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Effect of alloying elements on the elastic properties of γ-Ni and γ'-Ni_3Al from first-principles calculations

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I. ABSTRACT

The effect of alloying elements Ta, Mo, W, Cr, Re, Ru, Co, and Ir on the elastic properties of both γ-Ni and γ'-Ni_3Al is studied by first-principles method. Results for lattice properties, elastic moduli and the ductile/brittle behaviors are all presented. Our calculated values agree well with the existing experimental observations. Results show all the additions decrease the lattice misfit between γ and γ' phases. Different alloying elements are found to have different effect on the elastic moduli of γ-Ni. Whereas all the alloying elements slightly increase the moduli of γ'-Ni_3Al expect Co. Both of the two phases are becoming more brittle with alloying elements, but Co is excepted. The electronic structures of γ' phase alloyed with different elements are provided as example to elucidate the different strengthening mechanisms.

II. INTRODUCTION

Nickel-based single-crystal (SC) superalloys are a type of very important materials used in turbine blades for power generation and advanced aircraft engines due to their superior elevated-temperature mechanical properties[1–3]. The superalloys are constituted by precipitate γ' phase ($L1_2$, ordered fcc, Ni_3Al based) and matrix γ phase (disordered fcc, solid solution based on Ni). In general, the γ' precipitates play an important role in the mechanical properties of the two-phase γ/γ' alloy. It is well known that the mechanical properties, the lattice misfit, the precipitate morphology and the chemical compositions are all interrelated[4]. The chemical compositions of the constitutive phases controls the sign and the magnitude of the lattice misfit δ, which in turn influences sensitively the precipitate shape and the microstructure evolution during fabrication and application[5, 6]. As a result, the effect of alloying elements on the lattice misfit and elastic properties is critical for a fundamental understanding of the mechanical behaviors of the Ni-base superalloys. Advanced commercial superalloys usually contain many alloying elements. As an example, Re, Ru are the critical additions for the obvious improvement of the performance of alloys. However, to the best of our knowledge, the different strengthening mechanisms related to these alloying elements are not totally understood. Therefore, a deeper understanding of the influence of certain alloying elements on the elastic properties of superalloys is of high interest and should be systematically investigated. In view of the important role of density functional theory (DFT) on studying the mechanical properties of material[7–9], we present here the ab initio investigation of effect of alloying elements on the elastic properties of both γ-Ni and γ'-Ni_3Al. The essential alloying elements X (X=Ta, Mo, W, Cr, Re, Ru, Co, Ir) in the fourth generation Ni-base superalloys are all included in our study. Our calculated results are in good agreement with existing experiments[10, 11]. The electronic structures of doped γ'-Ni_3Al phase are given as example to elucidate the different alloying mechanisms related to these additions.

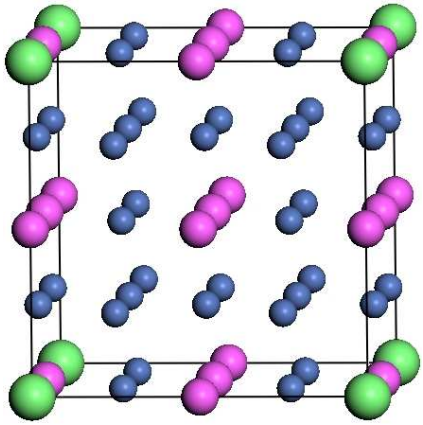

FIG. 1: Supercell of the $L1_2$ Ni_3(Al, X) compound, in which the small spheres are Ni atoms, the intermediate spheres Al atoms, and the large spheres alloying element X.

III. CALCULATION METHOD AND MODEL

The first-principles calculations presented here are based on DFT, and have been carried out using the Vienna *ab-initio* simulation package (VASP)[12]. The generalized gradient approximation (GGA) using the Perdew-Wang (PW91) functional[13] of projector augmented wave (PAW) method[14] is adopted for parametrization of the exchange-correlation functional. The cutoff energy of atomic wave functions is set to be 350 eV. A $10 \times 10 \times 10$ k-points in Brillouin zone is adopted with a regular Monkhorst-Pack scheme. The convergence of elastic moduli with respect to the cutoff energy and k-point is tested and gives a satisfactory result. All the internal freedoms of atoms in supercells are fully relaxed. The break condition for the electronic self-consistence and ionic relaxation are 10^{-5} eV and 10^{-4} eV, respectively.

Supercells of $2 \times 2 \times 2$ are adopted for both γ-Ni (or doped with X) and γ'-Ni_3(Al, X). Fig. 1 is an example shown for Ni_3(Al, X) system. The Al atom at the cube corner is substituted by different alloying elements X to represent the alloyed Ni_3(Al, X). Whereas the Ni atom at the Ni supercell corner are replaced by addition for alloyed Ni. The concentration of the alloying elements in our models are 1/32 atom %, which would lead to a obvious strengthening effect. It is should be pointed out that the direct substitution of atom is a rough approximation to investigate the alloying effects. This operation is adopted only for a qualitative estimate of these additions to the elastic properties of both Ni and Ni_3Al. If the real alloying effects of these additions are to be investigated, more advanced methods taking the statistical distribution of atoms into consideration are needed in this field.

The theoretical equilibrium volume V_0 and bulk modulus B are determined by fitting the total energies versus volume according to the Murnaghan equation of state [15]. The cubic shear constants $C' = \frac{C_{11}-C_{12}}{2}$ and C_{44} are determined by applying an appropriate set of distortions with the distortion parameters varying from δ=-0.06 to 0.06 in the step of 0.01. The applied strain configurations ϵ and the corresponding strain-energy density variations $\Delta E/V_0$ are given as follows: ϵ=(δ, δ, $(1+\delta)^{-2}$-1, 0, 0, 0) with $\Delta E/V_0 = 6C'\delta^2 + O(\delta^3)$, and ϵ=(0, 0, 0, δ, δ, δ) with $\Delta E/V_0 = \frac{3}{2}C_{44}\delta^2$.

The elastic constants are calculated using the Hill's averaging method[18]. First, the elastic constants C_{11} and C_{12} are separated from the bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$ and the shear constant C' of a crystal with cubic symmetry. Then, the shear modulus is calculated as the arithmetic Hill average $G = \frac{1}{2}(G_V + G_R)$, where $G_V = \frac{C_{11}-C_{12}+3C_{44}}{5}$ and $G_R = \frac{5}{4S_{11}-4S_{12}+3S_{44}}$ are the Voigt and Reuss bounds, respectively. S_{11}, S_{12}, and S_{44} here

TABLE I: Calculated equilibrium lattice parameters of pure metal γ-Ni, unalloyed γ'-Ni_3Al, and lattice misfit δ, in comparison with the experimental values.

	a_γ ($\AA$)	$a_{\gamma'}$ ($\AA$)	δ (%)
Present Calculation	3.515	3.568	1.50
Experiment	3.52[a]	3.57[b]	1.41

[a]Ref. [16]
[b]Ref. [17]

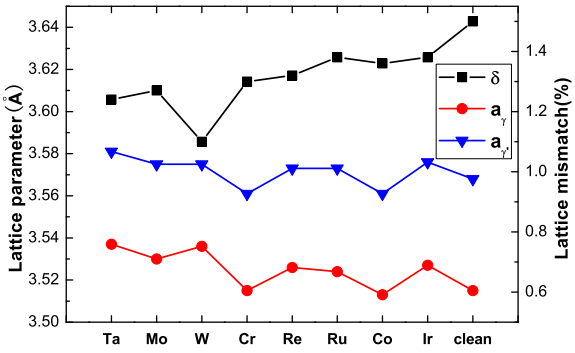

FIG. 2: The lattice parameters of Ni (alloyed with X) (a_γ), alloyed Ni_3(Al, X) ($a_{\gamma'}$), and lattice misfit(δ) as a function of the alloying element X.

are the elastic compliances[19]. Finally, the Young's modulus E and Poisson ratio ν are obtained as $E = \frac{9GB}{G+3B}$ and $\nu = \frac{1}{2}(\frac{3B-2G}{3B+G})$, respectively.

IV. RESULTS AND DISCUSSION

A. Variation in lattice properties

The equilibrium lattice parameters of pure metal Ni, pure Ni_3Al and the lattice misfit $\delta = \frac{a_{\gamma'}-a_\gamma}{2(a_{\gamma'}+a_\gamma)}$ are listed in Table I. The lattice misfit here is the difference in lattice parameters between doped Ni and doped Ni_3Al with the same addition and its concentration. It provides a benchmark for estimating the effect of alloying elements on the lattice properties of Ni-base superalloys. The experimental values are also listed in Table I for comparison. The lattice parameters of Ni and Ni_3Al are calculated to be 3.515 $\AA$ and 3.568 $\AA$, which is in excellent agreement with the experimental values of 3.52 $\AA$ and 3.57 $\AA$, respectively. Moreover, the present calculated lattice misfit is 1.50%, comparable with the experimental result of 1.41%. The consistence confirms the reliability of our calculation.

Furthermore, in order to study the effect of alloying elements on the mechanical properties of Ni-base superalloys, a Ni and an Al atom in the supercell of pure Ni and pure Ni_3Al are substituted by a X atom, respectively. The latter one is shown in Fig.1 as an example. The

TABLE II: Calculated elastic constants, bulk modulus, shear modulus, Young's modulus (GPa), G/B ratio, and Poisson ratio of unalloyed Ni_3Al and alloyed Ni_3(Al, Ta) in comparison with the experimental values.

		C_{11}	C_{12}	C_{44}	B	G	E	G/B	ν
Ni_3Al	Present Calculation	229.7	147.5	116.6	174.9	76.8	201	0.44	0.308
	Experiment[a]	227	148	120	174.3	77.0	201	0.44	0.308
Ni_3(Al, Ta)	Present Calculation	242.7	151.1	118.9	181.6	81.1	212	0.45	0.306
	Experiment[b]	238	154	130	182	82.8	216	0.45	0.303

[a]Ref. [10]
[b]Ref. [11]

lattice parameters of alloyed Ni and Ni_3Al, and the lattice misfit as a function of alloying elements X are shown in Fig.2, where "clean" means no addition in the systems. The alloying elements X in the figure are arranged in order of the Mendeleev number proposed by Pettifor[20]. It is obvious from Fig. 2 that the lattice parameters of both γ and γ' phases increase with most of the alloying elements, but Co and Cr are excepted. This variation in lattice parameters may correlate with the large atomic radii of alloying elements Ta, Mo, W, Re, Ru and Ir. Whereas the atomic radii of Co and Cr are comparably smaller, as a result the lattice parameters decrease. Fig. 2 also shows that the lattice misfit decreases with all the the alloying elements, in which W is the most effective one in decreasing δ. The decreases in δ with alloying element X may influence the microstructure, thereby the mechanical properties of alloys at high temperature[5, 6].

B. Elastic moduli

The elastic moduli of both γ-Ni and γ'-Ni_3Al doped with alloying elements X are all included in our calculations. In Table II, we list the results for Ni_3Al and Ni_3(Al, Ta) as example. The experimental observations are also listed for comparison. Our calculated elastic properties of Ni_3Al and Ni_3(Al, Ta) are in good agreement with the experimental values from Ref.[10] and Ref[11], respectively. Ta considerably increases the elastic moduli of γ' phase, which is consistent with experimental result[11]. This consistence also confirms the validity of our method.

Fig. 3 and Fig. 4 shows our predictions of the elastic properties of alloyed Ni and Ni_3(Al, X) as a function of alloying element, respectively. It is clear from Fig. 3 that different element has different effect on the elastic properties of γ matrix. First of all, all the alloying element except Ta considerably increase C_{11} of Ni. However, their effects on C_{12} behaves differently. Co is the only one that can increase the elastic constant C_{12} of Ni. It is also noticeable that the alloying elements have almost the same effect on C_{44} and C_{11}. Then, Cr, Re and Co consistently increase the bulk modulus of Ni. Interestingly, only Re is effective on increasing the shear modulus of Ni. Finally, all the elements increase the Young's modulus. Generally speaking, Re is the most effect alloying element in increasing the elastic moduli of γ phase. This is consistent with the fact that Re is a crucial alloying element in improving the mechanical performance of Ni-base superalloys[21].

From the elastic properties of alloyed Ni_3Al shown in Fig. 4, we can estimate their

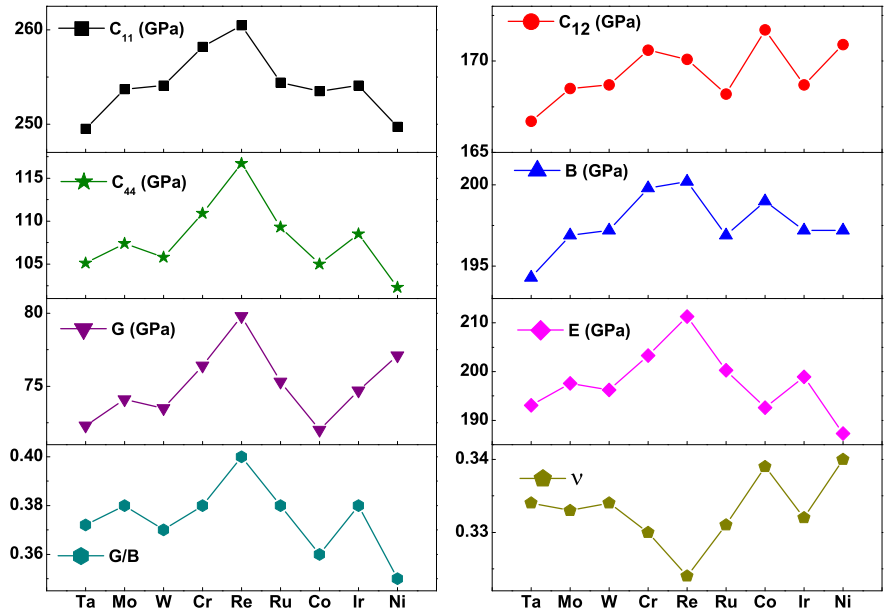

FIG. 3: The calculated elastic constants C_{ij}, bulk modulus B, shear modulus G, Young's modulus E, G/B ratio, and Poisson ratio ν of alloyed Ni as a function of the alloying element X.

different alloying effect on γ' precipitate. The elastic constants C_{11} and C_{12} of Ni_3Al increase with all the alloying elements, in which Re is the most effective one in increasing C_{11}, and Co in C_{12}. While Ru is found to be ineffective on increasing C_{12}. The curve of C_{44} is similar to that of C_{11}, except for Co. The elastic constant C_{44} of Ni_3(Al, Co) is a little smaller than pure Ni_3Al. In comparing elastic properties of various materials, it is sometimes more convenient to deal with the practical moduli such as bulk modulus B, shear modulus G, or Young's modulus E, rather than elastic constans C_{ij}. It is obvious that all the alloying element increasing the bulk modulus of Ni_3Al. Whereas Co has almost no influence on shear and Young's modulus of γ' phase. Similar to γ matrix, Re is also the most effective one on increasing the elastic moduli of γ'-Ni_3Al.

C. Ductile/brittle behavior

According to Pugh's empirical rule[22], the ductile/brittle behaviors of material are closely related to the ratio of G/B and Poisson ratio ν. A high value of G/B and low value of ν is associated with more brittle nature of material. Therefore the increase in G/B or decrease in ν indicates a decrease in ductility. On one hand, all the alloying elements in γ-Ni increase its G/B ratio and decrease its Poisson ratio ν, which is shown in Fig. 3. This variation suggests that all the additions considered in our calculations make Ni more brittle, in which Re is the most obvious one and Co has the most slight effect. As we can predict, a increase in moduli usually accompanies with lose of ductility. This change may be explained by the bonding nature of atoms in the next part. On the other hand, it is also interesting to notice from the G/B and ν curves in Fig. 4 that almost all the X elements can slightly increase G/B ratio and decrease ν value of Ni_3Al. As the circumstance for Ni, Re also has the most effect on the brittle/ductile behavior of Ni_3Al. However, the effect of Co is different. It is the only alloying element that makes an increase in ductility of the Ni_3Al.

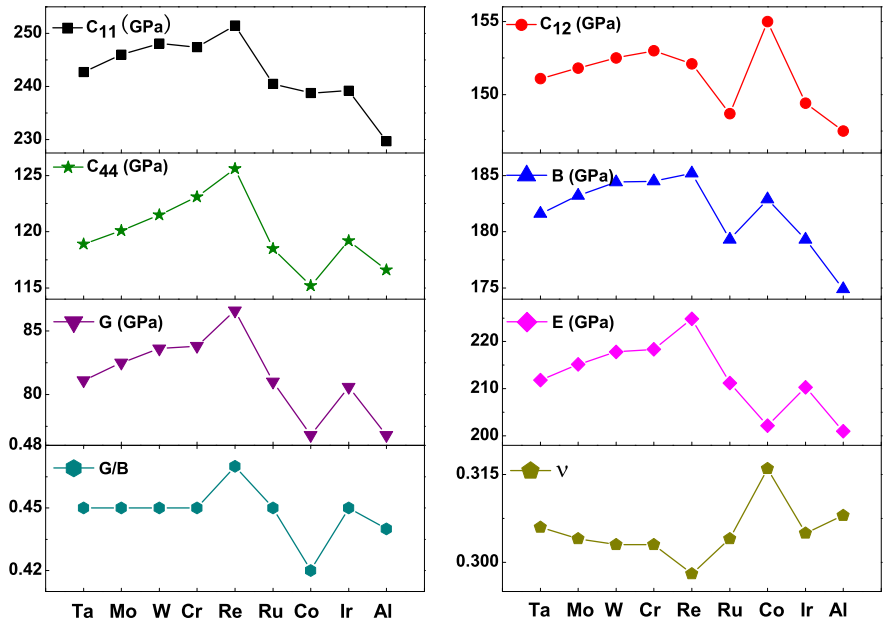

FIG. 4: The calculated elastic constants C_{ij}, bulk modulus B, shear modulus G, Young's modulus E, G/B ratio, and Poisson ratio ν of Ni_3(Al, X) as a function of the alloying element X.

D. Electronic structures of Ni_3(Al, X)

In order to develop a deeper understanding of the effect of these alloying elements on the elastic properties of both γ-Ni and γ'-Ni_3Al. Here we provide the electronic structures of the Ni_3(Al, X) systems as an example. Both Local Density of States (LDOS) and charge density difference are included in our calculations. The LDOS curves of the alloying elements X in doped Ni_3(Al, X) systems are plotted in Fig. 5. In contrast with Al, a deep valley separates the bonding and antibonding states of the LDOS for the alloying elements X (Ta, Mo, W, Cr, Re, Ru). The Fermi levels of X (Co, Ru, Ir are excluded) are located in the valleys, indicating those substitutions stabilize Ni_3(Al, X) phase[23]. This feature of LDOS also indicates a strong bonding strength between the alloying element and the host atoms. The bonding is partly covalent. These bonding nature usually suggests a higher elastic moduli[24]. Based on our result, the shear modulus G increases more quickly than the bulk modulus B. As a result G/B increase and leads to more brittleness. This is consistent with the increase of covalent-like bond in the alloyed Ni_3(Al, X) systems. In contrast, there is no obvious bonding and antibonding states of the LDOS of Co, and the Fermi level lies right in the peak of its LDOS. This feature of LDOS is closely related to the metallicity of the alloyed system, which is the reason why only Co addition increases the ductility of γ'-Ni_3Al.

Besides LDOS, the charge density difference on the (100) planes are plotted in Fig. 6. The purpose is to understand the effect of alloying atoms on the bonding properties of the Ni_3(Al, X) systems. The charge density difference of the Ni_3(Al, X) system is defined as $\Delta\rho$=ρ[Ni_3(Al, X)]-ρ_{free}[Ni_3(Al, X)]-[ρ(Ni_3Al)-ρ_{free}(Ni_3Al)], where ρ_{free} is the superposition of free atom charge density. It can directly reflect the bonding characteristic. From Fig. 6, it can be seen that charge correlation regions due to the electron accumulation appear around the alloying X atoms and their nearest neighbor (NN) Ni atoms. This sharp of charge difference suggests the bonding between X and its NN Ni atoms is stronger than that for Al and its NN Ni atoms in pure Ni_3Al. It indicates enhanced interaction between X and the host atom in Ni_3(Al, X). Except Co, there exists the relative strong bonding that has covalent-like character between X and NN Ni. One can believe that it is this bonding feature of X

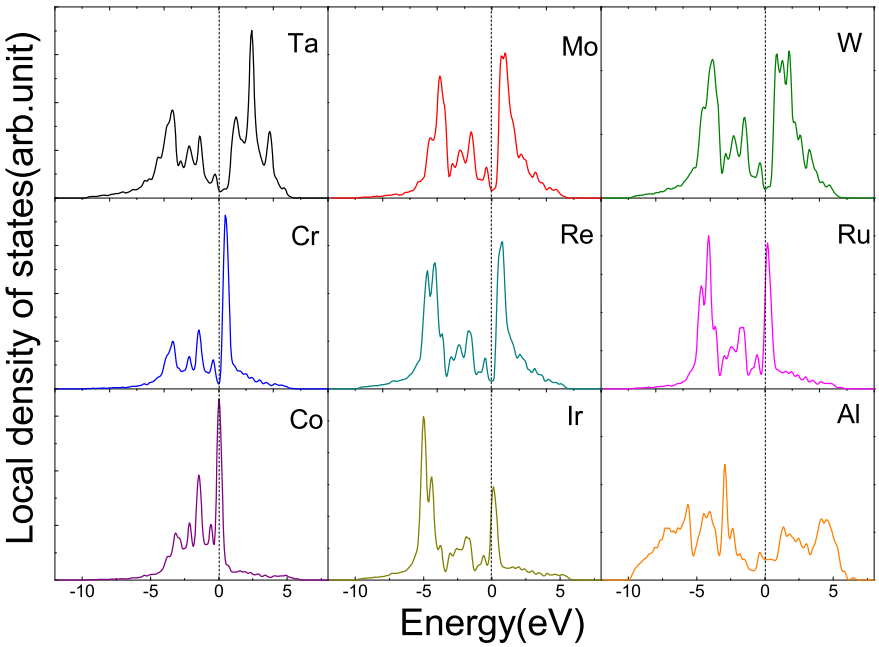

FIG. 5: The electronic Local Density of States of the alloying elements X in the Ni_3(Al, X) compounds. The Fermi levels has been shifted to zero.

that leads to more contributions to its elastic moduli. Because the directional distributed covalent-like bond will effectively resist the deformation of a material. It is in turn leading to a high modulus. It is also consistent with the result that the X additions give larger G/B values and decrease the ductility of Ni_3(Al, X). The directional distribution of charge different can be found obviously in Ni_3(Al, Re) shown in Fig. 6. Further more, we notice that the shape of the charge correlation region of Co in the Ni_3(Al, X) system is different from that of the other alloying X atoms. The charge accumulation around Co is spherically symmetric near the atomic site, which is in qualitative agreement with the standard picture of metallic bonding. The feathers of bonding shown in Fig. 6 is closely related to the results that Co increase the ductility of the alloyed system while other additions (X=Ta, Mo, W, Cr, Re, Ru, Ir) make Ni_3Al more brittle. Our charge density difference analysis here is consistent with the LDOS.

V. SUMMARY

In summary, the effect of alloying elements on the elastic properties of both γ-Ni and γ'-Ni_3Al are systematically investigated by the first-principles method. Results for lattice properties, elastic moduli and the ductile/brittle behaviors are all included in our calculations. The results show that all the additions decrease the lattice misfit, which may affect the mechanical properties of Ni-base superalloys at high temperature. The calculated elastic constants and other moduli of Ni_3Al and Ni_3(Al, Ta) are in good agreement with the existing experiments. Different alloying elements have different effect on the elastic moduli of γ-Ni. Whereas, all the alloying elements slightly increase the moduli of γ'-Ni_3Al expect Co. According to the calculated values of G/B and Poisson ratio, Both of the two phases are becoming more brittle with alloying elements, but Co is excepted. The LDOS and charge density difference of γ' phase alloyed with different elements are provided as example to elucidate the different strengthening mechanisms. The partly covalent-like bond exist be-

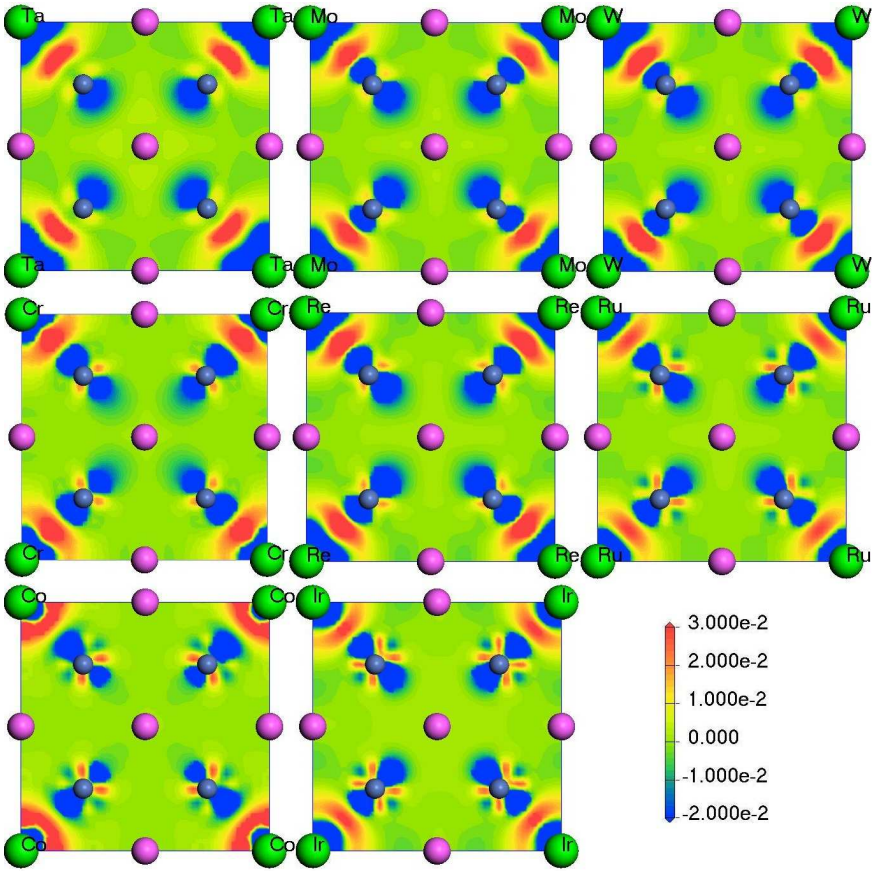

FIG. 6: The charge density difference on the (100) planes of the Ni_3(Al, X) systems and the Ni_3Al system. The small spheres are Ni atoms, the intermediate spheres Al atoms, and the large spheres doped X atoms. Positive (negative) values denote charge accumulation (depletion)[in unit of $e/(a.u.)^3$].

tween alloying element and the host atoms except Co. This is the reason why almost all the alloying elements increase the elastic moduli and brittleness of Ni_3(Al, X), while Co is different. These results may provide useful information for the design of more advanced SC Ni-base superalloys.

VI. ACKNOWLEDGEMENT

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VII. REFERENCES

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