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The first-principles study on the doping effect of Re in Ni_3Al

Song Yu [a,*], Chongyu Wang [a,b], Tao Yu [a]

[a] *Central Iron and Steel Research Institute, Beijing 100081, China*
[b] *Department of Physics, Tsinghua University, Beijing 100084, China*

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Abstract

Using first-principles density function for molecules method (DMol) and discrete variational method (DVM) based on the density functional theory, we studied the doping effect of Re in Ni_3Al. The structure relaxation and the alloying energy show that Re has a strong Al site preference and leads to the local deformation, which is in agreement with the experimental results and other theoretical results. In addition, the charge density difference and the bond order show that Re can strongly enhance the interatomic interaction between the nearest neighbor atoms. From the density of states and the Pauli spectrum, we find that resonance states and localized states are induced by doping Re, and the doped Re atom forms the hybridized bond with the nearest neighbor atoms.

Keywords: The first-principles; Re; Ni_3Al

1. Introduction

Because of the excellent properties of Ni-based superalloys, such as high-temperature strength, low density, and strong resistance to oxidation, they have attracted much attention from physicists and technicists in recent years [1]. Ni_3Al, as Ni-based superalloys with strengthening phase (γ' phase), is believed to be the cause of increased yield strength and creep resistance at high-temperature [1]. In order to improve the high-temperature property, researchers have added various alloying elements in Ni_3Al, such as Re, Cr, Ti, W, Co, and Ta [2–6]. Knowledge about the physical behavior of the alloying element is important for understanding the strengthening effect and developing practical superalloys.

In the past two decades, the first-principles have been used widely to study the physical behavior of alloying elements in Ni_3Al. Using all-electron linear muffin-tin orbitals-atomic spheres approximation (LMTO-ASA) and full-potential linearised augmented plane wave (LAPW) energy band methods, Freeman et al. [7–9] studied the phase stability in Ni_3Al and $Ni_3(Al, V)$ systems. They found that the cohesive energy of 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, and the magnetic interaction has little effect on the structural transition. Furthermore, they proposed that adding V can enhance the bonding effect, which can stabilize Ni_3Al in an $L1_2$-like structure. Employing the discrete variational method (DVM) on a series of small cluster models, Yang et al. [10] carried out a total energy calculation, considering only interactions between the nearest neighbor atoms and explaining the substitution behaviors of alloying elements in Ni_3Al. They found that Sc, Co, Cu, and Pd prefer the Ni site, while Ti, V, Nb, and Mo prefer the Al site, and Fe is attracted to both sites. Moreover, they suggested that these site preferences are insensitive to the interactions with the next nearest neighbor atoms. However, using the tight-binding method combining with the coherent potential approximation (CPA), Marcel et al.

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* Corresponding author. Tel.: +86 1062185838; fax: +86 1062185838.
E-mail address: yusong107@yahoo.com.cn (S. Yu).

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[11] found that Zn, Cd, Cu, and Au have weak tendency to occupy the Al and Ni sites, Ga, Si, Ge, Fe, Co, and Pd have strong tendency to occupy the Al and Ni sites, Cr and Cd show no evident preference for either site. In their calculations, the pair-potential interaction is extended to the sixth nearest neighbor atoms. In addition, with the first-principles interatomic potential, Shen et al. [12] studied the atom site preference of alloying elements, they gained the results in agreement with the experiment, and predicted the behavious of the alloying elements on the surface and boundary. Furthermore, using the first-principles methods, some researchers have studied the electronic effect of alloying elements. For instance, with the real-space recursion method, Wang et al. [13] studied the energy and electronic structure of Re and Ta in Ni_3Al, they found that Re prefers the Al site, while Ta prefers the Ni site. And utilizing the tight-binding linear muffin-tin orbitals (LMTO) method in conjunction with the multi-sublattice coherent potential approximation, Ruban et al. [14] studied the temperature and compositional dependency of site substitution behaviors for all 3d, 4d, 5d, and noble metals.

Re is a very important alloying element added in Ni-based superalloys, which can retard particle coarsening and improve the creep strength at very high-temperature [3–5], and so it has been widely used in the aeronautic field. However, the strength mechanism of Re is very little known. In this study, we will use two first-principles methods, density function for molecules method (DMol) [15,16], and discrete variational method (DVM) [17–19], to study the doping effect of Re in Ni_3Al.

2. Method and model

2.1. Theory method

The DMol and DVM are the real-space numerical self-consistent methods based on the density functional theory, which have been successfully used in the system of metal cluster, biomolecule, and organic matter, etc. The basic idea of the methods is that the basis set of atom orbit is set as the basis set of system, and the Kohn–Sham equation is self-consistently solved by the numerical integration

$$\varphi_i(r) = \sum_j C_{ji}\chi_j(r) \tag{1}$$

where ϕ_i is the wave function of single electronic orbit in molecule, $\chi_i(r)$ is the symmetrized basis set of atom, and C_{ji} is the expansion coefficient. Based on the Diophantine integral function, the error function is written as:

$$\begin{aligned}\Delta_{ij} &= \int \phi_i^*(r)(H-\varepsilon)\phi_j(r)\mathrm{d}\tau \\ &= \sum_k W(r_k)\phi_i^*(r_k)(H-\varepsilon)\phi_j(r_k)\end{aligned} \tag{2}$$

where $W(r_k)$ are the weight of sample points, r_k is the coordinate of discrete sample points. Based on Eq. (1), the error function can be rewritten as:

$$\Delta_{ij} = \sum_{lk} C_{ik}^*(H_{kl} - \varepsilon_{kl})C_{lj} \tag{3}$$

with $\partial\Delta_{ij}/\partial C_{ij} = 0$, the following equation can be obtained:

$$\sum_l (H_{kl} - \varepsilon_l S_{kl})C_{lj} = 0 \tag{4}$$

where

$$H_{kl} = \sum_i W(r_i)\chi_k^*(r_i)H\chi_l(r_i) \tag{5}$$

$$S_{kl} = \sum_i W(r_i)\chi_k^*(r_i)\chi_l(r_i) \tag{6}$$

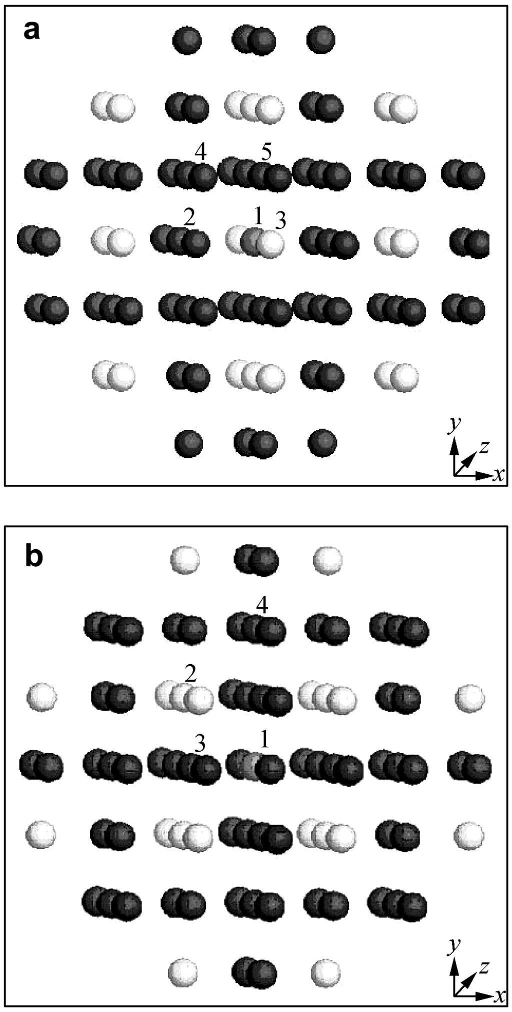

Fig. 1. The cluster model used in the DMol and DVM calculations. (a) The Ni_3Al [$Ni_3(Al,Re)$] cluster model. The cluster model centers on the Al (Re) atom. The central Al (Re) atom is labeled by No. 1, two NN Ni atoms are labeled by No. 2 and No. 4, respectively, the NNN Al atom is labeled by No. 3, and No. 5 denotes the NNN Ni atom. (b) The Ni_3Al [$(Ni,Re)_3Al$] cluster model. The cluster model centers on the Ni (Re) atom. The central Ni (Re) atom is labeled by No. 1, the NN Al atom and the NN Ni atom are labeled by No. 2 and No. 3, respectively, and the NNN Ni atom is labeled by No. 4.

Eqs. (5) and (6) can be solved by the numerical self-consistent method, and the eigen function, eigen values, and eigen orbits occupancy of the single electron can be obtained.

2.2. Model

Below its melting point (1390 °C), Ni_3Al has the $L1_2$-like ordered structure in which Al and Ni occupy a corner site and a face center site, respectively. Because Re has large atomic radii, Re 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 based on our simulation of molecular dynamics [20], we build the molecular cluster models as shown in Fig. 1. The cluster model consist of 87 atoms, including the sixth neighbor atoms. In the models, the number of neighbor atoms is enough that the boundary effect can be ignored.

Table 1
The alloying energy of Re (Unit: eV)

System	Binding energy	Alloying energy
Ni_3Al	−515.34	
$Ni_3(Al,Re)$	−518.51	−3.17
$(Ni,Re)_3Al$	−516.26	−0.92

In the DMol calculation, the convergence criteria for the energy gradient and the atomic displacement are 0.001 Ry/a.u. and 0.001 Å, respectively. The double numerical polarized (DNP) basis including the inner orbitals and the Vosko–Wilk–Nisair local exchange-correlation functional with the Becke–Perdew–Wang general gradient approximation (GGA) correction were used to obtain more precise results. The Re atom, the nearest neighbor (NN) atoms, and the next nearest neighbor (NNN) atoms were all allowed to relax in accordance with the force acting on them. In the DVM calculation, in order to reduce the effect of basis selection on the results, we used the single-site orbi-

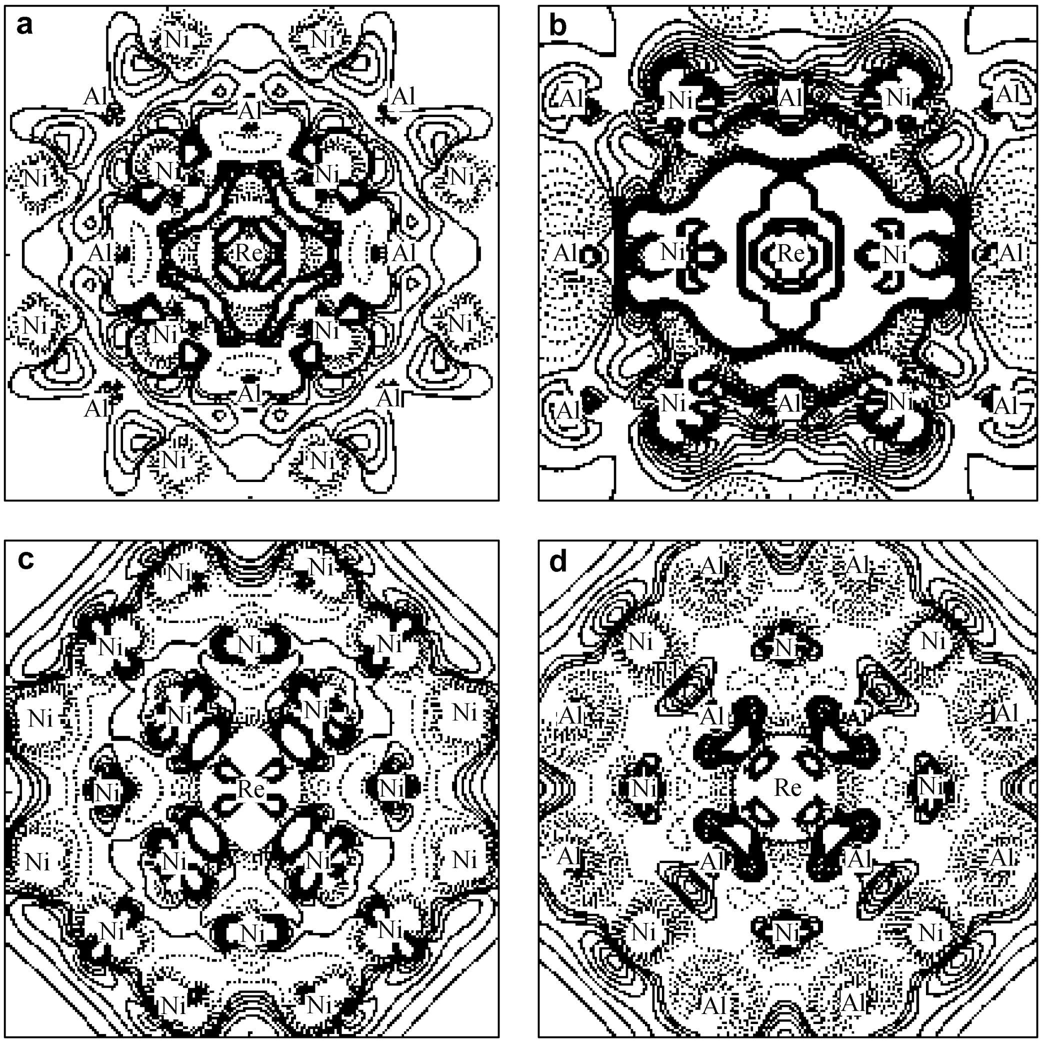

Fig. 2. The charge density difference (the contour spacing is 0.0001 e $a.u.^{-3}$, the solid lines and dashed lines correspond to the gain and loss of electrons, respectively). (a) The electron density difference on the [001] plane of the $Ni_3(Al,Re)$ system; (b) the electron density difference on the [011] plane of the $Ni_3(Al,Re)$ system; (c) the electron density difference on the [001] plane of the $(Ni,Re)_3Al$ system; (d) the electron density difference on the [011] plane of the $(Ni,Re)_3Al$ system.

Table 2
The bond order

Atoms	Bond order	
	Ideal system	Doping system
(Re,Al)1–Ni_2	0.2915	0.3883
(Re,Al)1–Al_3	0.0372	0.0471
(Re,Al)1–Ni_4	0.0201	0.0224
Ni_2–Al_3	0.0221	0.3049
Ni_2–Ni_5	0.0199	0.2538
Ni_2–Ni_4	0.0215	0.2770

tals as the basis set. In the generation of a basis, funnel potential was 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 assignments are $3s^23p^1$ for the Al atom, $3d^84s^24p^0$ for the Ni atom and $5d^56s^26p^0$ for the Re atom. The single-particle wave functions are solved by the self-consistent multipolar approximation. This way is at the cost of more computation time. However, more accurate and self-consistent charge densities can be obtained. In addition, the Vosko–Wilk–Nisair exchange-correlation potential and 1000 integration points per atom were used in the computation.

3. Result and analysis

3.1. Local deformation

After the DMol relaxation, the atoms can stay with a stable position. When Re atom substitutes for the Al site, the distance from Re to the NN atom increases 0.7%, and the distance from Re to the NNN atom increases only 0.2%, which is almost unchanged. However, when Re atom substitutes for the Ni site, the distance from Re to the NN atom increases 2.8% and the distance from Re to the NNN atom increases 0.6%. It is a larger local deformation that Re atom substitutes for the Ni site, which do harm to the structure and properties of alloys. Therefore, Re exhibits a strong Al site preference, which is in agreement with the experimental and other theoretical results [3,4,10].

3.2. Alloying energy

The energy is an important physic parameter to judge the atom site preference of alloying elements. In this study, the alloying energy is defined as follows:

$$E_{\mathrm{Re}}^{\mathrm{Al}} = E_{\mathrm{c}}^{\mathrm{Re-Al}} - E_{\mathrm{c}} \tag{7}$$

$$E_{\mathrm{Re}}^{\mathrm{Ni}} = E_{\mathrm{c}}^{\mathrm{Re-Ni}} - E_{\mathrm{c}} \tag{8}$$

where $E_{\mathrm{Re}}^{\mathrm{Al}}$ and $\mathrm{E}_{\mathrm{Re}}^{\mathrm{Ni}}$ denote the alloying energy for Re atom substituting for the Al and Ni sites, respectively; $E_{\mathrm{c}}^{\mathrm{Re-Al}}$ and $E_{\mathrm{c}}^{\mathrm{Re-Ni}}$ are the binding energy of systems for Re atom substituting for the Al and Ni sites, respectively; E_{c} is the

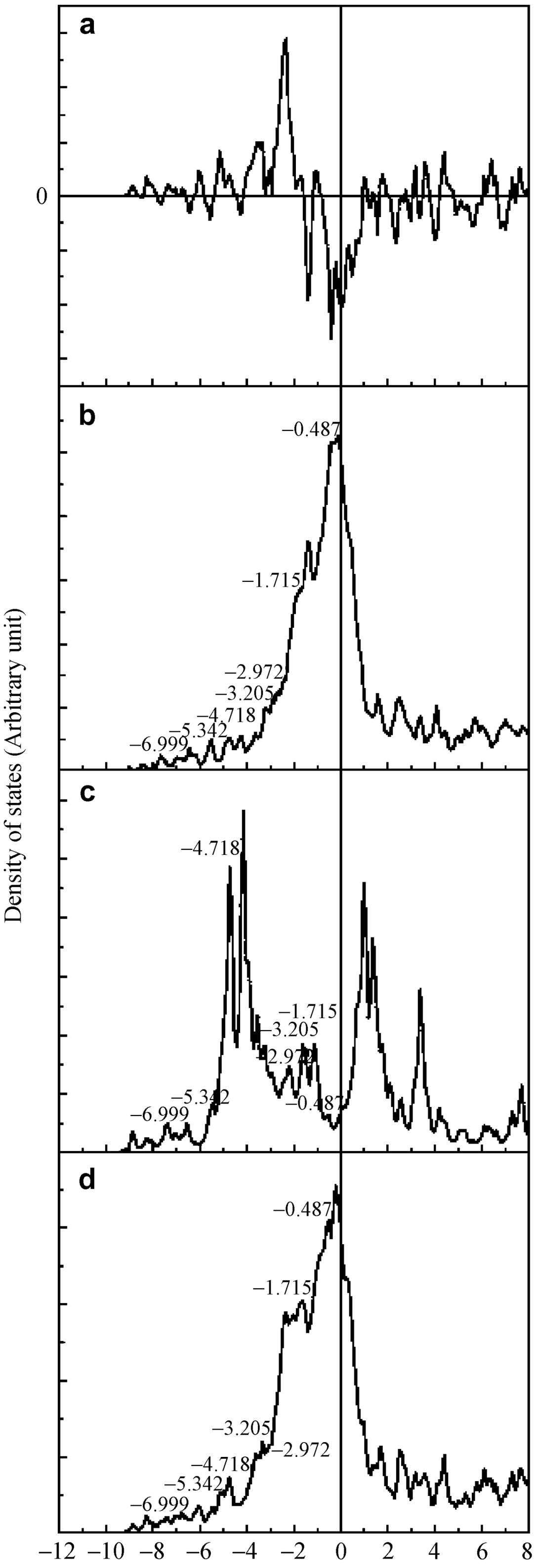

Fig. 3. The density of states of Re, $Ni_3(Al,Re)$, and Ni_3Al. (a) The difference of TDOS between the $Ni_3(Al,Re)$ and Ni_3Al system; (b) the TDOS of Ni_3Al system; (c) the LDOS of Re atom; (d) the TDOS of $Ni_3(Al,Re)$ system. The Fermi level is shifted to zero. The Arabic numerals correspond to that of Fig. 1.

binding energy of ideal Ni_3Al. The calculated results are shown in Table 1. It can be seen from Table 1 that the system binding energy descends 3.17 eV when Re atom substitutes for the Al site, which is lower than the atom activation energy. Therefore, Re atom can be stable at the Al site. However, when Re atom substitutes for the Ni site, the binding energy of the system decreases only 0.92 eV, which is less than that of Al atom, and so Re atom at the Ni site is unstable. This is also supported by the experimental and other theoretical results [3,4,10].

3.3. The charge density difference

The charge density difference can reflect the charge distribution directly. In this study, the charge density difference is defined as:

$$\Delta\rho = \rho[Ni_3(Al,Re)] - \rho_{free}[Ni_3(Al,Re)] - \rho[Ni_3Al] + \rho_{free}[Ni_3Al] \qquad (9)$$

The results are given in Fig. 2. It can be seen from Fig. 2(a) and (b) that the strong charge correlation regions due to electron accumulation appear around the Ni atoms and the Al atoms, which reflect the enhanced interaction between the NN Ni atoms as well as the enhanced interaction between NN Ni atom and the associated NNN Al atom. It can also be seen from Fig. 2(c) and (d) that the electron accumulation appears around the Ni atoms and the Al atoms. However, compared with Fig. 2(a) and (b), when the Re atom substitutes for the Ni site, the region of loss electron is larger than that of Al site. Consider the bonding, it is better that Re atom substitutes for the Al site, which is in agreement with the results presented in the previous section.

3.4. Bond order

In order to study the interatomic interaction, we calculated the bond order between atoms. Based on the above analyses, we can believe that Re atom has a strong Al site preference. Therefore, we only discuss the bond order which Re atom substitutes for the Al site. The results are shown in Table 2. It can be seen from Table 2 that the bond order between NN atoms (Ni_2–Ni_5, Ni_2–Al_3, and Ni_2–Ni_4) increases obviously after doping the Re atom, which means that Re in Ni_3Al can strongly enhance the interatomic interaction between nearest neighbor atoms. However, the bond order between Re and the associated atoms ((Re,Al)1–Ni_2, (Re,Al)1–Al_3 and (Re,Al)1–Ni_4) increases very little after doping the Re atom. The above results are consistent with the analyses on the charge density difference presented in Section 3.3.

3.5. Density of state

In order to study the interactions between atomic orbitals, being the same as Section 3.4, we only consider the situation that Re atom substitutes for the Al site. The total

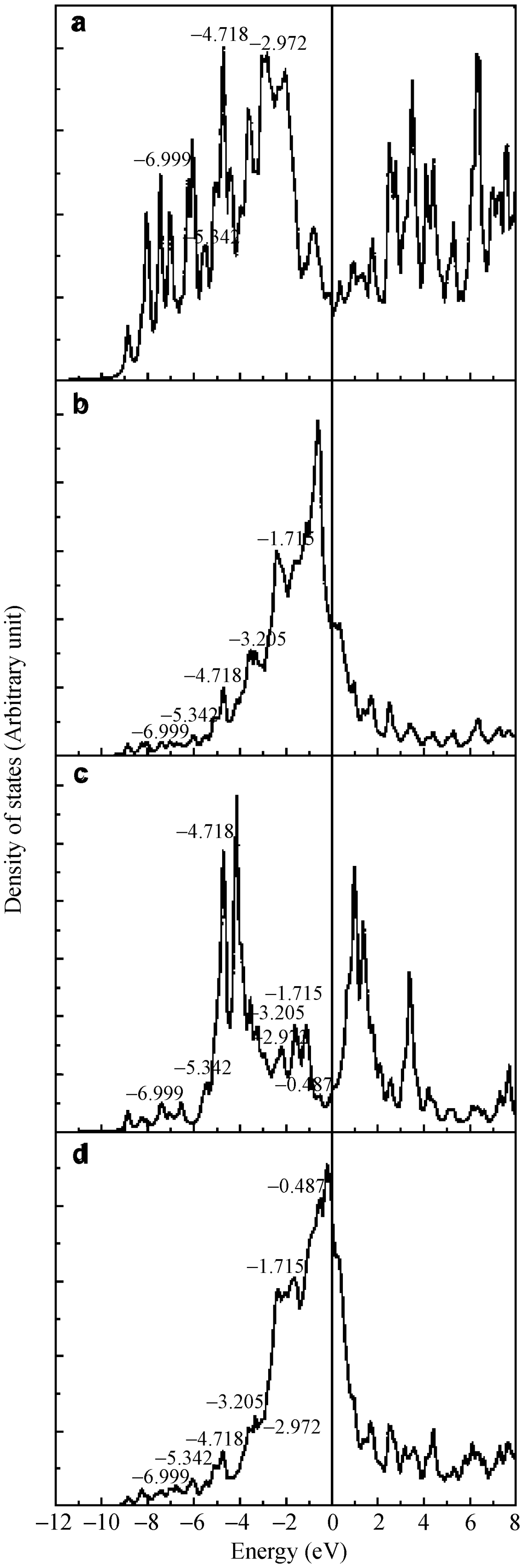

Fig. 4. The density of states of Re, Ni, Al, and $Ni_3(Al,Re)$. (a) The LDOS of NNN Al2 atom; (b) the LDOS of NN Ni1 atom; (c) the LDOS of Re atom; (d) the TDOS of $Ni_3(Al,Re)$. The Fermi level is shifted to zero. The Arabic numerals correspond to that of Fig. 1.

density of states (TDOS) and local density of states (LDOS) are calculated by the Lorenz broadening scheme combining with a Mulliken population analysis. The density of states (DOS) in DVM method is defined as follows

$$D_{\alpha l}(E) = \sum_n N^n_{\alpha l} \frac{\delta}{\pi[(E - \varepsilon_n) + \delta^2]} \tag{10}$$

where $N^n_{\alpha l}$ is the population of the atomic orbital $\phi_{\alpha l}$ of atom l in energy ε_n of the molecular orbital, and δ is the broaden parameter.

Fig. 3 shows the TDOS of the $Ni_3(Al,Re)$ and Ni_3Al systems and the LDOS of the Re atom. Based on the Pauli spectrum, it can be seen that Re atom can form some resonance states at the levels of −0.487, −1.715, −2.972, −3.205, −4.718, −5.342, and −6.999 eV, where the greatest effect of electronic state is near the Fermi level (−0.487 eV). Fig. 4 shows the TDOS of the $Ni_3(Al,Re)$ system and the LDOS of the Re atom and the associated atoms. Similar to the analyses of Fig. 3, it can be also seen from Pauli spectrum that the Re atom forms the hybridized bond with the NN Ni atom at the levels of −1.715, −3.205, −4.718, −5.342, and −6.999 eV, and forms the hybridized bond with the NNN Al atom at the levels of −2.972, −4.718, −5.342, and −6.999 eV. It is worth emphasizing that near the Fermi level (−0.487 eV), Re atom does not form the hybridized bond with the associated atoms. This electronic state is the localized state, which contributes to the TDOS of the system independently.

4. Conclusion

Using first-principles methods DMol and DVM based on density functional theory, we have studied the doping effect of Re in Ni_3Al. According to the calculation of local deformation and alloying energy, the Re atom has a strong Al site preference, and it can lead to the local deformation, which is in agreement with the experimental and other theoretical results. Furthermore, based on calculation of the charge distribution and bonding order, Re atom can strongly enhance the interatomic interaction between the nearest neighbor atoms. The density of states and the Pauli spectrum show that resonance states and localized states are induced by doping Re, and the doped Re atom forms the hybridized bond with the nearest neighbor atoms.

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