Energetics and electronic structure of Re and Ta in the γ' phase of Ni-based superalloys

Shan-Ying Wang,[1,2] Chong-Yu Wang,[1,2,3] Jia-Hua Sun,[2] Wen-Hui Duan,[1] and Dong-Liang Zhao[2]

[1]*Department of Physics, Tsinghua University, Beijing 100084, China*
[2]*Center Iron and Steel Research Institute, Beijing 100081, China*
[3]*International Centre for Materials Physics, Academia Sinica, Shenyang 110016, China*

By use of first-principles methods based on density functional theory, we study the alloying effect of Re and Ta in the γ' phase of Ni-based superalloy. We find that when Re (Ta) is substituted for Al, the binding energy of the system obtained by the DMol method decreases by 2.55 eV (4.04 eV). This is accompanied by a small local lattice distortion (less than 1% of the calculated lattice constant). In contrast, when Re (Ta) is substituted for Ni, the binding energy of the system decreases by only 0.68 eV (1.11 eV), but there is a larger local lattice distortion (more than 3% of the calculated lattice constant). The transfer energies obtained by the DMol method show that both Re and Ta exhibit a strong Al site preference, which is in agreement with experimental and recent theoretical results. Using the discrete variational method, we calculate the interatomic energy, the charge distribution and the partial density of states. Both Re and Ta in the γ' phase can strongly enhance the interatomic interaction between nearest neighboring atoms, as well as that between a nearest neighboring atom and the associated next nearest neighboring atom. However, the bonding between Re (Ta) itself and the host atoms is weak. We also examine the strong dependence of the binding energy on the substitution type by analyzing the interatomic energies, and discuss the charge distribution and the partial density of states for the systems in which Re (Ta) is substituted for Al.

I. INTRODUCTION

As a promising high-temperature structural material with excellent properties such as high-temperature strength, low density, and strong resistance to oxidation, Ni-based superalloy has attracted much attention from physicists and technological workers in recent years. The main microstructures of such material are a disordered Ni-based solid solution rich in Cr (the γ matrix) and the intermetallic compound Ni_3Al (the γ' precipitate). Solid-solution strengthening in the γ matrix and ordered strengthening in the γ' precipitate are the two main technologically important features found in Ni-based superalloy. Experiments[1−5] have shown that by properly increasing the total concentration of a refractory alloying element such as Re or Ta in both the γ and the γ' phases, the high-temperature mechanical properties of such material can be drastically improved. An important feature of the alloying effect for these $5d$ elements is that they can enhance the γ-γ' lattice mismatch and directly strengthen the γ' phase, resulting in a strong pinning effect on the dislocation motion in the superalloy.

Clearly, knowledge about the physical behavior of the alloying element in the γ' phase is important for gaining an understanding of the strengthening effect and for developing practical superalloys. Over the past two decades, first-principles investigations[6−12] have provided good characterizations of the site preferences of many alloying elements in the γ' phase. Using all-electron LMTO-ASA and full-potential LAPW energy band methods, Freeman *et al.*[6−8] thoroughly studied the phase stability in Ni_3Al and $Ni_3(Al,V)$ systems. They found that the cohesive energy of the Ni_3Al phase can be attributed primarily to the d-d electron interaction between Ni atoms and the d-p electron interaction between Ni and Al atoms. The small magnetic in-

teraction energy was found to have little effect on the structural transition. They further pointed out that, as a substitution with Al site preference, V addition can induce the strongest bonding effect that can stabilize Ni_3Al in an $L1_2$-like structure. Wang *et al.*[9] studied electronic structures of Mg-doped γ phase, γ' phase and γ-γ' phase interface using a real-space recursion method, and showed that Mg prefers to enter into the γ' phase at an Al site. Following these studies, Yang *et al.*[10] carried out a total energy calculation employing the discrete variational method on a series of small cluster models, considering only interactions between nearest neighboring atoms, in an effort to explain the substitution behaviors of Sc, Ti, Nb, etc., additions in Ni_3Al. They showed that Sc, Co, Cu, and Pd all prefer an Ni site, while Ti, V, Nb, and Mo prefer an Al site, and Fe was attracted to both sites. They also claimed that these site preferences are insensitive to interactions from the next nearest neighboring atoms. This, however, is inconsistent with the later study by Sluiter and Kawazoe[11] who used the tight-binding method combining with the coherent potential approximation (CPA). In Sluiter and Kawazoe's calculations, the pair-potential interactions involved extended out to the the sixth nearest neighboring atoms, automatically including the antisite factor. They found the following site preferences in Ni_3Al: Zn, Cd, Cu, and Au have weak tendencies to occupy Al and Ni sites; Ga, Si, Ge, Fe, Co, and Pd have strong tendencies to occupy Al and Ni sites; and Cr and Cd show no evident preference for either site. Recently, Ruban *et al.*[12] made a more comprehensive and careful study of the temperature and compositional dependencies of site substitution behaviors for all $3d$, $4d$, $5d$ and noble metals utilizing the tight-binding LMTO method in conjunction with the multisublattice CPA. Their total energy calculations demonstrated that, at high temperatures, Cu and Pd exhibit reverse substi-

tution behaviors. Since Co, Pd, Cu, and Ag each only showed a weak Ni site preference, the direction of the solution lobe in each's ternary phase diagram could not be taken as the evidence for a strong Ni site preference.

In spite of considerable theoretical efforts, the alloying effects of $5d$ elements such as Re and Ta in the Ni_3Al phase are still far from being fully understood. In an attempt to better explain the alloying effects of these elements, we have employed two widely used first-principles methods [the DMol method[13,14] and the discrete variational (DV) method[15–17] based on desity functional theory[18,19]] to determine the electronic structure of Re and Ta elements in the Ni_3Al phase and to study the associated energetics.

II. METHODS AND COMPUTATIONAL DETAILS

As is well known, it is convenient to use a cluster model to explore the electronic properties of systems with local defects. The DMol and DV methods enable us to use such a cluster model to study the real system without requiring an unreasonable and unattainable amount of computational power. In the present study, atomic configurations and total energies corresponding to the ground states are determined via a DMol relaxation calculation. Utilizing the atomic configurations obtained from DMol optimization, we then calculate the interatomic energies, charge density distributions, and partial density of states of the systems by use of DV method.

Below its melting point ($1390\,°C$), Ni_3Al has an $L1_2$-like ordered structure in which Al and Ni occupy a corner site and a face center site, respectively. Even at the very small concentration found in Ni-based superalloy, Re and Ta usually exhibit good alloying effects. Due to their large atomic radii, Re and Ta in the Ni_3Al phase should substitute for Ni or Al atoms rather than stay at interstitial sites. Thus, we consider only the substitution case and adopt a simple single impurity model which ignores the interactions between the $5d$ elements. In the DMol relaxation calculations, the same cluster model, shown in Fig. 1, was always employed so that results would be compatible. The cluster model constructed from the bulklike structure of Ni_3Al consists of 87 atoms and centers at an Al atom. We first determined the lattice constant for the Ni_3Al system by performing a series of total energy calculations using different lattice constants. The calculated lattice constant of the Ni_3Al system corresponding to the lowest binding energy (defined as the difference between the total energy of the interactive atom system and that of the free atom system) is about 3.44 Å, which is 4% smaller than the experimental value (3.58 Å). Then we substituted the central Al atom by an Re or Ta atom or a vacancy and performed a DMol relaxation calculation [we use the names $Ni_3(Al,Re)$, $Ni_3(Al,Ta)$ and $Ni_3(Al,Vac)$, respectively, for these systems after relaxation]. The Re or Ta atom, the twelve nearest neighboring (NN) Ni atoms, and the six next nearest neighboring (NNN) Al atoms were all allowed to relax in accordance with the forces acting on them and the preservation of the O_h symmetry. Next we substituted an Re or Ta atom or a vacancy for one of the twelve NN Ni atoms and performed a similar DMol relaxation calculation to that
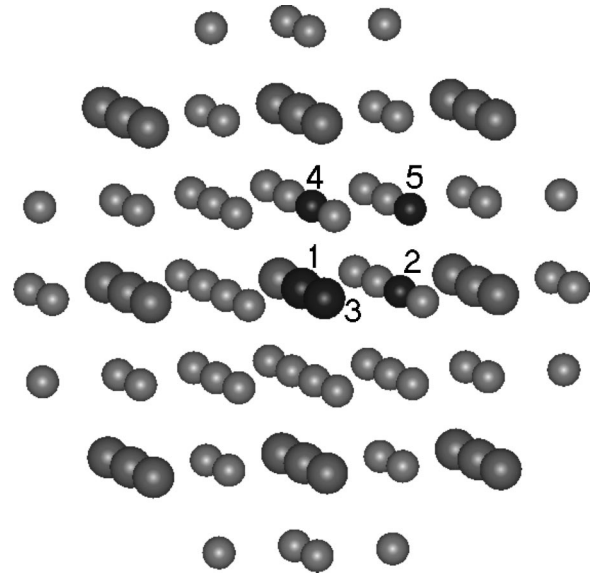

FIG. 1. Ni_3Al [$Ni_3(Al,Re)$, $Ni_3(Al,Ta)$, $Ni_3(Al,Vac)$] cluster model used in the DMol and the DV calculations. The cluster model centers on an Al (Re,Ta,Vac) atom. The large and the small balls denote an Al (Re,Ta,Vac) atom and an Ni atom, respectively. The central Al (Re,Ta,Vac) atom is labeled by the Arabic numeral 1. Two NN Ni atoms are labeled by the numerals 2 and 4, and one NNN Al atom is labeled by the numeral 3. The numeral 5 denotes a next NNN Ni atom. The thickened balls are to provide guidance in locating the numerals.

performed with the $Ni_3(Al,Re)$ system [these new systems, which preserve C_{2v} symmetry during relaxation, are labeled as $(Ni,Re)_3Al$, $(Ni,Ta)_3Al$, and $(Ni,Vac)_3Al$, respectively]. In the DMol calculations, the convergence criteria for the energy gradient and the atomic displacement are, respectively, 0.001 Ry/a.u. and 0.001 Å. The double numerical polarized (DNP) basis including the inner orbitals and the Vosko-Wilk-Nisair local exchange-correlation functional[20] with the Becke-Perdew-Wang general gradient approximation (GGA) correction[21,22] were used to obtain more precise results.

Using the atomic configurations taken from the DMol relaxation results, we calculated the interatomic energies, the charge density distributions, and the partial density of states for the Ni_3Al, $Ni_3(Al,Re)$, $Ni_3(Al,Ta)$, $(Ni,Re)_3Al$, and $(Ni,Ta)_3Al$ systems by the DV method. In the DV calculations, the same cluster models as those used in DMol calculation (as shown in Fig. 1) were adopted for the $Ni_3(Al,Re)$ and $Ni_3(Al,Ta)$ systems, but different cluster models (as shown in Fig. 2) were adopted for the $(Ni,Re)_3Al$ and $(Ni,Ta)_3Al$ systems. The reason for using two different kinds of cluster models is that there is no strict "unit cell" definition in the DV method. With large clusters, the distinctions between the different cluster models used do not have a significant effect on the results obtained. Naturally, for the sake of better comparison between calculated results, we used two Ni_3Al cluster models as reference systems. One centers at an Al site, and the other centers at an Ni site. The DV method is not as well developed as the DMol method. The former is
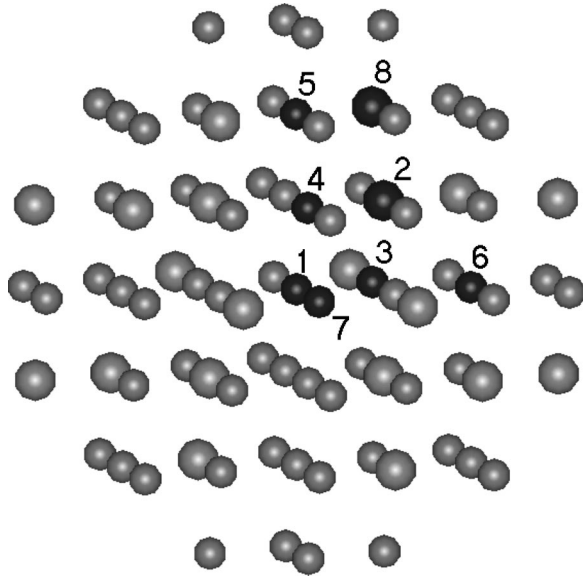
FIG. 2. Ni_3Al [$(Ni,Re)_3Al$, $(Ni,Ta)_3Al$] cluster model used only in the DV calculation. The cluster model centers on an Ni site. The large and small balls denote an Al atom and an Ni (Re,Ta) atom, respectively. The central Ni (Re,Ta) atom is labeled by the Arabic numeral 1. One NN Al atom and two NN Ni atoms are labeled by numerals 2, 3, and 4, respectively; and three NNN Ni atoms are labeled by numerals 5, 6, and 7. The numeral 8 denotes a next NNN Al atom. The thickened balls are to provide guidance in locating the numerals.

short many features commonly found in the present state-of-the-art electronic structure calculation methods, such as use of the DNP basis, the GGA correction and, more importantly, structural optimization. At least three aspects need to be considered when using of DV method: the choice of the basis set, the boundary effect and the numerical accuracy. To reduce the effect of basis selection on the results, we used the single-site orbitals as the basis set. In the generation of a basis, funnel potentials were added to contract the radial part of atomic orbital and to induce bond states. This is particularly important in treating some unoccupied and expanded atomic orbitals such as Ni-4p. The variational basis functions assignmets are $3s^2 3p^1$ for an Al atom, $3d^8 4s^2 4p^0$ for an Ni atom and $5d^5(5d^3)6s^2 6p^0$ for an Re (Ta) atom. A cluster embedding potential was added to remove the boundary effect from the cluster model. It was constructed by adding together the charge densities of several hundred environment atoms to generate Coulomb and exchange-correlation potentials. The single-particle wave functions are solved by way of a self-consistent multipolar approximation. This expends significant time in computation; but can, by a fitting process, yield more accurate and self-consistent charge densities. The Vosko-Wilk-Nisair exchange-correlation potential and about 1000 integration points per atom were used in the computation. By utilizing the methods just outlined, DV calculations can be expected to yield reasonable and reliable results. Since the magnetic interaction energy makes only a small contribution to the binding energy,[6] all DMol and DV calculations are spinrestricted.

TABLE I. The binding energies (in eV) of the Ni_3Al system with and without the presence of an Re (Ta, Vac) atom. ΔE denotes the difference in binding energies between the Ni_3Al system in the presence of an Re (Ta, Vac) atom and the unsubstituted Ni_3Al system.

	Binding energy	ΔE
Ni_3Al	-514.46	
$Ni_3(Al,Re)$	-517.01	2.55
$Ni_3(Al,Ta)$	-518.50	4.04
$Ni_3(Al,Vac)$	-506.80	-7.66
$(Ni,Re)_3Al$	-515.14	0.68
$(Ni,Ta)_3Al$	-515.57	1.11
$(Ni,Vac)_3Al$	-505.91	-8.55

III. BINDING ENERGY AND INTERATOMIC INTERACTION

In Table I, we present the binding energies obtained by the DMol method for the Ni_3Al system and Ni_3Al system with the substitution of an Re or Ta atom or a vacancy. It is clear seen that, in comparison with Ni_3Al system, the binding energies of the systems containing Re or Ta are lower. When an Re (Ta) atom occupies an Al site, the binding energy decreases by as much as 2.55 eV (4.04 eV). The magnitude of this shift is much larger than the usual thermal activation energy for an atom jumping from one lattice site to another. When an Ta atom occupies an Ni site, the binding energy decreases by 1.11 eV; however, for an Re atom, it decreases by only 0.68 eV. These results imply that both Re and Ta can stabilize the Ni_3Al phase, and that both have the possibility of occupying either an Al site or an Ni site.

Knowledge of the transfer energy is needed to illucidate the site substitution behavior of an Re (Ta) atom in the Ni_3Al phase (see Ref. 12). In the present work, the transfer energy is defined as the energy required to move a single Re (Ta) atom from an Ni site to an Al site. Thus, the site preference can be determined from the sign and the magnitude of the transfer energy. For a quasistoichiometric alloy in the dilute limit of the alloying element, the transfer energy is directly related to the binding energies of the alloying system and the vacancy system. In this study, the transfer energy of a substitutional atom (for example, Re) in the Ni_3Al phase (denoted by E_t^{Re}) is defined as

$$E_t^{Re} = \{E_b[Ni_3(Al,Re)] - E_b[Ni_3(Al,Vac)]\}$$
$$- \{E_b[(Ni,Re)_3Al] - E_b[(Ni,Vac)_3Al]\},$$

where $E_b[Ni_3(Al,Re)]$ is the binding energy of the $Ni_3(Al,Re)$ system, $E_b[Ni_3(Al,Vac)]$ is the binding energy of the Al vacancy system, and so on.

The calculated transfer energies of Re and Ta atoms are -0.98 and -2.04 eV, respectively. These highly negative transfer energies show that both Re and Ta atoms in the Ni_3Al phase have strong Al site preferences; that is, they can stably remain at an Al site. Actually, for a quasistoichiometric alloy in the dilute limit of the alloying element, the substitution behavior of the alloying element is closely tied to

two factors: a chemical factor and a geometric factor (here, the alloying element can be treated as a single impurity in a compound). The chemical factor mainly refers to binding characteristics including the bonding strength between the alloying element and the host atom. The geometric factor incorporates the effects induced by atomic radii, atomic arrangement and so on. The binding energy just reflects the chemical effect. In fact, the atomic radii of Re and Ta are very close to that of Al, but quite different from that of Ni (the atomic radii of Re, Ta, Al, and Ni are 1.37, 1.44, 1.43, and 1.24 Å, respectively). Therefore, from the point of view of atomic size, one might assume that Re and Ta would prefer to occupy an Al site, and thus not induce a severe local lattice distortion in the Ni_3Al phase. Indeed, the DMol relaxation results confirm this assumption. When Re occupies an Al site, the NN Ni atoms and the NNN Al atoms are almost completely undisturbed. A similar result is obtained for Ta except that the NNN Al atoms move outside by a mere $\sim 1\%$ of the calculated lattice constant. We found that noticeable lattice distortions appear when an Re (Ta) occupies an Ni site. The NN atomic sites around a Re (Ta) atom expand by an average of 3% (5%) of the calculated lattice constant, and the NNN atomic sites around a Re or Ta atom expand by an average of 2% of the calculated lattice constant. Note that the NN atoms and the NNN atoms around an Re or an Ta atom include both Al and Ni atoms. From the above findings, we can conclude that, in the Ni_3Al phase, Re and Ta atoms both prefer to occupy an Al site, which is in agreement with the experimental[5] and the recent theoretical[12] results. One possible caveat should be addressed here: the effect of the cluster size on the transfer energy. To test this, we performed calculations using cluster systems each containing only 55 atoms. The calculated binding energies for Ni_3Al, $Ni_3(Al,Re)$, $Ni_3(Al,Ta)$, $Ni_3(Al,Vac)$, $(Ni,Re)_3Al$, $(Ni,Ta)_3Al$, and $(Ni,Vac)_3Al$ systems were -315.84, -318.22, -320.05, -308.32, -316.20, -316.89, and -307.22 eV, respectively. The transfer energies of Re and Ta were -0.92 and -2.06 eV, respectively. These values differ only slightly from those calculated using cluster models of 87 atoms. This implies that the transfer energy calculated will be insensitive to the cluster size if the number of atoms in the cluster model is raised beyond 87.

In order to study the interatomic interaction, we have calculated the interatomic energy (IE) E_{lm} between atom l and atom m by the DV method.[23,24] The interatomic energy is defined as

$$E_{lm} = \sum_n \sum_{\alpha\beta} N_n a_{n\alpha l}^* a_{n\beta m} H_{\beta m \alpha l},$$

where N_n is the electron occupation number for the molecular orbital ψ_n, $a_{n\alpha l} = \langle \phi_{\alpha l} | \psi_n \rangle$, and $H_{\beta m \alpha l}$ is the Hamiltonian matrix element connecting the atomic orbital $\phi_{\alpha l}$ of atom l to the atomic orbital $\phi_{\beta m}$ of atom m. Since the IE is related to the Hamiltonian matrix element, it can be used to estimate the bonding capability of the two atoms. Usually, a negative number with a large absolute value means a strong interatomic interaction. IE values proved very useful in studies on Ni_3Al grain boundary problems.[23,24]

TABLE II. The interatomic energies (in eV) for selected atomic pairs in the Ni_3Al, $Ni_3(Al,Re)$ and $Ni_3(Al,Ta)$ systems. The Arabic numerals in Al1, Ni2, etc., correspond to those in Fig. 1.

Atom pairs	Ni_3Al	$Ni_3(Al,Re)$	$Ni_3(Al,Ta)$
Al1 (Re1,Ta1)-Ni2	-2.25	-0.95	-1.53
Al1 (Re1,Ta1)-Al3	1.41	0.22	-0.48
Ni2-Ni4	-2.05	-2.54	-3.28
Ni2-Al3	-3.76	-3.81	-3.86

Tables II and III present the IE's of some interesting atomic pairs where substitution is for an Al atom and for an Ni atom, respectively. From Table II, we can see that when an Re (Ta) atom is substituted for an Al atom, the IE between the Re (Ta) atom and an NN Ni atom greatly increases, while that between the Re (Ta) atom and an NNN Al atom drastically decreases. The IE between two NN Ni atoms as well as that between an NN Ni atom and the associated NNN Al atom are strongly enhanced. From Table III, we can see that when an Re (Ta) atom is substituted for an Ni atom, the change in the IE is similar to that which occurs with substitution for an Al atom, even though the coordination conditions in the two cases are quite different. The IE's between the Re (Ta) and the NN atoms, which include both Ni and Al atoms, are greatly weakened relative to the analogous IE's in the unsubstituted Ni_3Al system. On the other hand, the reverse is true for the IE's between the NN atoms themselves which are strongly enhanced, with the exception of cases where two atoms have a NN relationship such as Al2 and Ni6 (or a NNN relationship such as Ni3 and Ni8) where the IE is only slightly enhanced.

The above results provide concrete information giving insight into the alloying effects for Re and Ta atoms, including their effects on the crystal cohesion of the Ni_3Al phase. When substituted for an Al atom, an Re (Ta) atom will form only weakly bonding states with the surrounding host atoms, but nonetheless the substitution strongly enhances the interatomic interaction between two adjacent Ni atoms as well as that between an NN Ni atom and the associated NNN Al atom. According to a study by Freeman et al.,[6] the abovementioned interatomic interactions among the host atoms (which are enhanced by the introduction of Re or Ta atoms)

TABLE III. The interatomic energies (in eV) for selected atomic pairs in the Ni_3Al, $(Ni,Re)_3Al$ and $(Ni,Ta)_3Al$ systems. The Arabic numerals in Ni1, Al2, etc., correspond to those in Fig. 2.

Atom pairs	Ni_3Al	$(Ni,Re)_3Al$	$(Ni,Ta)_3Al$
Ni1 (Re1,Ta1)-Al2	-1.70	-0.26	1.98
Ni1 (Re1,Ta1)-Ni3	-0.99	-0.58	1.50
Al2-Ni3	-2.43	-3.22	-3.91
Al2-Ni6	-2.45	-2.67	-2.56
Ni3-Ni4	-1.44	-2.59	-3.78
Ni3-Ni5	-1.23	-1.29	-1.08
Ni3-Ni7	-2.03	-1.87	-1.64
Ni3-Al8	-0.90	-1.22	-1.14

TABLE IV. The electron occupation number N ($N_{(Al,Re)}$, $N_{(Al,Ta)}$) in the valence orbitals for each atom in the Ni_3Al [$Ni_3(Al,Re)$, $Ni_3(Al,Ta)$] system. $\Delta N_{(Al,Re)} = N_{(Al,Re)} - N$, etc., $\Delta Q_{(Al,Re)} = Q_{(Al,Re)} - Q$, etc., where Q ($Q_{(Al,Re)}$, $Q_{(Al,Ta)}$) is the net number of electrons in the valence orbitals for each atom in the Ni_3Al [$Ni_3(Al,Re)$, $Ni_3(Al,Ta)$] system. Here $Q = N - Z_{val}$, where Z_{val} is the standard number of valence electrons per atom. The Arabic numerals in Al1, Ni2, etc., correspond to those in Fig. 1.

		N	$N_{(Al,Re)}$	$N_{(Al,Ta)}$	$\Delta N_{(Al,Re)}$	$\Delta N_{(Al,Ta)}$	$\Delta Q_{(Al,Re)}$	$\Delta Q_{(Al,Ta)}$
Al1 (Re1,Ta1)	$3(6)s$	0.51	0.64	1.26				
	$3(6)p$	2.14	0.34	0.22				
	$(5)d$		5.98	3.77				
	Q	-0.35	-0.04	0.25			0.31	0.60
Ni2	$4s$	0.23	0.36	0.38	0.13	0.16		
	$4p$	1.28	1.16	1.06	-0.12	-0.22		
	$3d$	8.65	8.57	8.59	-0.08	-0.06		
	Q	0.15	0.09	0.03			-0.06	-0.12
Al3	$3s$	0.64	0.61	0.60	-0.03	-0.04		
	$3p$	2.22	2.18	2.19	-0.04	-0.03		
	Q	-0.14	-0.21	-0.21			-0.07	-0.07
Ni5	$4s$	0.49	0.49	0.50	0.00	0.01		
	$4p$	0.94	0.94	0.95	0.00	0.01		
	$3d$	8.74	8.74	8.74	0.00	0.00		
	Q	0.17	0.17	0.18			0.00	0.01

are the primary contributions to the cohesive energy of the Ni_3Al phase. Thus at an Al site, substitution by an Re or an Ta atom greatly improves the crystal cohesion and accounts for the large decrease in the binding energy of the $Ni_3(Al,Re)$ or $Ni_3(Al,Ta)$ system relative to the the Ni_3Al system. When substituted for an Ni atom, an Re or an Ta atom will still strongly enhance the interatomic interaction between two adjacent host atoms. However, one should keep in mind that Ni atoms dominate the crystal cohesion of the Ni_3Al phase. Thus, the magnitude of the binding energy of the $(Ni,Re)_3Al$ or the $(Ni,Re)_3Al$ system can not be significantly larger than that of the Ni_3Al system because the energy loss caused by the absence of the Ni atom can not be fully compensated. In addition, Ta clearly exhibits an stronger alloying effect than Re and, consequently, substitution by Ta results in a larger decrease in the binding energy of the system.

IV. CHARGE DISTRIBUTION AND DENSITY OF STATES

Having found that an Re (Ta) atom at an Al site exhibits a strong alloying effect, in this section, we discuss the charge distribution and the density of states obtained by the DV method for the Ni_3Al, $Ni_3(Al,Re)$ and $Ni_3(Al,Ta)$ systems.

It is well known that the charge transfer between the alloying element and the host atom can greatly affect the interatomic bonding behavior. Table IV lists the electron occupation numbers in the valence orbitals calculated by a Mulliken population analysis.[25] For the Ni_3Al system, an Ni atom obtains a small quantity of charge ($\sim 0.16e$) from the adjacent Al atoms, with the acquired charge mainly assigned to the $4p$ orbitals. However, more electrons transfer from the Ni-$4s$ orbital to the Ni-$4p,3d$ orbitals, and from the Al-$3s$

orbital to the Al-$3p$ orbitals. In the $Ni_3(Al,Re)$ system, Re neither gains nor loses charge, and thus exhibits weak interactions with the host atoms. Consequently, the amount of charge transferred to the adjacent Ni2 atoms decreases relative to the case of the Ni_3Al system. Surprisingly, unlike with Re, Ta can obtain a small quantity of charge ($\sim 0.25e$) from the environment, leading to a considerable decrease in the amount of charge transferred to the adjacent Ni2 atoms. Therefore, the bonding strength of an Ta atom to the host atoms is somewhat stronger than that of a Re atom to the host atoms. For the $Ni_3(Al,Re)$ and the $Ni_3(Al,Ta)$ systems, we see a remarkable charge redistribution in the Ni2-$4s,4p$ orbitals, but the charge distributions in the Ni2-$3d$ and the Al3-$3s,3p$ orbitals are only slightly affected. The charge distributions in the orbitals of the Ni5 atoms, which are the next NNN atoms relative to the Re (Ta) atom, are also barely affected. The charge transfers for an Re (Ta) atom mainly occur between its own orbitals, namely from the $6s$ to the $5d$ orbitals and from $6s$ orbital to the $6p$ orbitals, via s-d and s-p hybridization, respectively. This behavior is analogous to that of an $3d$ transition metal element.

To complete the analysis of the interactions between atomic orbitals, we have calculated the partial density of states (PDOS) by means of the Lorenz broadening scheme combining with a Mulliken population analysis. The PDOS in the DV method is defined as

$$D_{\alpha l}(E) = \sum_n N_{\alpha l}^n \frac{\delta}{\pi[(E - \varepsilon_n) + \delta^2]},$$

where $N_{\alpha l}^n$ is the population of the atomic orbital $\phi_{\alpha l}$ of atom l in energy level ε_n of the molecular orbital, and δ is the
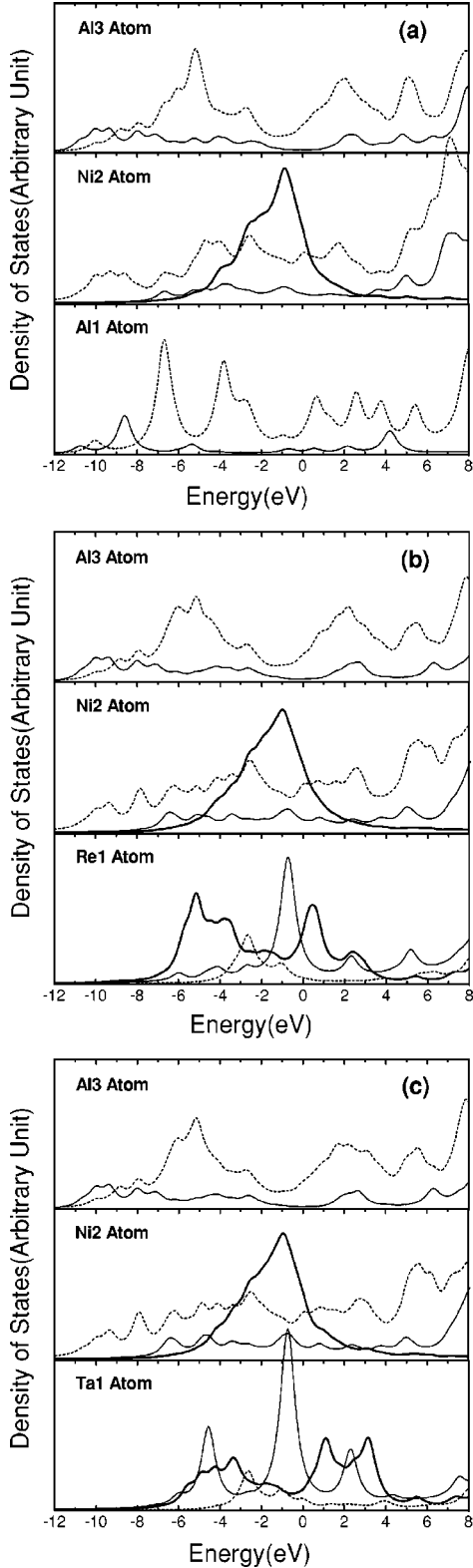
FIG. 4. The electron density difference on the (011) plane between (a) the $Ni_3(Al,Re)$ system and the Ni_3Al system and (b) the $Ni_3(Al,Ta)$ system and the Ni_3Al system. The contour spacing is $0.0001e$ a.u.$^{-3}$. Solid lines and dashed lines correspond to the gain and the loss of electrons, respectively.

FIG. 3. The atomic partial density of states in (a) the Ni_3Al system, (b) the $Ni_3(Al,Re)$ system, and (c) the $Ni_3(Al,Ta)$ system. The thick solid lines, thin solid lines and dashed lines denote d, s, and p electronic states, respectively. The Fermi level is shifted to zero. The Arabic numerals in Al1, Ni2, etc., correspond to those in Fig. 1.
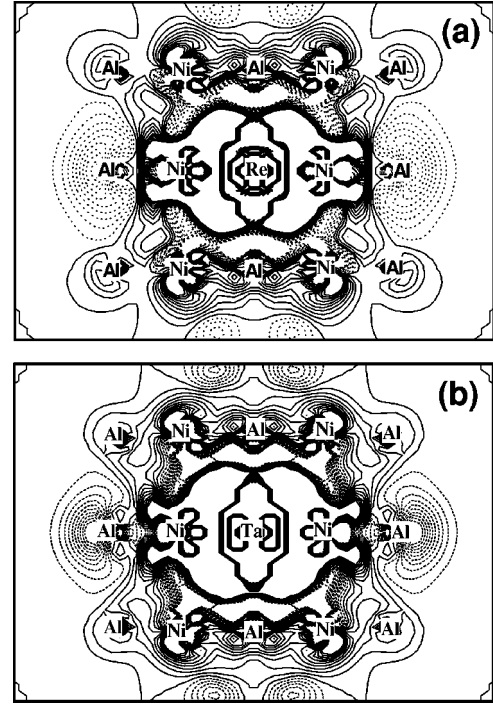
broaden parametering (chosen as 0.25 eV in the present work). Figures 3(a) [3(b), 3(c)] shows PDOS curves for the center Al1 (Re1,Ta1), the NN Ni2 and the NNN Al3 atoms in the Ni_3Al [$Ni_3(Al,Re)$, $Ni_3(Al,Ta)$] system. Two main atomic bonding features previously observed in the Ni_3Al system[6] are reproduced and are clearly visible in Fig. 3(a). We see that the Al-$3s$,$3p$ orbitals hybridize with the Ni-$4s$,$4p$ orbitals, leading to the energy bands smearing out over a wide energy range. The bonding states show up primarily as the characteristic peaks in the low energy range from -12 to -6.0 eV, while the antibonding states are mainly seen as characteristic peaks in the high energy range from 2.0 to 6.0 eV. On the other hand, the local features of the Ni-$3d$ states remain intact, except that a small proportion of the charge is rendered itineratelike by $4s$,$4p$-$3d$ hybridization. In the $Ni_3(Al,Re)$ and the $Ni_3(Al,Ta)$ systems, the PDOS curves of the Ni2-$4s$,$4p$ orbitals are considerably changed in the regions of the bonding states and the antibonding states. While the PDOS curves of the Ni2-$3d$ orbitals and the Al3-$3s$,$3p$ orbitals show some small changes around -3.2 and -5.5 eV, respectively. The additional resonant peaks which appear over a broad low energy range from -8.5 to -2.0 eV imply enhanced interactions of the Ni2-Ni2 and the Ni2-Al3 atomic orbitals. In Fig. 3(b) [3(c)], some clean and isolated PDOS peaks of Re (Ta) appear at both sides of the Fermi level, resulting from the weak interactions between the orbitals of the alloying atoms and those of the host atoms.

The charge density differences on the (011) plane are plot-

ted in Fig. 4. The charge density difference is defined as $\Delta \rho = \rho[\text{Ni}_3(\text{Al},\text{Re})] - \rho_{\text{free}}[\text{Ni}_3(\text{Al},\text{Re})] - \rho(\text{Ni}_3\text{Al}) + \rho_{\text{free}}(\text{Ni}_3\text{Al})$ for the $\text{Ni}_3(\text{Al},\text{Re})$ system (other systems have similar definitions). From Fig. 4, we can see that strong charge correlation regions due to electron accumulation appear around the Ni atoms and the Al atoms, reflecting enhanced interactions between the NN Ni atoms as well as enhanced interactions between NN Ni atoms and the associated NNN Al atoms in the $\text{Ni}_3(\text{Al},\text{Re})$ and the $\text{Ni}_3(\text{Al},\text{Ta})$ systems. The sparse charge correlation curves connecting an Re (Ta) atom with the Ni atoms imply their weak bonding. The above results are consistent with the analyses on interatomic energy presented in the previous section.

V. SUMMARY

We have studied alloying effect of Re (Ta) atom in the γ' phase of Ni-based superalloy using first-principles methods. The calculated transfer energies obtained by the DMol method show that an Re (Ta) atom prefers to occupy an Al site in the γ' phase. The effects of an Re (Ta) atom at an Al site and at an Ni site are different. At an Al site, an Re (Ta) atom induces a large decrease of 2.55 eV (4.04 eV) in the binding energy of the system, without leading to tremendous local lattice distortion. While at an Ni site, an Re (Ta) atom induces a small decrease of 0.68 eV (1.11 eV) in the binding energy and large local lattice distortion. Thus the binding energy of the system in the γ' phase strongly depends on the substitution type. The results for the interatomic energy obtained by the DV method suggest that an Re atom or an Ta atom, no matter whether it is at an Al site or at an Ni site, will greatly enhance the interaction between nearest neighboring atoms, as well as that between a nearest neighboring atom and the associated next nearest neighboring atom. However, the Re and Ta atoms only weakly bond with the host atoms. In addition, the charge distribution and PDOS results obtained by the DV method for the systems where an Re atom or an Ta atom is substituted for an Al atom confirm the conclusions drawn from the interatomic energy analyses.

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