)** show the contour plots of the components of the strain tensor in the basal plane of (001) for FeCoNiCr. In addition to the shear strains, we also computed the local atomic hydrostatic strain via $\varepsilon_i^m = \frac{1}{6} \left(Tr \mathbf{J}_i^T \mathbf{J}_i - 3 \right)$ [53, 54]. As we can see in **Fig. 4(a)-(d)**, although their averages are small, the local value of each strain component is highly fluctuating and varies from one atom to another, breaking the symmetry and smoothness of a regular strain field one could obtain for a dilute solution. As a result, the local strain components

around the individual atoms depend strongly on the local packing environment, not just determined by the species of the chemical elements alone. According to the distribution of each strain component as shown in **Fig. 5(a)-(d)**, the average residual volumetric strain is finite while the average residual shear strain approaches zero. By comparison, the fluctuation of the residual shear strains is prominent, ranging from -0.01 to 0.01.

4. Theoretical Modeling

In general, local lattice distortion generates both volumetric and shear residual strains, which raises the elastic energy stored in the alloys. For the volumetric strain, the elastic energy density is given by $u_v = \frac{3}{2}(C_{11} + 2C_{12})\sum_{i=1,n}(\varepsilon_i^m)^2 \big/ n$, where n is the total number of particles, C_{11} and C_{12} are the elastic constants in Voigt notation [54]; while for the shear strain, the elastic energy density is given by $u_d = \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}(\gamma_i^{Mises})^2 \big/ n + [2C_{44} - (C_{11} - C_{12})]\sum_{i=1,n}[(\varepsilon_i^{xy})^2 + (\varepsilon_i^{xz})^2 + (\varepsilon_i^{yz})^2] \big/ n$, where

$\gamma_i^{Mises} = \sqrt{\frac{2}{3}Tr(\mathbf{F}_i - \varepsilon_i^m \mathbf{I})}$ is the *von Mises* equivalent atomic shear strain, $\mathbf{F}_i$ is the local Lagrangian strain tensor at atom *i* and $\mathbf{I}$ is the identity strain tensor [53, 54] (see **Appendix A**). Since the second term of u_d is negligibly small relative to the first term for most metallic alloys, we can approximately take $u_d \approx \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}(\gamma_i^{Mises})^2 \big/ n$ for simplicity (see **Appendix A**). As a result, the total lattice distortion induced elastic energy density is

$u_p = u_v + u_d \approx \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}\left[\frac{2(C_{11} + 2C_{12})}{(C_{11} - C_{12})}(\varepsilon_i^m)^2 + (\gamma_i^{Mises})^2\right]\big/ n$. As an analogy to the equivalent *von Mises* strain [54], we here define an effective strain γ_i^{eq} for atom *i* to quantify the local effect of the lattice distortion, which can be expressed as:

$$\gamma_i^{eq} = \sqrt{\frac{2(C_{11} + 2C_{12})}{(C_{11} - C_{12})}\left(\varepsilon_i^m\right)^2 + \left(\gamma_i^{Mises}\right)^2} \tag{1}$$

With this newly defined γ_i^{eq}, the total energy density can be re-written as $u_p = \frac{3}{4}(C_{11} - C_{12})\gamma^2$,

where $\gamma = \sqrt{\sum_{i=1,n}\left(\gamma_i^{eq}\right)^2 \Big/ n}$ is the average equivalent strain (see **Appendix A**). As demonstrated in

Fig. 6(a), in the pristine structure, there is no local distortion and hence $\gamma_i^{eq} = 0$ everywhere in the

lattice. After the distortion, local shear and volumetric strains are developed around the individual

atoms. As seen in **Fig. 6(b)**, the magnitude of γ_i^{eq} mainly ranges from 0.01 and 0.025 on the (001)

plane, suggestive of highly fluctuating local lattice distortions. For the whole alloy, we compute

an average equivalent strain $\gamma = \sqrt{\sum_{i=1,n}\left(\gamma_i^{eq}\right)^2 \Big/ n}$, to quantify the overall lattice distortion.

    Table 1 lists the important properties and attributes of the pristine and distorted structure

extracted from our DFT simulations for the 11 types of FCC equimolar alloys. These include the

simulated lattice constants a^{DFT} of the pristine and distorted structures, and the simulated

equivalent strain γ^{DFT} in the distorted structures. To understand these results in a quantitative

manner, we herein develop a simple physical model, which takes into account the efficient packing

of different sized atoms interacting through an effective elastic medium. The basic idea can be

illustrated in **Fig. 7**. From a thermodynamic viewpoint, the pristine structure corresponds to a

fictitious mean lattice at the local energy minimum E_1 in the energy well without any local

distortions; while the distorted structure corresponds to the local energy minimum E_2 in the energy

well that allows both dilatations and shear distortions. Following the method in Froyen's work [55],

the fictitious pristine lattice can act as a reference lattice, from which atomic displacements can

result. In theory, lattice distortion is energetically favorable only when $\Delta E = E_2 - E_1 < 0$. For the

simulated atomic configurations, ΔE is mainly due to the change in the elastic energy storage. From a structural perspective, this is only possible if local shearing can relax part of the radial strains developed around the individual atoms in the pristine structure, due to the atomic size misfit as seen in **Fig. 7**. According to Ref. [26], the elastic energy stored per unit volume in the pristine structure can be expressed as $u_1 = \frac{3}{2}(C_{11} + 2C_{12})(\varepsilon^{fluc})^2$ (see **Appendix A**), while that in the distorted structure can be derived as $u_2 = \frac{3}{2}(C_{11} + 2C_{12})(\varepsilon^{fluc*})^2 + u_p$ (see **Appendix A**), where ε^{fluc} and ε^{fluc*} denote the standard deviation of the residual radial strains in the pristine and distorted structure, respectively; u_p denotes the additional energy increase due to the lattice distortion. Thus, the driving force $\Delta u = u_2 - u_1$ for the distortion can be expressed as:

$$\Delta u = \frac{3}{2}(C_{11} + 2C_{12})\left[(\varepsilon^{fluc*})^2 - (\varepsilon^{fluc})^2\right] + \frac{3}{4}(C_{11} - C_{12})\gamma^2 \tag{2}$$

Note that ε^{fluc*} and ε^{fluc} are related theoretically, the relation of which may be generally written as $\varepsilon^{fluc*} = \varepsilon^{fluc}(\gamma)$. Now we seek a first-order approximation of the above relation, which is $\varepsilon^{fluc*} = \varepsilon^{fluc} - \alpha\gamma$ with α a parameter yet to be determined. Substituting this equation into (2) gives $\Delta u = \frac{3}{2}(C_{11} + 2C_{12})\left[(\varepsilon^{fluc} - \alpha\gamma)^2 - (\varepsilon^{fluc})^2\right] + \frac{3}{4}(C_{11} - C_{12})\gamma^2$. Minimizing the energy difference Δu requires $\partial\Delta u / \partial\gamma = 0$, which yields:

$$\gamma = \left(\frac{2(C_{11} + 2C_{12})\alpha}{(C_{11} - C_{12}) + 2(C_{11} + 2C_{12})\alpha^2}\right)\varepsilon^{fluc} \tag{3}$$

Eq. (3) is important and provides the critical condition under which distortion becomes energetically favorable. Here, we further propose that, among all admissible distorted lattice

configurations as predicted by Eq. (3), the real distorted lattice should take on the configuration that maximizes the overall atomic displacement or the effective average strain γ. This is consistent with the idea that lattice distortion is generally in favor of phase transition [9]. Following the above thinking that γ should be maximized, we have $\partial\gamma/\partial\alpha = 0$ which yields $\alpha = \sqrt{(C_{11}-C_{12})/2(C_{11}+2C_{12})}$. For an isotropic system, $\dfrac{(C_{11}-C_{12})}{(C_{11}+2C_{12})} = \dfrac{(1-2\nu)}{(1+\nu)}$, in which ν is the Poisson's ratio. Substituting this expression into Eq. (3), we thereby obtain the critical equivalent strain $\gamma^{th} = \dfrac{1}{2}\sqrt{\dfrac{2(1+\nu)}{(1-2\nu)}}\varepsilon^{fluc}$ (see **Appendix A**).

To verify the above analyses, we calculated γ^{th} for the pristine structures of the 11 FCC equimolar alloys with ε^{fluc} determined via the method detailed in Ref. [26]. Afterwards we compared them with the DFT derived ones, which can be computed via $\gamma^{DFT} = \sqrt{\sum_{i=1,n}(\gamma_i^{eq})^2 \big/ n}$. As shown in **Fig. 8(a)**, one can see a general trend that γ^{DFT} correlates well with γ^{th}. This delivers a clear message that our theoretical model captures the equivalent strain γ very well. Based on the above results, we can further derive that the elastic driving force to be $\Delta u = -\dfrac{3}{2}(C_{11}-C_{12})\gamma^2$ with $\varepsilon^{fluc*} = \varepsilon^{fluc} - \dfrac{1}{2}\varepsilon^{fluc} = \dfrac{1}{2}\varepsilon^{fluc}$. According to Eq. (2), one can infer that the change in the elastic energies should be $\Delta u = \dfrac{3}{2}(C_{11}+2C_{12})\left[(\varepsilon^{fluc*})^2 - (\varepsilon^{fluc})^2\right]$ in the presence of only atomic contraction and expansion. Therefore, our results indicate that, in order to offset the elastic energy resulting from lattice distortion, a maximum of 75% of the elastic energy stored in the pristine structure could be released out. More importantly, one can infer from the data, as shown in **Fig. 8(a)**, that the lattice distortion does not generally follow the proposition that lattice distortion

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would increase with the number of elements, as early proposed in the HEA literature [26]. Since ε^{fluc} is correlated with the atomic size difference $\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - r_i \big/ \sum_{j=1}^{n} c_j r_j\right)^2}$ [16] and $\varepsilon^{fluc} \approx 0.97\delta$ [26, 56], the equivalent strain γ can be expressed as $\gamma = f(\nu)\delta$, where $f(\nu) = 0.485 \sqrt{\dfrac{2(1+\nu)}{(1-2\nu)}}$. The above expression suggests that the lattice distortion induced residual strain in the chemically complex alloys depends on not only the atomic size misfit, as quantified by δ, but also on the attribute of the chemical bonding reflected by the Poisson's ratio. As shown in **Fig. 8(b)**, by mixing different sized elements in a multicomponent alloy, such as FeCoNiCr or FeCoNiCrMn, one can reduce the atomic size difference without significantly altering the Poisson ratio, and thus partly relax the elastic energy induced by the large lattice distortion in the binary system being composed of the largest and smallest elements, such as FeCr.

Furthermore, we evaluated the lattice constants of the pristine and distorted structures for the equimolar alloys we considered. In general, the lattice constant of an alloy can be expressed as[26]: $a = \sum_{i=1}^{n} c_i a_i (1 + \varepsilon_i)$, where a_i is the lattice constant of the FCC lattice made up of only the ith element. On the basis of our theoretical model (Eqs. (2) - (3)), it can be shown that a complete set of equations can be developed to solve for the radial strains ε_i around the constituent elements in the pristine and distorted structures (see **Appendix B**). As a result, we obtained the lattice constant a^{th} of the alloys in their pristine and distorted structures respectively, as tabulated in Table 1. Evidently, shear distortion does not significantly change the lattice constant of the alloys, which is within our expectation because of the decoupling between shear and volumetric strains. To justify our theoretical results, we compare the lattice constant a^{DFT} derived from the DFT calculations with the theoretical value a^{th}. As seen in **Fig. 9** and the inset, the theoretical predictions

agree remarkably well with the DFT calculations.

5. Discussions

5.1 Solid solution strengthening

As noted in the recent works[35, 57], the fluctuation of local residual strains is important to the mechanical properties of equimolar complex alloys or HEAs even though the average residual strain in them may be small. According to the solid-solution strengthening model [4, 6, 7], the critical shear stress $\tau_0(T=0K) \sim \Delta E_p^{4/3}$, where ΔE_p is the binding energy of a dislocation to a local region which can be associated with the standard deviation of the energy difference when a dislocation segment moves over a distance of ω. In theory, this binding energy is closely related to the elastic field around solute atoms [7]. In the presence of atomic size difference and lattice distortion, this elastic field can be intensified, thereby leading to solute strengthening [3]. According to Labusch [3], solute strengthening comes about owing to two types of misfit: one is the volumetric misfit and the other is the shear misfit. In our model, the equivalent strain γ_i^{eq} quantifies both the volumetric and shear misfits between a central atom i and its surroundings. Therefore, we may speculate that $\Delta E_p \propto \sqrt{\sum_{i=1,n}(c_{11}-c_{12})(\gamma_i^{eq})^2 \big/ n}$ or $\tau_0(T=0K) \propto \left[(c_{11}-c_{12})\gamma^2\right]^{2/3}$.

To verify the above speculation, we plot $\sigma_{alloy}^{\text{exp.}}$ vs. $\left[(c_{11}-c_{12})(\gamma^{DFT})^2\right]^{2/3}$, where $\sigma_{alloy}^{\text{exp.}}$ can be viewed as an equivalent of τ_0 (T=0K) and was extracted from previous experiments [6] after subtraction of other strengthening effects, such as the Hall-Patch effect. Evidently, $\sigma_{alloy}^{\text{exp.}}$ is in a good linear correlation with $\left[(c_{11}-c_{12})(\gamma^{DFT})^2\right]^{2/3}$ as shown in Fig. 10. This is encouraging and suggests that further investigation is worthwhile to explore the strengthening mechanisms in the chemically complex solid-solution alloys by linking the generalized residual strain of a highly

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fluctuation residual strain field to dislocation movements in it.

5.2 Magnetic effect

Before moving to the Summary, we would like to stress that all the above calculations were based on non-spin polarized formulation of DFT. However, some recent works [35, 49, 58] already showed that there might be a magnetic effect on the local lattice distortions in HEAs at a finite temperature. To have a further check, we performed additional DFT simulations on four equimolar alloys, as mentioned earlier, by switching on magnetic calculations and, compared the magnitude of γ_i^{eq} around each atom computed before and after taking magnetism into consideration. As seen in **Fig. 11**, the distribution of γ_i^{eq} for the four model alloys only varies a little after switching on the magnetism option, which is consistent with the previous results [35]. To be specific, a small peak shift can be observed (left for FeCoNi, FeCrNi and FeCoNiCrMn, while right for FeCoNiCr) although the curve of the overall distribution remains almost unchanged. Such a peak shift indicates that magnetism could either relax or intensify the overall residual strain caused by lattice distortion.

Given the results in **Fig. 11**, an updated γ^{DFT} is expected after considering magnetism. As shown in **Fig. 8(a)**, the values of γ^{DFT} of the magnetic systems become slightly different from those of their non-magnetic counterparts. However, it can be clearly observed that these γ^{DFT}'s still have a good correlation with the theoretically predicted values [**Fig. 8(a)**], if the updated Poisson's ratios of these magnetic systems were used in $\gamma^{th} = \dfrac{1}{2}\sqrt{\dfrac{2\left(1+\nu^{mag.}\right)}{\left(1-2\nu^{mag.}\right)}}\varepsilon^{fluc}$. Since γ^{DFT} is an equivalent strain which quantifies the lattice distortion, the relative change of γ^{DFT}, either positive or negative, thereby suggests that the magnetic effect is quite diversified with respect to lattice distortion and thus solute strengthening in different alloys. Seemingly, this may add additional difficulties for the

understanding of lattice distortion in a magnetic field. Nevertheless, since the magnetic effect also manifests itself in the alloy elastic properties, such as the Poisson's ratio, our results suggest that the theoretical modeling laid out in the present work still gives a very good prediction of the lattice distortion with the updated elastic properties.

6. Summary

In summary, through the first-principles calculations, we reveal the details of a non-symmetric residual strain field with atomic scale fluctuations in a series of equimolar complex alloys, which results from atomic scale lattice distortion and would be impossible to study via the conventional experimental means. Subsequently, we develop a simple theory to quantitatively understand our simulation results by considering the efficient packing of different sized atoms interacting in an effective elastic medium. It is shown that our theory captures the general trend of the lattice constants and the magnitude of the distortion induced effective strain very well, either with or without considering the magnetism. Since dislocation strengthening in these complex alloys is closely related to the distribution of the residual strain field, we envision that our current findings should be valuable to further our understanding of plasticity enhancement in chemically complex alloys, such as HEAs.

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Appendix A: The equivalent strain due to the shear induced energy penalty

According to the previous works [26, 59], when incorporating different sized atoms to form an alloy with a simple lattice structure, the radii of the constituent elements need to be adjusted in order to accommodate the atomic size differences. Therefore, the resultant sizes can be very different from those in the corresponding simple metallic form, leading to the development of the intrinsic residual strain [26]. For the perfect pristine structure without any shear, all bond lengths are equal, and the local residual strains are purely volumetric. According to Ref. [26], in this case, the residual radial strain surrounding element i can be derived as

$$\varepsilon_i = \sum_{j=1}^{n} \omega_{ij} c_j \Big/ \sum_{k=1}^{n} A_{ik} c_k - 4\pi\overline{\eta} \Big/ \Big(N_i \sum_{k=1}^{n} A_{ik} c_k\Big),$$ where ω_{ij} is the solid angle subtended by atom j around atom i; c_i is the atomic fraction of element i; N_i is the coordinate number of element i;

$$\overline{\eta} = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} c_j c_i N_i \left[1 - \frac{\sqrt{x_{ij}(x_{ij}+2)}}{x_{ij}+1}\right] \text{ and } A_{ij} = \frac{2\pi x_{ij}}{(x_{ij}+1)^2 \sqrt{x_{ij}(x_{ij}+2)}} \text{ in which } x_{ij} = r_i/r_j \text{ and } r_i \text{ is the}$$

radius of element i. To compute the residual radial strains for a given alloy, one simply needs to know the atomic radius of the constituent element before mixing. For this purpose, we also carried out additional DFT simulations on the pure metals to obtain their respective radius at 0K, as listed in **Table 1**. Once ε_i was obtained, it can be shown that the average radial strain $\overline{\varepsilon}$ is zero in absence of residual shear strains [26]. In such a case, the fluctuation of these local radial strains, in terms of the standard deviation of their distribution, can be simply computed as $\varepsilon^{fluc} = \sqrt{\sum c_i \varepsilon_i^2}$. According to Ye et al. [26], this radial strain fluctuation is strongly correlated with the atomic size misfit in a multicomponent alloy, which can be used further as a metric to gage the lattice stability.

Following the assumptions in previous works [29, 35], the above model was built without considering the existence of shear strains. However, recent work shows shear strains might also

play a very important role in solute strengthening effect[7]. Hence it is necessary for us to revisit the formula of residual strains. First, let's start from a thermodynamic viewpoint. In theory, without outside stimuli, distortions occur only when the energy state after distortion is lower than that of the pristine configuration. According to Ref. [26], when applying the continuum elastic theory to HEAs, the strain energy density in the pristine structure can be expressed as $u_1 = \frac{3}{2}(C_{11} + 2C_{12})(\varepsilon^{fluc})^2$, in which C_{11} and C_{12} are elastic constants and ε^{fluc} the standard deviation of residual radial strains in the pristine structure. While the strain energy density in the distorted structure can be derived as $u_2 = \frac{3}{2}(C_{11} + 2C_{12})(\varepsilon^{fluc*})^2 + u_p$, where u_p is the energy penalty due to the lattice distortion, ε^{fluc*} denote the corresponding standard deviation in the distorted structure, respectively. In theory, lattice distortion will cause two parts of energy penalty: one is the distortion induced hydrostatic strain energy u_v and the other is the distortional shear strain energy u_d. Following the previous work [53], with the relative displacements of the particle's neighbors r_{ji}, where atom j is one of atoms i's nearest neighbors, the local deformation gradient tensor $\mathbf{J}_i$ for each particle can be derived by minimizing $\sum_{j \in N_i^0} |\mathbf{r}_{ji}^0 \mathbf{J}_i - \mathbf{r}_{ji}|^2$, which yields

$$\mathbf{J}_i = \left(\sum_{j \in N_i^0} \mathbf{r}_{ji}^{0T} \mathbf{r}_{ji}^0 \right)^{-1} \left(\sum_{j \in N_i^0} \mathbf{r}_{ji}^{0T} \mathbf{r}_{ji} \right).$$ Here N_i^0 is the total number of nearest neighbors of atom i and superscript "0" refers the reference configuration[53]. As the local Lagrangian strain at atom i is $\mathbf{F}_i = \frac{1}{2}(\mathbf{J}_i^T \mathbf{J}_i - \mathbf{I})$, the local hydrostatic strain can be calculated via $\varepsilon_i^m = \frac{1}{3}Tr(\mathbf{F}_i)$, and the local shear strain invariant is $\gamma_i^{Mises} = \sqrt{\frac{2}{3}Tr(\mathbf{F}_i - \varepsilon_i^m \mathbf{I})}$ [53, 54]. For a cubic system, the hydrostatic strain energy density can be calculated via $u_v = \frac{3}{2}(C_{11} + 2C_{12}) \sum_{i=1,n} (\varepsilon_i^m)^2 / n$, while the distortional strain

energy   density   is

$$u_d = \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}(\gamma_i^{Mises})^2 \Big/ n + [2C_{44} - (C_{11} - C_{12})]\sum_{i=1,n}\left[(\varepsilon_i^{xy})^2 + (\varepsilon_i^{xz})^2 + (\varepsilon_i^{yz})^2\right] \Big/ n, \text{ where n is}$$

the total number of particles. Hence the total shear induced energy penalty is:

$$u_p = u_v + u_d$$
$$= \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}\left\{\frac{2(C_{11} + 2C_{12})}{(C_{11} - C_{12})}(\varepsilon_i^m)^2 + (\gamma_i^{Mises})^2 + \frac{4[2C_{44} - (C_{11} - C_{12})]}{3(C_{11} - C_{12})}\left[(\varepsilon_i^{xy})^2 + (\varepsilon_i^{xz})^2 + (\varepsilon_i^{yz})^2\right]\right\} \Big/ n$$

(A.1)

As an analogy of the definition of the equivalent Von Mises strain [54], here we define an

equivalent strain γ_i^{eq} to be:

$$\gamma_i^{eq} = \sqrt{\frac{2(C_{11} + 2C_{12})}{(C_{11} - C_{12})}(\varepsilon_i^m)^2 + (\gamma_i^{Mises})^2 + \frac{4[2C_{44} - (C_{11} - C_{12})]}{3(C_{11} - C_{12})}\left[(\varepsilon_i^{xy})^2 + (\varepsilon_i^{xz})^2 + (\varepsilon_i^{yz})^2\right]}$$ (A.2)

Thus Eq. (A.1) can be simplified into

$$u_p = \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}(\gamma_i^{eq})^2 \Big/ n = \frac{3}{4}(C_{11} - C_{12})\gamma^2$$

(A.3)

For metallic alloys, the second term in the expression of u_d is relatively small compared to the first

term,   we   can   approximately   take $u_d \approx \frac{3}{4}(C_{11} - C_{12})\sum_{i=1,n}(\gamma_i^{Mises})^2 \Big/ n$ and   hence

$\gamma_i^{eq} \approx \sqrt{\frac{2(C_{11} + 2C_{12})}{(C_{11} - C_{12})}(\varepsilon_i^m)^2 + (\gamma_i^{Mises})^2}$. From the energy viewpoint, distortions occur when:

$$\Delta u = u_2 - u_1 = \frac{3}{2}(C_{11} + 2C_{12})\left[(\varepsilon^{fluc})^2 - (\varepsilon^{fluc*})^2\right] + \frac{3}{4}(C_{11} - C_{12})\gamma^2 < 0$$

(A.4)

Conceptually, ε^{fluc*} and ε^{fluc} are related, the relation of which may be generally written as

$\varepsilon^{fluc*} = \varepsilon^{fluc}(\gamma)$. For a first order approximation, assuming that $\varepsilon^{fluc*} = \varepsilon^{fluc} - \alpha\gamma$ with α a

parameter   yet   to   be   determined,   Eq.   (A.4)   can   be   rewritten   as

$$\Delta u = u_2 - u_1 = \frac{3}{2}(C_{11} + 2C_{12})\left[(\varepsilon^{fluc} - \alpha\gamma)^2 - (\varepsilon^{fluc})^2\right] + \frac{3}{4}(C_{11} - C_{12})\gamma^2 < 0 \quad .$$ Minimizing the

energy difference Δu requires $\partial\Delta u/\partial\gamma = 0$, which yields:

$$\gamma = \left(\frac{2(C_{11} + 2C_{12})\alpha}{(C_{11} - C_{12}) + 2(C_{11} + 2C_{12})\alpha^2}\right)\varepsilon^{fluc} \tag{A.5}$$

In theory, the above expression gives all γ's which are energetically favorable. In general, in a size-mismatched disordered system, atoms will be driven to move away from their ideal lattice positions, leading to a sustainable increase of lattice distortion if there is no further energy barrier [9]. Following this thinking, it is natural for one to assume that γ will be pushed to reach a critical value, where the reduced energy can no longer balance the energy penalty due to the large distortion. In such case, γ will be maximized requiring $\partial\gamma/\partial\alpha = 0$ which yields that

$\alpha = \sqrt{(C_{11} - C_{12})/2(C_{11} + 2C_{12})}$. For an isotropic cubic system, $\dfrac{(C_{11} - C_{12})}{(C_{11} + 2C_{12})} = \dfrac{(1 - 2v)}{(1 + v)}$, in which v is the

poisson's ratio, hence an expression of α that weakly depends on the Poisson's ratio of an alloy can be thereby derived. Substituting this expression into Eq. (A.5), we thereby have the critical

equivalent strain $\gamma^{th} = \dfrac{1}{2}\sqrt{\dfrac{2(1 + v)}{(1 - 2v)}}\varepsilon^{fluc}$, and consequently the energy difference is derived to be

$$\Delta u = -\frac{3}{2}(C_{11} - C_{12})\gamma^2 , \text{ and } \varepsilon^{fluc*} = \varepsilon^{fluc} - \frac{1}{2}\varepsilon^{fluc} = \frac{1}{2}\varepsilon^{fluc}.$$

Appendix B: Residual Radial Strains in the Distorted Lattice

Since the shear strain is decoupled with the volumetric strain and given that the lattice still retains a FCC structure after adjustment, the lattice constant can be generally expressed as:

$a = \sum_{i=1}^{n} c_i a_i(1 + \varepsilon_i)$, where a_i is the constant of the FCC lattice made up of the pure ith element.

According to Ref. [26], since the average residual radial strain is finite and none-zero in the

distorted structure, the residual radial strain of element i can be generally rewritten as:

$$\varepsilon_i = \frac{\sum_{j=1}^n \omega_{ij} c_j}{\sum_{k=1}^n A_{ik} c_k} - \frac{4\pi\overline{\eta}}{N\sum_{k=1}^n A_{ik} c_k} + \frac{\sum_{j=1}^n c_j A_{ij} \varepsilon_j}{\sum_{k=1}^n A_{ik} c_k} \tag{B.1}$$

In theory, by solving a complete set of Eq. (B.1) with the constraint condition $\varepsilon^{fluc*} = \frac{1}{2}\varepsilon^{fluc}$, one

can mathematically work out the residual radial strain ε_i^* for each element and the equilibrium

packing efficiency $\overline{\eta}^*$ in the distorted structure.

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List of Table Captions

Table 1 The lattice constants, elastic constants, polycrystalline Poisson's ratio v as well as the effective strain γ for the various alloys and pure elements obtained from the DFT simulations at T = 0 K compared with those obtained from our elastic theory. The pristine lattice refers to the ideal reference FCC structure without distortion while the distorted one refers to the distorted FCC structure after relaxation.

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Figure 1. The results of the DFT simulation on the FCC FeCoNiCr alloy. (a) atoms of the pristine structure occupies the ideal lattice positions, which subsequently stray from their ideal positions after lattice distortion in (b). In the 3D configurations, white balls stand for Fe, blue ones for Co, red ones for Ni and yellow ones for Cr. The simulated XRD results of the pristine structure (black dash line) as well as the distorted structure (red solid line) are shown in (c).

Figure 2. Theoretical XRD of (a) Fe (b) Cr (c) Ni (d) Co and (e) Mn with FCC structure.

Figure 3. (a) and (b) show the contour plots of the partial electron density (PED) of the pristine structure and the distorted structure, respectively. The black circles in (b) highlight the distorted electron cloud frontiers. Note the colors in the center of each atom are only used to lable different elements, which do not provide any PED information. All are derived from the (001) plane in FCC FeCoNiCr.

Figure 4. The contour plots of the local atomic strain tensor components derived from the (001) plane in the FCC FeCoNiCr. Here the contour images were plotted following the way in Ref. [60].

Figure 5. The distributions of the local atomic strain tensor components in FCC FeCoNiCr.

Figure 6. (a) and (b) show the γ_i^{eq} contour map of the pristine structure and the distorted structure, respectively. All are derived from the (001) plane in FCC FeCoNiCr and the contour images were plotted following the method in Ref. [60].

Figure 7. The schematics demonstrates the transition of a pristine structure to a distorted structure. In principle, the pristine structure corresponds to the configuration with the lowest energy state with local shear being prohibited. Distortion becomes energetically favorable only when local shear relaxes part of the radial strains developed in the pristine structure.

Figure 8. (a) The equivalent strain γ^{DFT} obtained through the simulations for the distorted atomic structure can be well predicted by our theoretical model, with or without considering magnetism. (b) γ^{DFT} is in good correlation with $f(v)\delta$, where $f(v)$ is the function of Poisson's ratio as defined in the main text.

Figure 9. The DFT derived lattice constant can be well predicted by our theoretical model.

Figure 10. The correlation between the experimentally derived lattice friction and the lattice distortion characterized by the product of elastic constants and equivalent strain.

Figure 11. The comparison of the distribution of γ_i^{eq} around each atom with and without considering the magnetic effect. The solid line is the visual guide for the γ_i^{eq} distribution considering magnetism while the dash line is for the γ_i^{eq} distribution without considering magnetism.