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# Effects of alloying element Ti on $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al from first principles

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## Abstract

The energies and electronic structures of the alloying element Ti in the Nb–Si–Al–Ti three-phase alloy, Nb<sub>ss</sub> (Nb solid solution), Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al, have been studied by the first-principles pseudopotential plane-wave method based on density functional theory. It is found that the preferred sites for the alloying element Ti are the Nb I sublattice sites of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and then the Nb sublattice sites of Nb<sub>3</sub>Al phase according to the calculations of impurity formation energies. Using a sum of overlap populations of all bonds in the conventional cell, we evaluate the covalent bonding of intermetallic compounds quantitatively. It is found that Ti can decrease the covalent bonding of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al. We also analyse the bond characters using valence charge densities and total density of states.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

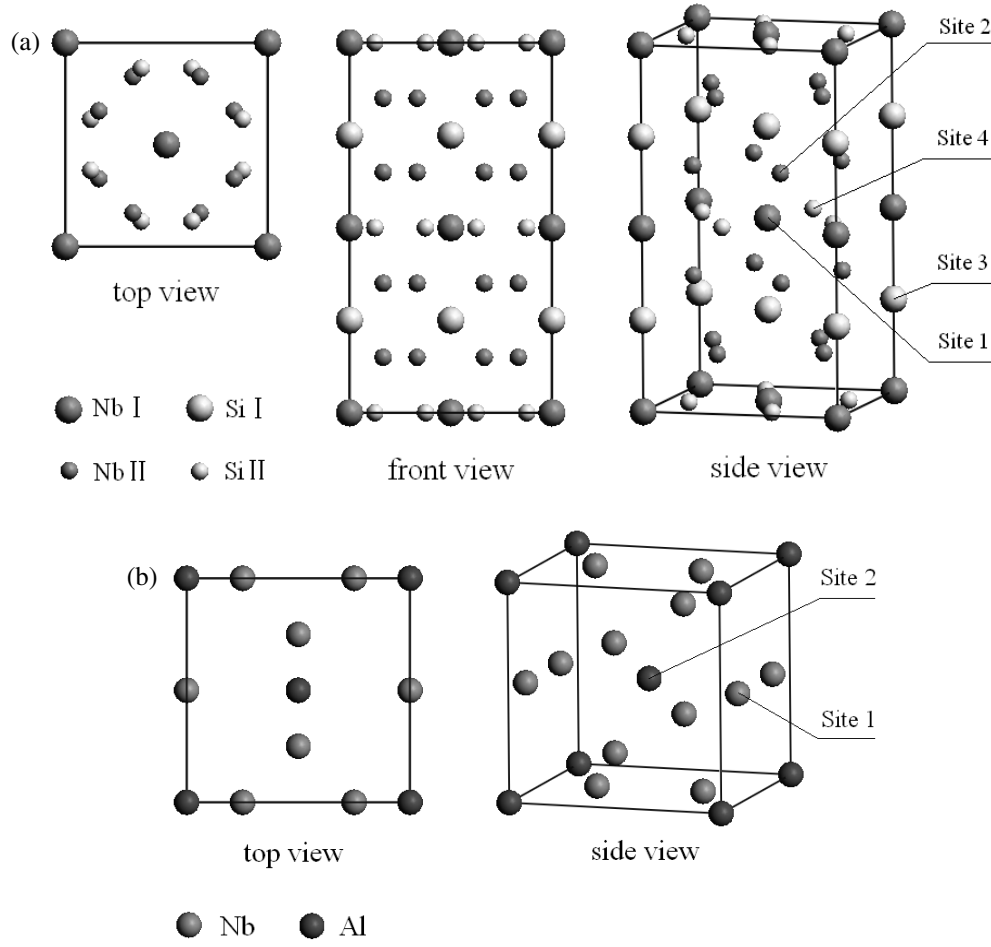
Recently, the development of high-temperature structure materials whose operating temperature exceeds that of conventional nickel-based superalloys has been required in various fields. Refractory intermetallic compounds such as Nb<sub>5</sub>Si<sub>3</sub> [1] and Nb<sub>3</sub>Al [2, 3] have been studied as candidate materials due to their excellent high-temperature strength and low density. The intermetallic compounds Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al have severe brittleness at ambient temperature. To overcome this frailty, the Nb<sub>ss</sub>/Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>ss</sub>/Nb<sub>3</sub>Al *in situ* composites have been studied [4–9] extensively; in these composites the Nb solid solution (Nb<sub>ss</sub>) provides toughness at ambient temperature and the intermetallic compounds supply excellent strength at high temperature. To be considered as a new material for ultra-high-temperature structural applications, Nb<sub>ss</sub>/Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>ss</sub>/Nb<sub>3</sub>Al *in situ* composites must be ductile, oxidation resistant, and show resistance to creep [10, 11]. For this purpose, Murayama *et al* [12] fabricated the Nb–Si–Al three-phase alloy (Nb<sub>ss</sub>, Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al). They reported that the high-temperature strength and fracture toughness at room temperature of the three-phase alloy consisting of Nb<sub>ss</sub>, Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al are higher than those of alloys in Nb–Si or Nb–Al binary

systems. By the addition of titanium, the fracture toughness at room temperature of the three-phase alloy ( $\text{Nb}_{\text{ss}}$ ,  $\text{Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$ ) is increased to over  $12 \text{ MPa m}^{1/2}$  without sacrificing the high-temperature strength; at the same time the oxidation resistance is also improved [12]. Why can the addition of titanium increase the fracture toughness at room temperature and improve the oxidation resistance of the three-phase alloy? How can we understand the effect of the alloying element Ti on the three-phase alloy from bonding characters? The answers to these questions are meaningful. However, all the research mentioned above is concerned with the composition, processing and properties. There is only one investigation about  $\text{Nb}_5\text{Si}_3$  thermal expansion anisotropy from first principles [13]. Therefore, our research is concentrated on how titanium influences the electronic structures of the intermetallic compounds  $\alpha\text{-Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$ , and gives a method to evaluate the covalent bonding of the intermetallic compounds quantitatively from first principles.

## 2. Computational method and models

We performed first-principles calculations within the density functional theory (DFT) using the Cambridge Serial Total Energy Package (CASTEP) [14]. CASTEP uses a plane-wave basis set for the expansion of the single-particle Kohn–Sham wavefunctions, and pseudopotentials to describe the computationally expensive electron–ion interaction, in which the exchange–correlation energy by the generalized gradient approximation (GGA) of Perdew was adopted for all elements in our models by adopting Perdew–Burke–Ernzerhof parameters [15, 16]. Ultrasoft pseudopotentials [17] were used. In the present calculations, the cutoff energy was set at 320 eV. Sampling of the irreducible wedge of the Brillouin zone was performed with a regular Monkhorst–Pack grid of special  $k$ -points, which are respectively  $4 \times 4 \times 4$ ,  $6 \times 6 \times 6$  and  $4 \times 4 \times 2$  for  $\text{Nb}_{\text{ss}}$ ,  $\text{Nb}_3\text{Al}$  and  $\alpha\text{-Nb}_5\text{Si}_3$ . A finite basis set correction and the Pulay scheme of density mixing [18] were applied for the evaluation of energy and stress. All atomic positions in our models were relaxed until the forces were less than  $0.03 \text{ eV \AA}^{-1}$ . In order to investigate the effect of the alloying element Ti on the three phases alloy ( $\text{Nb}_{\text{ss}}$ ,  $\text{Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$ ), we built the  $2 \times 2 \times 2$  bcc Nb supercell,  $\alpha\text{-Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$  structures.

The structure of  $\alpha\text{-Nb}_5\text{Si}_3$  is shown in figure 1(a). Its space group is  $I4/mcm$ , and the lattice parameters are  $a = b = 6.557 \text{ \AA}$ ,  $c = 11.86 \text{ \AA}$ . The atomic coordinates in the unit cell are Nb (0, 0, 0), Nb (0.166, 0.666, 0.15), Si (0, 0, 0.25) and Si (0.375, 0.875, 0). It can be seen from figure 1(a) that there are 20 niobium atoms and 12 silicon atoms in the conventional cell of  $\alpha\text{-Nb}_5\text{Si}_3$ . It can be determined that there are two groups of niobium atoms (Nb I and Nb II) and two groups of silicon atoms (Si I and Si II) in the conventional cell from their geometry positions. We use Nb I and Si II to denote the niobium atoms and silicon atoms in the niobium silicon mixing layers, respectively. Nb II and Si I denote the niobium atoms in the pure niobium layers and the silicon atoms in the pure silicon layers, respectively. That is to say there are four nonequivalent solute positions for titanium in  $\alpha\text{-Nb}_5\text{Si}_3$  unit cells and the corresponding sites are pointed out in figure 1(a). The total number of atoms of each group are four for Nb I, sixteen for Nb II, four for Si I and eight for Si II. The structure of the  $\text{Nb}_3\text{Al}$  phase is shown in figure 1(b). The space group of it is  $Pm\bar{3}n$ , and the lattice parameters are  $a = b = c = 5.184 \text{ \AA}$ . The atomic coordinates in the unit cell are Nb (0.25, 0.0, 0.5) and Al (0, 0, 0). There are six Nb atoms and two Al atoms in  $\text{Nb}_3\text{Al}$  unit cell. We can determine the equivalent atoms in the conventional cell according to the atomic geometry positions. It can be found that all the Nb atoms are equivalent and all the Al atoms are also equivalent; thus there are only two kinds of substituted sites for Ti in  $\text{Nb}_3\text{Al}$  unit cells. The corresponding sites are labelled in figure 1(b). Site 1 is related to the Nb sublattice and site 2 is related to Al sublattice.



**Figure 1.** The atomic structures. (a) Conventional cell of  $\alpha$ - $\text{Nb}_5\text{Si}_3$ ; (b) conventional cell of  $\text{Nb}_3\text{Al}$ .

### 3. Results and discussion

#### 3.1. Site preference of Ti

To study the site preference of Ti in the three-phase alloy ( $\text{Nb}_{\text{ss}}$ ,  $\text{Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$ ), the impurity formation energies were calculated by definition

$$E_{f-\text{im}}^{\text{M}} = E_f^{\text{M-Ti}} - E_f^{\text{M}} = E_t^{\text{M-Ti}} - E_t^{\text{M}} + E_{\text{solid}}^{\text{X}} - E_{\text{solid}}^{\text{Ti}} \quad (1)$$

where M denotes Nb,  $\alpha$ - $\text{Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$ , respectively; X represents the substituted atom;  $E_f^{\text{M}}$  and  $E_f^{\text{M-Ti}}$  refer to the formation energies of the unit cell of M and Ti-doped M;  $E_{\text{solid}}^{\text{X}}$  and  $E_{\text{solid}}^{\text{Ti}}$  are the total energies of X and Ti atoms in their bulk states, respectively;  $E_t^{\text{M}}$  and  $E_t^{\text{M-Ti}}$  refer to the total energies of the unit cell of M and Ti-doped M at their equilibrium lattice constant.

We calculated the impurity formation energies of Ti in the three phases,  $\alpha$ - $\text{Nb}_5\text{Si}_3$ ,  $\text{Nb}_3\text{Al}$  and  $\text{Nb}_{\text{ss}}$ , at different sites. In the calculation only one atom is substituted by Ti atom in the 16-atom  $\alpha$ - $\text{Nb}_5\text{Si}_3$ , 8-atom  $\text{Nb}_3\text{Al}$  and 16-atom bcc Nb cells, respectively. The results of our calculated impurity formation energies of Ti are listed in table 1. From table 1, we can see

**Table 1.** The system total energies  $E_t$  (eV), formation energies  $E_f$  (eV) and impurity formation energies  $E_{f-im}$  (eV) of titanium at different substitution sites of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>, Nb<sub>3</sub>Al and Nb.

Systems	Sites of Ti	$E_t$ (eV)	$E_f$ (eV)	$E_{f-im}$ (eV)
Clean $\alpha$ -Nb <sub>5</sub> Si <sub>3</sub>	—	-16 179.37	-12.13	—
	Nb I	-16 233.73	-12.66	-0.53
Ti-doped $\alpha$ -Nb <sub>5</sub> Si <sub>3</sub>	Nb II	-16 232.94	-11.87	0.26
	Si I	-17 673.50	-9.29	2.84
	Si II	-17 672.39	-8.18	3.95
Clean Nb <sub>3</sub> Al	—	-9 425.96	-1.76	—
Ti-doped Nb <sub>3</sub> Al	Nb	-9 479.91	-1.88	-0.12
Nb <sub>3</sub> Al	Al	-10 973.53	-1.08	0.68
Clean Nb	—	-24 826.08	0	—
Ti-doped Nb	Nb	-24 879.62	0.29	0.29

that the impurity formation energy of Ti in the  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> phase is increased gradually when the Nb I, Nb II, Si I, Si II sites are substituted, respectively. The first group of Nb atoms (Nb I) is the most favourable site to be replaced by titanium atoms according to the negative impurity formation energy result. The impurity formation energy of Ti in Nb<sub>3</sub>Al is larger when Al is substituted than that when Nb is substituted. The negative impurity formation energy of Ti in the Nb site and positive impurity formation energy of Ti in the Al site means that the Nb atoms are more easily substituted by Ti in the Nb<sub>3</sub>Al phase, which accords with the other experimental result [3]. The impurity formation energy of Ti in the 16-atom Nb supercell is positive, which means the Ti atom cannot replace the Nb to form Nb<sub>ss</sub>.

Comparing the impurity formation energies of Ti in  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>, Nb<sub>3</sub>Al and Nb<sub>ss</sub> at different sites, it is clearly shown that Ti atoms first replace atoms on the Nb I sublattice in  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and then replace the Nb atoms in the Nb<sub>3</sub>Al phase. Therefore, our following discussion will just focus on these cases.

### 3.2. Overlap population analysis

It is widely accepted that a large value of the bond overlap population indicates a covalent bond [19, 20]. The larger the overlap population is, the stronger the covalence bond is. To study the change of bonds, we calculate the bond overlap populations of the clean and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al systems, respectively.

The overlap populations of Nb I–Si I and Nb I–Si II bonds in pure  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and the overlap populations of the corresponding Ti–Si I and Ti–Si II bonds in Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> are listed in table 2. As can be seen from table 2, the overlap populations of Nb I–Si I and Nb I–Si II bonds in clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> have larger values than those of the corresponding Ti–Si I and Ti–Si II bonds in Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>. Therefore, the Ti–Si I and Ti–Si II bonds are weaker and less covalent in Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> than the Nb I–Si I and Nb I–Si II bonds in clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>. However, the overlap populations of some other bonds in the Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> are a little larger than those of the clean system. This makes it confusing to analyse how titanium has changed the covalent bonding of the  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> phase. In light of this problem, we propose a new method to evaluate the covalent bonding quantitatively according to the overlap populations. We sum up the overlap populations of all bonds in the clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> unit cell and the Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> unit cell, respectively. The total overlap population in the unit cell decreases by 0.66% after titanium is doped. The total overlap population decrease shows that the bonds in Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> are less covalent after titanium is doped in the system. Covalent bonding is one of

**Table 2.** The overlap populations of bonds in clean and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al phases.

	Clean systems		Ti-doped systems	
	Bonds	Overlap population	Bonds	Overlap population
$\alpha$ -Nb <sub>5</sub> Si <sub>3</sub>	Nb I–Si I	0.22	Ti–Si I	0.18
	Nb I–Si II	0.17	Ti–Si II	0.12
Nb <sub>3</sub> Al	Nb–Nb	0.88	Ti–Nb	0.84
	Nb–Al	0.42	Ti–Al	0.30

the reasons that makes the refractory intermetallic compounds brittle [21]; therefore titanium doping is good for improving the ductility of the  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> phase.

The overlap populations of Nb–Nb and Nb–Al bonds in clean Nb<sub>3</sub>Al and the overlap populations of the corresponding Ti–Nb and Ti–Al bonds in Ti-doped Nb<sub>3</sub>Al are also summarized in table 2. It can be seen that the overlap populations of Ti–Nb and Ti–Al in Ti-doped Nb<sub>3</sub>Al have lower values than those of the corresponding Nb–Nb and Nb–Al bonds in clean Nb<sub>3</sub>Al. Therefore, the Ti–Nb and Ti–Al bonds in Ti-doped Nb<sub>3</sub>Al are weaker and less covalent than Nb–Nb and Nb–Al bonds in clean Nb<sub>3</sub>Al, which is good for improving the ductility of the Nb<sub>3</sub>Al phase. Although the above bonds' overlap populations decrease, some other bonds' overlap populations increase for Ti-doped Nb<sub>3</sub>Al. Once again this makes it confusing to analyse how titanium influences the covalent bonding of the Nb<sub>3</sub>Al phase. We have used the above model to calculate the total overlap populations of the unit cell of clean Nb<sub>3</sub>Al and that of the unit cell of Ti-doped Nb<sub>3</sub>Al. The total overlap population of the unit cell decreases by 5.21% after Ti is doped in Nb<sub>3</sub>Al.

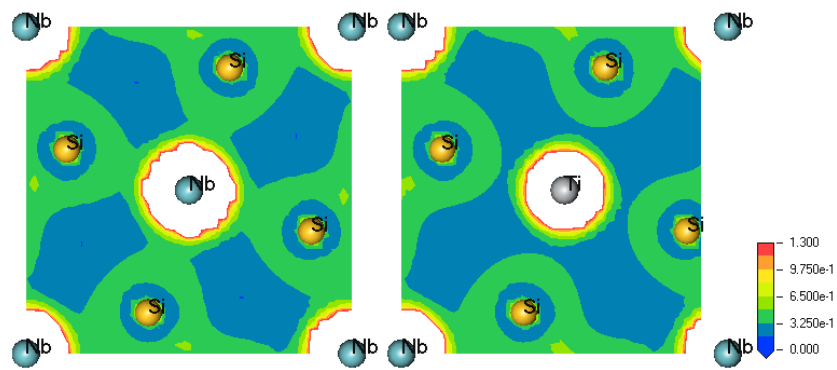
Comparing the total overlap population decrease of Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> with Ti-doped Nb<sub>3</sub>Al, we find that the relative decrease of the total overlap population of Nb<sub>3</sub>Al is much larger than that of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>. The overlap populations can be used to qualitatively measure the covalent content of atomic bonds [19–21]. Thus we come to the conclusion that the decrease of the covalent bonding in Nb<sub>3</sub>Al is larger than that in  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> after titanium is doped.

In order to further study the effects of titanium on the mechanical properties of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al, the bulk moduli of clean and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al have been calculated. The bulk moduli of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> are 191.0 and 188.3 GPa for clean and Ti-doped, respectively, which decrease about 1.41%. The bulk moduli of Nb<sub>3</sub>Al are 156.9 and 147.7 GPa for clean and Ti-doped, respectively, which decreases about 5.86%. The change of bulk moduli shows the same tendency as the change of total overlap populations.

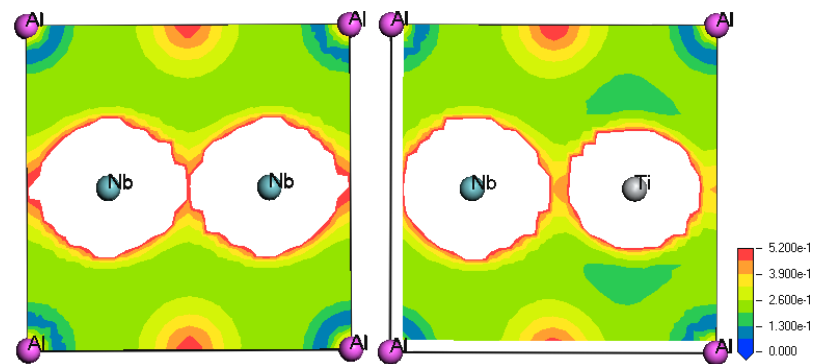
### 3.3. Valence charge densities

An important quantity which helps us characterize the bonds is the valence charge densities. To gain insight into the nature of the bonding, we calculated the valence charge densities of clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> conventional cells. Figure 2 presents the valence charge densities of clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> in the (002) planes. Comparing the valence charge densities of clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>, we can notice that it is less between the titanium and silicon atoms than between the niobium and silicon atoms. Therefore, the Ti–Si bonds in the (002) plane of Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> are weaker than the Nb–Si bonds in the (002) plane of clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub>. This is consistent with the overlap population analysis above. From figure 2, we can see that the valence charge density in the (002) plane of clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> is not uniform, which is one of the characters of covalent bonds.

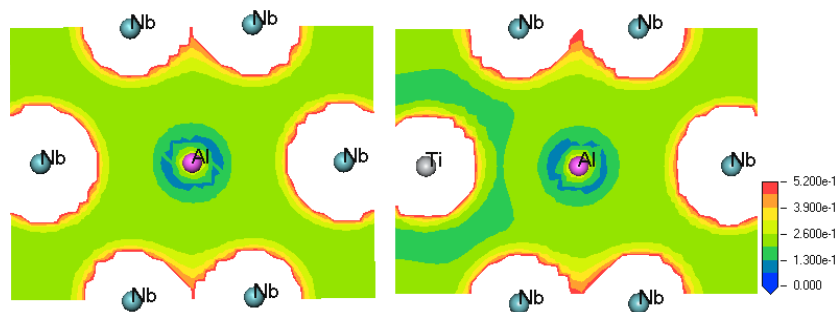
In order to further study the valence charge densities of Nb<sub>3</sub>Al conventional cell, we calculated the valence charge densities of clean Nb<sub>3</sub>Al and Ti-doped Nb<sub>3</sub>Al. Figures 3 and 4



**Figure 2.** The valence charge densities of clean  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> in the (002) planes.



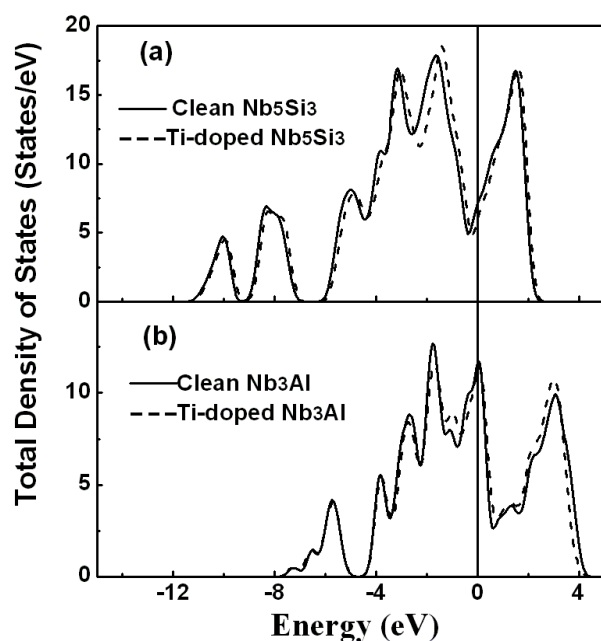
**Figure 3.** The valence charge densities of clean Nb<sub>3</sub>Al and Ti-doped Nb<sub>3</sub>Al in the (001) planes.



**Figure 4.** The valence charge densities of clean Nb<sub>3</sub>Al and Ti-doped Nb<sub>3</sub>Al in the (210) planes.

present the valence charge densities of clean Nb<sub>3</sub>Al and Ti-doped Nb<sub>3</sub>Al in the (001) (figure 3) and (210) planes (figure 4), respectively.

From figure 3 it can be seen clearly that in the Nb<sub>3</sub>Al (001) plane the valence charge density between Ti and Nb atoms is less than that between Nb and Nb atoms. From figure 4 we can see that in the (210) plane the valence charge density between Ti and Al atoms is less than that between Nb and Al atoms. Therefore, the Ti–Nb and Ti–Al bonds in Ti-doped Nb<sub>3</sub>Al are weaker than the Nb–Nb and Nb–Al bonds in clean Nb<sub>3</sub>Al. This is also consistent with the



**Figure 5.** The total density of states of (a)  $\alpha$ - $\text{Nb}_5\text{Si}_3$  and (b)  $\text{Nb}_3\text{Al}$ ; the Fermi level is set to zero.

overlap population calculations. From figures 3 and 4, the valence charge density in  $\text{Nb}_3\text{Al}$  is uniform, which is one of the characters of metallic bonds.

### 3.4. Density of states

In order to better understand how the doping Ti affect the bonds in  $\alpha$ - $\text{Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$ , we calculated the total density of states of clean and Ti-doped  $\alpha$ - $\text{Nb}_5\text{Si}_3$  (figure 5(a)) and  $\text{Nb}_3\text{Al}$  (figure 5(b)), respectively. Figure 5(a) compares the total density of states (TDOS) of clean  $\alpha$ - $\text{Nb}_5\text{Si}_3$  and Ti-doped  $\alpha$ - $\text{Nb}_5\text{Si}_3$ . A notable difference between them is that the total density of states of the Ti-doped  $\alpha$ - $\text{Nb}_5\text{Si}_3$  shifts appreciably to higher energy. This is because each niobium atom has two more d electrons than each titanium atom, which leads to the fact that the direct d–d bonds between Nb and Ti atoms are weaker than that between two Nb atoms. From figure 5(a), it can be seen clearly that there is a pseudo-gap near the Fermi energy level, which means coexistence of covalent and metallic bonds in  $\alpha$ - $\text{Nb}_5\text{Si}_3$  [22].  $\alpha$ - $\text{Nb}_5\text{Si}_3$  is stable and has strong covalent and metallic mixing bonds due to the Fermi energy being at the pseudo-gap. The system becomes more stable after titanium is doped because the TDOS moves to a higher energy relative to the Fermi energy and makes the bottom of the pseudo-gap closer to the Fermi energy. The change of the bonding of  $\alpha$ - $\text{Nb}_5\text{Si}_3$  is not dramatic because the density of states at the Fermi energy decreases slightly. All these features are consistent with the above analysis of impurity formation energies and overlap populations.

In figure 5(b) we present the total density of states of clean  $\text{Nb}_3\text{Al}$  and Ti-doped  $\text{Nb}_3\text{Al}$ . The bonds in the  $\text{Nb}_3\text{Al}$  phase are more metallic than that in the  $\alpha$ - $\text{Nb}_5\text{Si}_3$  phase due to the Fermi energy being at one of the peaks of the total density of states. The appearance of the pseudo-gap above the Fermi energy means that the bonds are partly covalent as well. The bonds of  $\text{Nb}_3\text{Al}$  become more metallic and less covalent after titanium is doped because the pseudo-gap becomes shallower. From both the analyses of overlap populations and total density of states, we come to the conclusion that the bonds in the  $\alpha$ - $\text{Nb}_5\text{Si}_3$  and  $\text{Nb}_3\text{Al}$  phases become less covalent after titanium is doped. Thus, the intrinsic brittleness of the two intermetallic



compounds will be improved due to the decrease of the content of covalent bonds by titanium doping.

Finally, the influence of titanium on the densities of  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al has been studied. As a new potential material for structural applications, low density is one of the most important properties. The calculated results show that the densities of clean and Ti-doped  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> are 7077 and 6992 kg m<sup>-3</sup>, respectively; the densities are 7275 and 6795 kg m<sup>-3</sup> for pure and Ti-doped Nb<sub>3</sub>Al, respectively, for the given content of titanium. It is obvious that titanium can significantly lower the densities of both  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al and has good influence on the structural applications.

#### 4. Conclusions

Based on the first-principles method within the framework of density functional theory, we have studied the effects of titanium on Nb–Si–Al–Ti three-phase superalloy (Nb<sub>ss</sub>, Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al). The impurity formation energies of the alloying element Ti in Nb<sub>ss</sub>,  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al at different substitution sites have been calculated. According to the impurity formation energies, Ti atoms prefer to occupy the Nb I sublattice sites in  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and then the Nb sublattice sites in Nb<sub>3</sub>Al phase. We have also calculated the overlap populations and valence charge densities. It is observed that the bonds between titanium atoms and the neighbouring atoms are weaker than the corresponding bonds between the substituted atoms and the neighbouring atoms in both  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al phases. The bonds in the  $\alpha$ -Nb<sub>5</sub>Si<sub>3</sub> and Nb<sub>3</sub>Al phases become less covalent after titanium is doped, and this will result in the improvement of intrinsic brittleness of these intermetallic compounds.

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