

Full length article

## A generally reliable model for composition-dependent lattice constants of substitutional solid solutions

Mingxu Wang<sup>a</sup>, Hong Zhu<sup>b</sup>, Gongji Yang<sup>c</sup>, Jinfu Li<sup>a</sup>, Lingti Kong<sup>a,\*</sup><sup>a</sup> School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Minhang, Shanghai 200240, China<sup>b</sup> University of Michigan–Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China<sup>c</sup> Hunan Provincial Key Laboratory of Advanced Materials for New Energy Storage and Conversion, School of Materials Science and Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

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## ABSTRACT

Solid solutioning has long been employed to improve the performance of engineering materials, the degree of improvement generally correlates closely with the resultant lattice parameters. It is therefore of great importance for materials design to describe accurately the composition-dependent lattice constants of the solid solutions (SSs). However, existing models could hardly reproduce the usually non-linear relationship between the compositions and the lattice constants. Herein, we present a new model within the framework of virtual crystal approximation by taking into account both the size factor and the electronic effect. The model takes inputs as simple as the fundamental property parameters of the elementary substances and  $N$  referential SSs for an  $N$ -component system, and can then predict the lattice constant of SS with any composition within the system. Systematical validation using datasets obtained from high-throughput first-principles calculations and available experiments confirmed the high reliability and general applicability of our model for various substitutional SSs. Applications and limitations of the model as well as outlooks were also discussed. It is expected that this model will deepen the understanding of the relationship between the composition and the properties of materials.

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## 1. Introduction

A full utilization of materials relies on the comprehensive understanding of the relationship among their compositions, structures and properties. In this regard, pure substances are barely used as structural and/or functional materials. Instead, appropriate amount of solutes are added to enhance/tune their mechanical behavior or physical properties so as to meet engineering requirements. [1] The lattice constants of the solid solutions (SSs), as one of the most fundamental parameters, vary with the composition, temperature and pressure. Meanwhile, they correlate closely with the bulk properties of the SSs, such as the elastic constants, thermal expansion coefficients, chemical bonding, thermal conductivity, and also with the onset of phase transition, occurrence of stacking faults, dislocation nucleation, etc. [2,3] It is therefore of great interest to evaluate accurately the composition dependence of the lattice constants for SSs. On the one hand, a quantitative insight of the composition-dependent lattice constants is the basis to evaluate other physical parameters, e.g., the misfit factor for

SS hardening [4–8]. On the other hand, a prior knowledge of the composition-dependent lattice constants can facilitate the tailoring of the physical and chemical properties of multiphase materials dominated by lattice misfits at the phase boundaries. [3,7,9–14] Moreover, lattice constants are at times necessary input parameters for mesoscopic and/or macroscopic scale calculations. Consequently, an accurate description/prediction of the composition-dependent lattice constants is one of the important prerequisites for composition design of advanced materials.

Establishing an analytical description of the lattice constants for SSs in terms of the properties of the constituting elements has been a long-pursued objective in solid state physics and materials science. [15] It is well-documented that two factors dominate the structure of alloy phases, namely the atomic size factor and the electronic effect. [16] While most of the existing models focus on the former, aiming to predict lattice constants of SSs based on the atomic radii or volumes [17–20], lattice constants [21,22] and/or elastic parameters such as the compressibility [23–25], shear modulus [26,27], Poisson's ratio [23,26,28], etc., of the elementary substances corresponding to the constituting elements. Among them, the famous Vegard's law [21] predicts a composition-weighted average of the lattice constants of the solute and solvent. In practice, however, deviation from Vegard's law is frequently observed. And

\* Corresponding author.

E-mail address: [konglt@sjtu.edu.cn](mailto:konglt@sjtu.edu.cn) (L. Kong).

many efforts have been devoted to address this problem. For example, the first-order elasticity model proposed by Eshelby [26] combined the atomic radius with the bulk modulus and Poisson's ratio, leading to an accurate description of the approximately linear composition dependence of the lattice constant for dilute SSs. In most cases, however, the dependence is nonlinear, especially in the concentrated range. To this end, Lubarda and Richmond [29] developed a second-order elasticity model, which was capable of describing the nonlinear relationship between lattice constants and compositions to some extent for merely several systems. Considering the differences in primary crystal structures for the constituting elements, Lubarda [2] recently modified the first-order elasticity model by adopting the effective atomic radii [30], and extended the description of the effective lattice constants to the concentrated range. Nevertheless, the modified model showed a limited success, because its inherent linear relationship failed to describe the actual situation in most cases.

Meanwhile, the electronic factors, such as the electronegativity [31], the number of valence electrons [31–33] and the electron density [16], were also considered. However, these models were found to make satisfactory prediction only in certain systems. For instance, Zhang and Li [16] recently considered the continuity requirement of electron density at the interface between different constituting atoms, and calculated the lattice constants of more than 100 binary SSs based on the atomic radii, electron densities and cohesive energies of the corresponding elemental components. The agreement with the experimental measurements is however not that satisfactory.

The recently developed concentrated multi-component SSs, high-entropy alloys, place further challenges in developing reliable models to predict the lattice constants for such complex systems. Most attempts are based on linear approximations, such as extension of Vegard's law or linear extrapolation around a reference composition [14]. Recently, To-Caraballo et al. [34,35] evaluated the statistical bond lengths in high-entropy alloys based on the bond matrix proposed by Moreen et al. [56] and then predicted the lattice constants of CrCoFeNi high-entropy alloys. Despite good agreement with the experimental data, the proposed approach is rather complicated with many fitting parameters [14], and its universality and accuracy still await further verification.

In short, describing/predicting the composition-dependent lattice constants for SSs is of both scientific and practical importance.

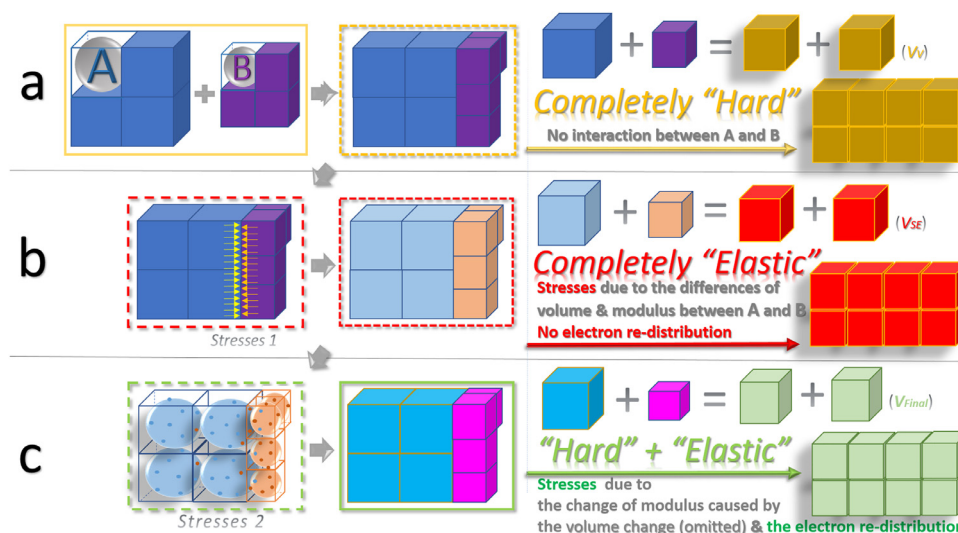
Yet most of the existing models are reliable only in the dilute region, and few if not none of them could describe the nonlinear relationship with high accuracy. To this end, a new model was proposed in this work within the framework of virtual crystal approximation (VCA) [36,37]. It takes the fundamental property parameters of the constituting elements and some reference SSs as inputs, and is seen to be capable of predicting the non-linear composition dependence of lattice constants for substitutional SSs in the whole composition range. Extensive validations with large amount of data obtained from high-throughput first-principles calculations and reported experiments suggest that the model is easy to use, of high reliability, and applicable to a wide range of SS systems, including the most challenging high entropy alloys.

## 2. Models

Imagining mixing solute and solvent atoms under constant temperature and pressure to form a substitutional SS with all atoms sitting at the lattice sites, the atomic volume is expected to change, induced by the internal stresses resulting from differences in the atomic size, modulus, and electronic structure of the constituting elements. Eventually, equilibrium will be established, and the lattice constant can be evaluated according to the crystal structure and the average atomic volume following the VCA. The development of the present model for binary SSs is schematically illustrated in Fig. 1, where the spatial distribution of the solute is left out.

### 2.1. Virtual crystal approximation and average volume

Assuming the solute atoms distribute randomly on the lattice sites, the overall shape of the crystal structure would remain invariant upon the formation of SS from a statistical point of view. Following the VCA, all atoms can be assumed as entities to share the same shape, volume, and composition, as illustrated in the right part of Fig. 1. In this way, the average volume for each micro-zone where an atom stays, rather than those complex factors, such as the distribution of solutes, local lattice distortion effect [38–41], electron cloud shape, and/or the change of space utilization, should be adopted as the central parameter, which would greatly simplify the problem. Furthermore, since all the micro-zones are identical with each other based on VCA, the bulk modulus for any



**Fig. 1.** Schematic diagram of the present model in the case of binary solid solutions. The left part shows the changes of average volumes during the process forming a solid solution, where the distribution of solute atoms is omitted. The right part shows the average volumes based on virtual crystal approximation. Different colors correspond to different values of average volumes.

micro-zone would also be the same as the macroscopic one. Consequently,

$$V_{\text{avg}}^{\text{alloy}} = V_{\text{tot}}^{\text{alloy}} / N, \quad (1)$$

$$K_{\text{avg}} = K_{\text{tot}}, \quad (2)$$

where  $V_{\text{avg}}^{\text{alloy}}$ ,  $V_{\text{tot}}^{\text{alloy}}$  and  $N$  are the average atomic volume, total volume, and total number of atoms of the SS, respectively. While  $K_{\text{avg}}$  and  $K_{\text{tot}}$  are the average bulk moduli for each micro-zone and the overall SS, respectively.

Within the framework of VCA, we will develop our model by dividing the formation process of a SS into three sequential imaginary scenarios, namely *mechanical mixing*, *internal stress equilibration without electronic coupling*, and *further adjustment due to the electronic coupling*, which correspond to the *Completely "Hard"*, *Completely "Elastic"*, and *"Hard" + "Elastic"* parts in Fig. 1a-c, respectively.

## 2.2. Mechanical mixing approximation

In the simplest picture, when mixed together to form SSs, each atom or micro-zone could be seen as a completely "hard" particle, whose average volume remains as its corresponding value in the elemental state (see Fig. 1a). In other words, no interaction between atoms of different species is assumed, while the interaction between atoms of the same species still remains the same as that in the elemental state. The SS can therefore be treated as a "mechanical mixture" of different atoms. And its average atomic volume could then be evaluated by a composition weighted average of the corresponding atomic volume of each component in their respective elemental state,

$$V_V = \sum_i V_{\text{avg}}^i c_i, \quad (3)$$

where  $V_V$  is the average atomic volume after the "mechanical mixing", while  $V_{\text{avg}}^i$  is the average atomic volume of component  $i$  in its elemental state and  $c_i$  is the content of component  $i$  in the SS.

## 2.3. Internal stress equilibration without electronic coupling

In reality, atoms of different species are generally of different sizes and moduli. When mixed together to form substitutional SSs, interactions between atoms of different species are inevitable. And internal stresses will be induced if all atoms remain their original sizes (see Fig. 1b). Assuming there is no electronic coupling between the atoms of different species, the modulus for each micro-zone could still be assumed to be the same as that of the elemental state, while the volume of each micro-zone would change elastically to reduce the internal stress, until a balance is reached. Upon equilibrium, we would have

$$\sum_i \sigma_i c_i = 0, \quad (4)$$

$$\sigma_i = K_{\text{avg}}^i (V_{\text{SE}} - V_{\text{avg}}^i) / V_{\text{SE}}, \quad (5)$$

where  $\sigma_i$  is the average internal stress on each micro-zone of component  $i$ ; and  $V_{\text{SE}}$  is the average atomic volume of the SS after the internal stress equilibration.  $K_{\text{avg}}^i$  and  $V_{\text{avg}}^i$  are the bulk modulus and the average atomic volume of component  $i$  in the elemental state, respectively. In the general case, the internal stress would be a tensor, and one should replace the bulk moduli and volumes with their corresponding tensor form. Assuming an isotropic deformation, all the parameters in Eq. (5) will be reduced to scalars, which simplifies the model considerably.

## 2.4. Further adjustment due to the electronic coupling

Actually, electronic coupling would be expected once the atoms of different species are mixed together. In turn, the bulk moduli of the micro-zones in the SS would differ from those in the elemental state, which requires further adjustment of the local atomic volumes so as to arrive at a complete internal stress balance (see Fig. 1c). The final average atomic volume of the SS predicted ( $V_P$ ) could be expressed by

$$V_P = V_V + \beta (V_{\text{SE}} - V_V), \quad (6)$$

where the first term on the right-hand side is the one from the mechanical mixing approximation. While the second term represents the deviation from the mechanical mixing, where  $(V_{\text{SE}} - V_V)$  stands for the volume change if internal stresses are considered without taking into account the electronic coupling. The parameter  $\beta$  accounts for the contribution of the electronic coupling effect to the volume deviation. Combining Eq. (6) with Eqs. (3–5), one obtains

$$V_P = V_V + \beta \frac{\sum_i K_{\text{avg}}^i V_{\text{avg}}^i c_i (1 - c_i) - \sum_i \sum_{j \neq i} K_{\text{avg}}^i K_{\text{avg}}^j V_{\text{avg}}^i V_{\text{avg}}^j c_i c_j}{\sum_i K_i c_i}. \quad (7)$$

One sees from Eq. (7) that the deviation from the mechanical mixing originates mainly from two factors, namely the size effect ( $V, K$ ) and the electronic one ( $\beta$ ). Besides, both the interaction between atoms of the same type, e.g.  $\sum_i K_{\text{avg}}^i V_{\text{avg}}^i c_i (1 - c_i)$ , and that between the different types, e.g.  $\sum_i \sum_{j \neq i} (K_{\text{avg}}^i K_{\text{avg}}^j V_{\text{avg}}^i V_{\text{avg}}^j c_i c_j)$ , contribute to the deviation. Alternatively, Eq. (6) or Eq. (7) can also be expressed as

$$V_P = (1 - \beta)V_V + \beta V_{\text{SE}}, \quad (8)$$

where  $(1 - \beta)V_V$  and  $\beta V_{\text{SE}}$  can be considered as the average atomic volumes contributed by the interaction between atoms of the same species (mechanical mixing approximation) and that of different species (internal stress equilibration).

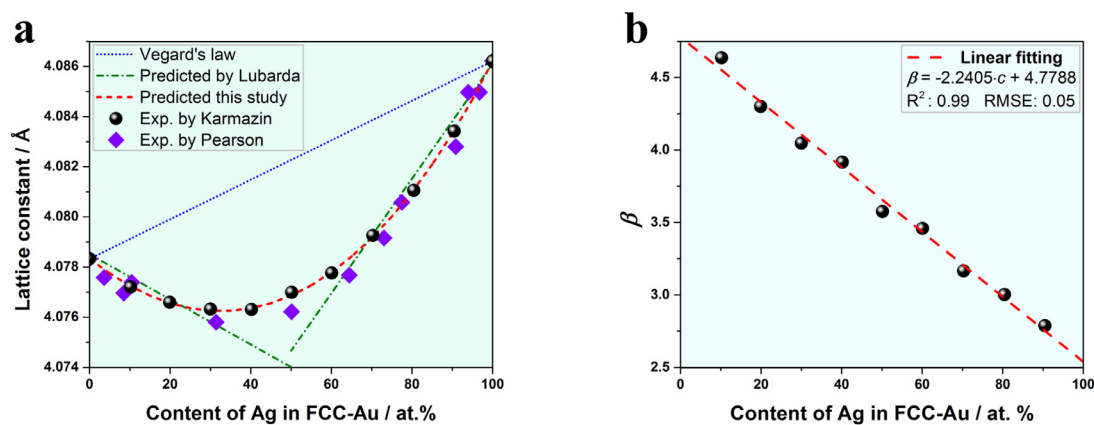
## 2.5. Determination of the parameter $\beta$

One sees from Eqs. (6–8) that to describe the average atomic volume of the SS within the framework of the VCA, all the parameters except for  $\beta$  can be obtained from the elemental state of the constituting elements. Consequently, determination of  $\beta$  is crucial to predict the average atomic volume and in turn the lattice constant of the SS with the current model. As  $\beta$  reflects the effect of electron coupling between the different elements, its value will therefore depend on the electron density of the SS. The latter however scales with the composition of the system. In turn,  $\beta$  depends on the concentrations of the constituting elements as well. Assuming a linear dependence, we will have

$$\beta = \sum_i \beta_i c_i, \quad (9)$$

where  $\beta_i$  scales the electronic coupling effects between component  $i$  and the other components on the average volume of the micro-zone for component  $i$ . It can be considered as a constant for element  $i$  in the solid solution, while its value depends on the constituting elements of the solid solution although regardless of the concentrations.

In this way, the necessary fitting parameters for an  $N$ -component SS are therefore the  $\beta_i$ 's. To determine these  $\beta_i$ 's, the lattice constants of at least  $N$  referential SSs for an  $N$ -component system as well as the bulk moduli and volumes of the end components are therefore needed. Once these  $\beta_i$ 's are determined, the lattice constant for the SS in the whole composition range can be deduced according to Eq. (6) or Eq. (8). Moreover, combining Eqs. (7) and (9), one sees that the composition dependence of lattice constants of SSs is inherently neither linear nor quadratic with



**Fig. 2.** Composition-dependent lattice constants of Au-Ag solid solutions (a) and the linear fitting for parameter  $\beta$  determined as a function of composition for the current model. Experimental data are from Refs. [51–53], while the data measured by Pearson [52] were not used in the fitting.

the current model. While a linear dependence will be overwhelming in the dilute range, and deviation from the linearity in nature could be reasonably elucidated within the present model.

### 3. Methods

High-throughput calculations were carried out by using the ATOMATE codes as the driver to automate the workflows [42]. The equilibrium lattice constants and bulk moduli were computed by adopting the preset workflow that computes and then fits the energy-volume relation of the SS models to the Birch-Murnaghan equation of state [43]. The SS models were generated by following the recipes of Monte-Carlo special quasi-random structure (MC-SQS) [44] within the ATAT codes [45].

All first-principle calculations were performed by using the VASP codes [46,47] based on density functional theory, where the ion-electron interactions were described by the projector augmented wave method [48] and the GGA-PBE exchange correlation functionals [49] were employed. A plane wave cutoff energy of 520 eV was adopted. The integration in the Brillouin zone was performed on a  $\Gamma$ -centered  $k$ -mesh with a grid density of 7000, where the partial occupations of the bands were set following the first-order Methfessel-Paxton method [50] with a smearing width of 0.05 eV. The energy tolerance for the electronic relaxations was  $10^{-7}$  eV per atom, and the Hellmann-Feynman force tolerance for the ion relaxations was set to be 0.01 eV/Å. A  $2 \times 2 \times 2$  supercell containing 32 atoms and a  $3 \times 3 \times 3$  supercell containing 54 atoms were adopted to model the FCC and BCC/HCP based SSs, respectively.

### 4. Results

To validate the proposed model, several typical systems were examined and the results were shown in Figs. 2–5, while more examples were compiled in the Supplementary file.

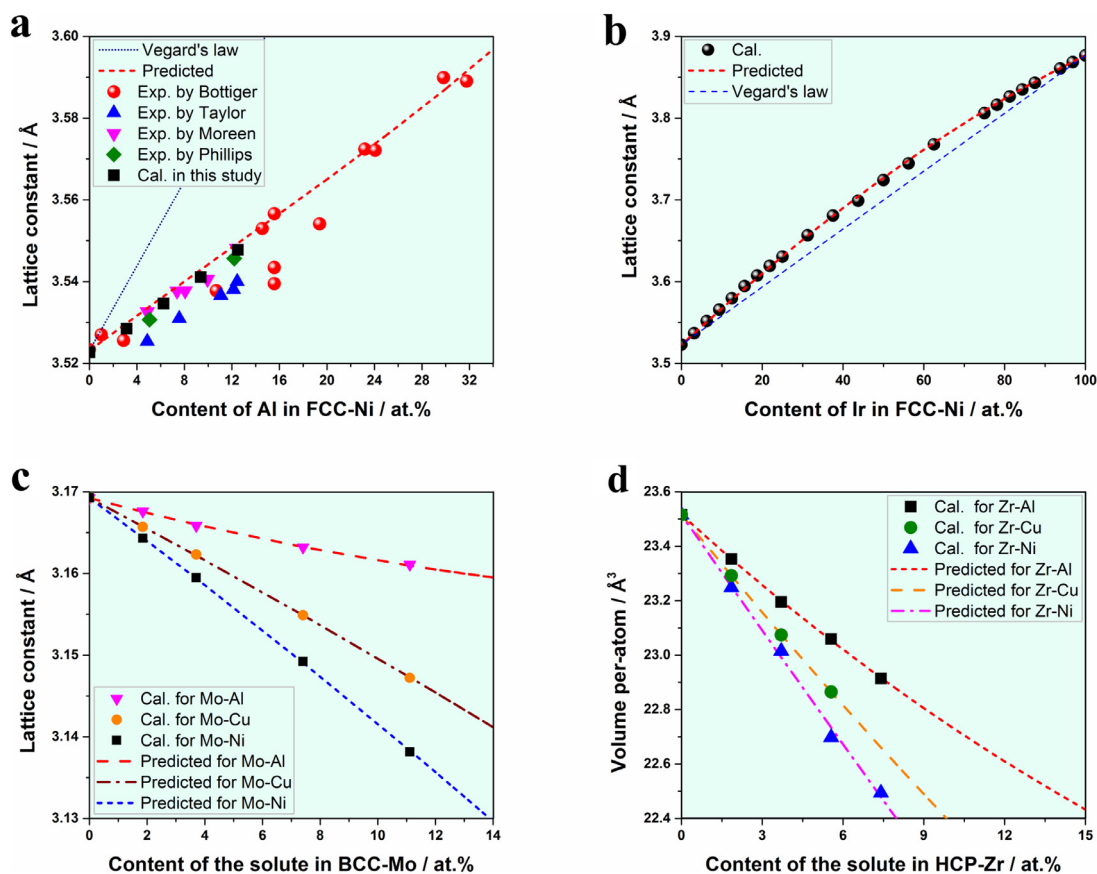
#### 4.1. Application in binary solid solutions

As the first example, the Au-Ag system which forms a continuous SS was examined. Firstly, the experimentally determined lattice constants ( $a^i$ ) [51,52] and bulk moduli ( $K_{avg}^i$ ) [53] were employed to calculate the  $V_{SE}$  according to Eq. (5) and then to determine the parameter  $\beta$  in Eqs. (6–8), so as to confirm the validity of the assumption introduced in Eq. (9). Fig. 2b shows the derived  $\beta$  for FCC Au-based SSs as a function of Ag concentration, where one

finds that indeed a linear correlation between  $\beta$  and  $c$  is observed. Incorporating the linearly fitted  $\beta_{Au}$  and  $\beta_{Ag}$  back into Eqs. (9) and (7), one can “predict” the lattice constant of the Au-Ag SS at any composition. Fig. 2a compares the predicted lattice constants to the experimentally determined ones [51,52], where one sees a perfect agreement ( $R^2 = 1.00$ , RMSE = 0.00). Instead, the Vegard’s law can hardly reproduce the experimentally revealed composition-dependent lattice constants. The Lubarda’s model [2] works better than the Vegard’s law, although it also fails to predict the non-linear composition dependence of lattice constants in the concentrated range. The perfect agreement between the predictions from the current model and the experimental data suggests the validity of the current model. In particular, the linearity of  $\beta$ - $c$  revealed in Fig. 2b demonstrates that the unknown parameter  $\beta$  could be easily determined if the lattice constants of  $N$  distinct referential SSs are available for an  $N$ -component system. It should be noted that the linearity of  $\beta$ - $c$  observed in Au-Ag is not unique, instead, it is rather universal. For simplicity, figures evidencing the linear dependence of  $\beta$  against  $c$  for all systems considered in this work were shown in the Supplementary file. It should be noted that the present model is essentially an isothermal one, i.e., it describes the composition dependent lattice parameters at a prescribed temperature. For other temperatures, one should plug the corresponding moduli and lattice parameters under the desired condition into the present model and then make the predictions.

One might doubt that the success of the proposed model in the Au-Ag system could be a coincidence. To rule it out, some typical binary SSs with different crystal structures were examined, e.g. FCC Ni-Al with limited solubility and Ni-Ir continuous SSs, BCC Mo-based and HCP Zr-based SSs with limited solubility (see Fig. 3). More cases can be found in the Supplementary file. Fig. 3 compares the respective lattice constants derived with the proposed model to the data from first-principles calculations or experimental measurements. One sees that in all cases, the current model can describe accurately the nonlinear composition dependence of the lattice constants/average atomic volumes for substitutional SSs, regardless of the underlying crystal structure or the equilibrium solubility limit. It should be noted that for HCP-based SSs, the shape of the lattice, i.e., the  $c/a$  ratio, generally also varies with the addition of the solute, which however cannot be derived by the current model. Nonetheless, the composition-dependent average atomic volume can be accurately reproduced, as shown in Fig. 3d. Incidentally, one also sees from Fig. 3a that the measured data reported by different researchers differ from each other considerably, indicating the relatively large errors in experimental





**Fig. 3.** Composition dependence of the lattice constants or average volumes for binary solid solutions. Measured data (Exp.) [54–57] for limited Ni-Al solid solutions (a), calculated data based on DFT in this study (Cal.) for continuous Ni-Ir solid solutions (b), limited Mo-based solid solutions (c), and limited Zr-based solid solutions (d) are shown. The data measured by Böttiger [55] were adopted to get the  $\beta_i$ 's for the Ni-Al system.  $R^2 \approx 1.00$ ,  $RMSE \approx 0.00$  for all the curves.

measurements; for consistency, most examples shown here adopt the lattice constants calculated from first principles calculations.

#### 4.2. Applications in ternary and quasi-binary solid solutions

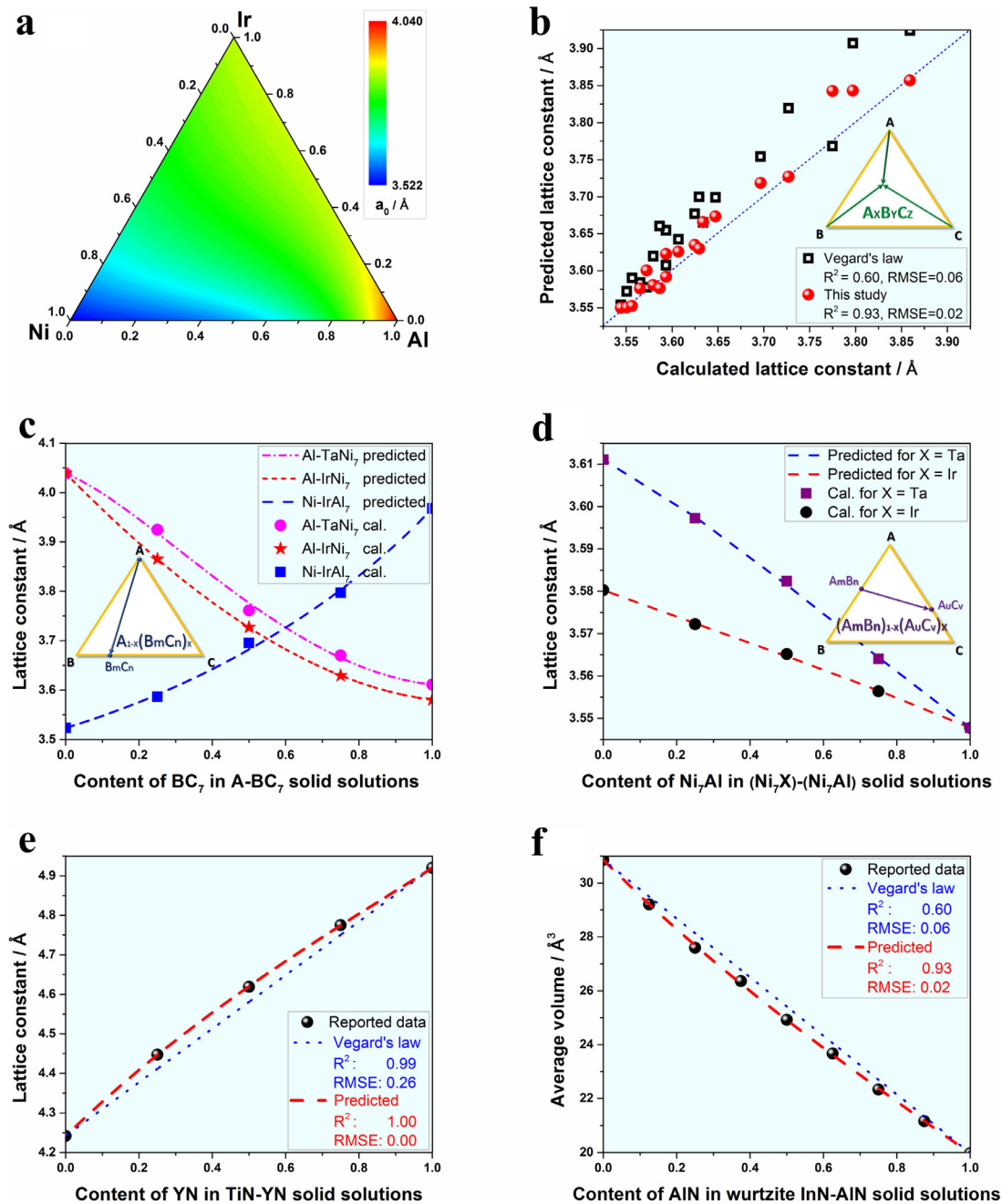
To showcase the application of the current model in ternary systems, we take the FCC Ni-Ir-Al system as an example, assuming a continuous SS in the whole composition range. Due to the shortage of experimental data, the lattice constants for the Ni-Ir-Al SSs at a series of compositions were computed by first principles high-throughput calculations and then fitted to the current model. Fig. 4a shows the contour map of the lattice constants predicted from the model, and Fig. 4b compares the calculated and predicted values. The values of  $\beta_{Ni}$ ,  $\beta_{Ir}$  and  $\beta_{Al}$  were obtained by linear fitting of  $\beta \sim c$ , where the corresponding  $\beta$ 's were derived using the eight referential Ni-Ir-Al ternary SSs (see Supplementary file). One sees from Fig. 4b that the proposed model works well for the ternary system as well, the agreement between the calculated lattice constants and the predicted ones by our model are much better than that by the Vegard's law, confirming the reliability and versatility of the current model.

Ternary systems with a fixed concentration for one component or with a fixed stoichiometric ratio between two components could be seen as quasi-binary ones, and one can also use the current model to derive their composition-dependent lattice constants. Fig. 4c-f show some hypothetical ternary SSs that can be treated as quasi-binary ones. One finds again that the current model works as well for such systems. One of the benefits of such treatment is that it enables one to evaluate the composition-

dependent lattice constants for SSs containing elements such as N, O, and/or S, whose elemental ground states differ considerably from the SS and in turn their bulk moduli and/or lattice constants for the elemental states are difficult to acquire. Nonetheless, comparing Fig. 4c with Fig. 4d, one sees that the non-linearity in the composition dependence of the lattice constants becomes less obvious with the increasing number of components for quasi-binary SSs, which should originate from the averaging effect of the interactions among different types of atoms.

#### 4.3. Application to concentrated multi-component solid solutions

For multi-component SSs, especially for the concentrated ones, e.g. high-entropy alloys, it has been a great challenge to describe their composition-dependent lattice constants. The current model is capable of making reliable predictions for them as well. In this regard, the CoCrFeNi high-entropy alloys whose lattice constants have been reported experimentally [14] were adopted to further demonstrate the reliability and universality of our model. The available experimental results were fitted to the current model, and the parameter  $\beta$  were found to be  $\beta = 3.7643c_{Co} + 10.0556c_{Cr} + 8.7098c_{Fe} - 8.6460c_{Ni}$  ( $R^2 = 0.94$ ,  $RMSE = 0.23$ ). One sees from Fig. 5 that the current model accurately reproduces the experimental data ( $R^2 = 0.97$ ,  $RMSE = 0.00$ ), which is superior over the predictions by Wang et al [14] based on a linear fitting from a reference composition ( $R^2 = 0.86$ ,  $RMSE = 0.00$ ). The Vegard's law, however, fails to yield reliable predictions for the lattice constants of CoCrFeNi high-entropy alloys ( $R^2 = -3.36$ ,  $RMSE = 0.01$ ).



**Fig. 4.** Composition dependence of lattice constants for ternary and quasi-binary solid solutions. (a) and (b) are the whole composition map for lattice constants of Ni-Ir-Al solid solutions and the corresponding fitting data used for the map, respectively; (c-f) are predictions for quasi-binary solid solutions[58,59].

## 5. Discussions

### 5.1. Error analysis

According to Eqs. (6–9), the credibility of the current model relies largely on the accuracy of the parameter  $\beta_i$ , which is determined by fitting to available data of the referential SSs. In general, lattice constants of at least  $N$  referential SSs are needed to determine these  $\beta_i$ 's for an  $N$ -component system. The accuracy of the data for the referential SSs is therefore rather critical. One sees from Fig. 2 and Supplementary file that the  $\beta$ - $c$  correlation usually fluctuates. And a relatively small error in the lattice constants of the referential SSs would translate into a large one for the linear fitting of  $\beta$ - $c$ , especially in the concentrated range. It is therefore

expected that accurate inputs from the referential SSs in the non-dilute range are essential for reliable predictions. More input data with high accuracy would certainly be helpful to improve the reliability of the predictions made based on our model.

Furthermore, it is noteworthy that there is no overfitting problem within the present model. Exactly  $N$  fitting parameters are needed for SSs of  $N$ -components. And nearly all the linear fits to determine  $\beta_i$ 's were found to have relatively large values of  $R^2$  and quite small RMSEs (see Supplementary File), confirming the linear assumption adopted in Eq. (9) is reasonable. It can also be seen in the Supplementary file that, on the premise of accurate input data, the choice of the dataset used for the fitting of  $\beta_i$ 's has little influence on the accuracy of the predictions. While errors in the predicted lattice constants and the determined  $\beta_i$ 's mainly come from

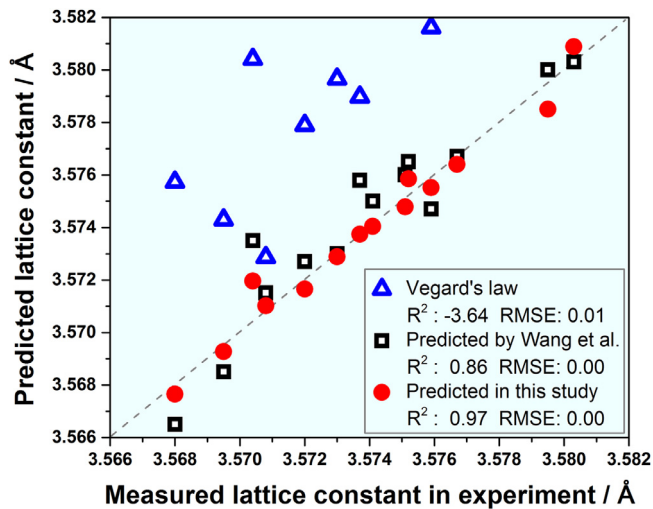


Fig. 5. Application in quaternary CoCrFeNi high-entropy alloys. The measured data are from Ref. [14].

those of the input from the referential SSs. For the latter, however, errors in experiment can have many sources, such as the material purity, measurement error, and temperature variation, while the errors in the first-principles calculated data mainly come from the finite supercell adopted to model SSs, especially for the multicomponent and/or concentrated systems. As error in the raw data is inevitable and merely four data points are available for most system in this study, all data points available were therefore used to fit the  $\beta_i$ 's to ensure high accuracy.

### 5.2. Interpretation of $\beta$ and the corresponding volumes

The parameter  $\beta$  is defined to account for the electronic coupling effect on the average atomic volumes. To further understand its physical essence, as well as to clarify the relative contributions to the final average atomic volume, data obtained from high-throughput first-principles calculations under 0 K and 0 Pa were analyzed. As revealed by the data shown in the Supplementary file, the values of  $\beta$  can be classified into three categories, each category corresponds to two possible relative relationships among  $V_P$ ,  $V_{SE}$ , and  $V_V$ . The origin can be understood in terms of the framework of the current model. Upon the mixing of different elements to form SSs, the valence electrons would redistribute, which will change the local electron density and bulk modulus for each micro-zone. As a result, further adjustment of the average atomic volume will occur to balance the internal stresses. The value of  $\beta$  characterizes quantitatively the contribution of the electronic factor to the adjustment of the average atomic volume (defined as  $\Delta V_1 = V_P - V_{SE}$ ), mainly through changing the bulk moduli of the micro-zones. Accordingly, the total change in the average atomic volume and the contribution from the size factor could be characterized by  $\Delta V = V_P - V_V$  and  $\Delta V_2 = V_{SE} - V_V$ , respectively. That is,  $\Delta V = \Delta V_1 + \Delta V_2$ . In turn, for each category of  $\beta$ , there will be two possible relative relationships among  $V_P$ ,  $V_{SE}$ , and  $V_V$  that correspond to  $\Delta V < 0$  for volume contraction and  $\Delta V > 0$  for volume dilation, respectively.

$\beta \in (0, 1)$ ,  $V_V > V_P > V_{SE}$  or  $V_V < V_P < V_{SE}$ . From Eq. (8), one would expect that the value of  $\beta$  should lie within (0, 1). This however corresponds to the case when the electronic coupling between different species in the SS is relatively weak. Under such circumstances, the electronic effect would counteract partially that of the size effect, i.e., we would have  $|\Delta V_1| < |\Delta V_2|$  and  $\Delta V_1 \cdot \Delta V_2 < 0$ . That is to say, the size factor dominates the volume change. The final average atomic volume would lie between  $V_V$  and  $V_{SE}$ .

Such situations were observed in the Al-end of the Al-Mg SSs ( $V_V > V_P > V_{SE}$ ) and the Ni-end of Ni-Pt SSs ( $V_V < V_P < V_{SE}$ ). Furthermore, it can be suspected that for  $\beta = 0$  ( $V_P = V_V$ , e.g., Ni-end of Ni-Ag SSs), the electron coupling effect is rather weak and can be neglected ( $\Delta V_1 = 0$ ), while for  $\beta = 1$  ( $V_P = V_{SE}$ , e.g., Cu-end of Cu-Nb SSs) the electronic coupling effect just cancels that by the size factor ( $\Delta V_1 = -\Delta V_2$ ).

$\beta > 1$ ,  $V_V > V_{SE} > V_P$  or  $V_V < V_{SE} < V_P$ . When the electronic coupling effect is relatively strong, the electron coupling would enhance the volume change caused by the size factor:  $|\Delta V_1| \geq |\Delta V_2|$  and  $\Delta V_1 \cdot \Delta V_2 > 0$ . As a result, the final average atomic volume would either contract considerably, e.g., for Al-Re SSs ( $V_V > V_{SE} > V_P$ ), or expand significantly, e.g., for Al-end of Al-Zn SSs ( $V_V < V_{SE} < V_P$ ).

$\beta < 0$ ,  $V_P < V_V < V_{SE}$  or  $V_P > V_V > V_{SE}$ . When the electronic coupling effect is strong enough to dominate the volume change while it counteracts the size effect, the value of  $\beta$  would be negative. The volume change caused by the size factor can only counteracts partially that by the electronic coupling ( $|\Delta V_1| > |\Delta V_2|$  and  $\Delta V_1 \cdot \Delta V_2 < 0$ ). This was observed in, e.g., Al-end of Al-Cd SSs ( $V_P > V_V > V_{SE}$ ) and Al-Ta SSs ( $V_P < V_V < V_{SE}$ ).

## 6. Conclusions

To summarize, a simple yet reliable and general model was proposed based on VCA to accurately describe the composition-dependent lattice constants of substitutional SSs, which was seen to be generally successful in reproducing the nonlinear composition dependence of lattice constants for binary and ternary SSs, even high entropy alloys.

Comparing to existing models, the current model has mainly three advantages. Firstly, it is inherently nonlinear, and would therefore be highly reliable in describing the nonlinear composition dependence for the lattice constants of substitutional SSs. Secondly, it is generally applicable to all substitutional SSs. Applications in metallic and non-metallic systems with different crystalline structures of different equilibrium solubility limits are seen to be successful. Although the temperature and pressure dependence are not explicitly incorporated in the model, they could easily be considered by adopting the input parameters ( $K$  and  $V$ ) under the desired temperature and pressure. Thirdly, it is relatively simple and convenient, as only  $N$  fitting parameters are required for an  $N$ -component system. And the method is also easy to implement, making it rather promising for future studies.

Nonetheless, limitations of the current model are also apparent. Firstly, the determination of  $\beta_i$ 's requires the lattice constants of at least  $N$  referential SSs for an  $N$ -component system, which are generally unavailable. Nonetheless, the ever growing computational power and constantly improving of scientific computing algorithms however make it possible to overcome such difficulties. Secondly, the model assumes an isotropic variation of the lattice constants upon the formation of SSs, while anisotropic variations are frequently observed for systems like HCP ones. In such cases, the predicted average atomic volume is expected to be reliable. Besides, the model cannot be used to describe the composition-dependent lattice constants for interstitial SSs, which could however be treated with existing models within the dilute limit.

Accordingly, further improvement of this model will focus on two aspects. On the one hand, more high-throughput first-principles calculations will be carried out to produce large amount of standard data, from which the related  $\beta_i$  for each system can be deduced. Combined with data mining and machine learning techniques, the relationship between  $\beta_i$  and the intrinsic properties of the constituting elements would be revealed. In this way, one might be able to derive  $\beta_i$  directly from the related parameters of the constituting elements rather than from linear fitting, and the

current model could then be employed to predict the lattice constants of SSs readily. On the other hand, the model can be further extended to account for the anisotropic behavior of the crystal lattice, e.g., by replacing the bulk modulus with the elastic constants. And then the composition dependent lattice constants for systems with internal freedoms could also be described. Furthermore, by extending the ideas in this study, models that describe the composition dependent bulk moduli and/or elastic constants of the solid solutions could also be developed based on the mean field approximation. It is expected that this study as well as further study can deepen the understanding of the relationship between the composition and properties of materials.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Data availability

The data that support the plots within this paper are available from the corresponding author (konglt@sju.edu.cn) upon reasonable request.

### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2021.116865.

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