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## A tight-binding analysis of cohesive properties in the Ni–Al system

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**Abstract.** A simple tight-binding model is used for a quantitative study of hybridisation effects in nickel-aluminium compounds. The model is not an *ab initio* calculation but it requires only the data on elemental properties of pure metal constituents which are readily available in the literature. Combined with an extended Cluster Bethe Lattice Method, this approach allows the energy of formation of these compounds to be calculated and the chemical trends in the bonding properties to be analysed.

### 1. Introduction

Compounds formed between transition metals and elements with only s and p electrons in their valence shells display interesting magnetic, superconducting and structural properties. The alloying behaviour of such compounds was first studied in details by Guard and Westbrook [1]; their results suggested that the alloying behaviour is determined by chemical effects (e.g. the electronic structure) rather than simply by size factors. The first approach using these electronic arguments has been the rigid band theory [2]; it gives a simple analysis of the thermodynamic data, characterised by an electronic charge rearrangement due to the sp–d interaction. However the limitations of such an approach are obvious and a better understanding of the hybridisation effect is necessary to get a more precise interpretation of thermodynamic data. Recently, Mayou *et al* [3] used a Bethe lattice-type approximation to study the effect of s–d hybridisation and showed that a pseudogap in the electronic density of states may appear at the top of the d band. The existence of this pseudogap allowed these authors to give a new interpretation of thermodynamic properties in *T–Al* compounds, the *T* atom constituent varying through the 3d transition metal series [4, 5]. This approach has been also used by Colinet *et al* [6] to interpret the strong asymmetry in the curve of the enthalpy of formation versus composition which is found in Gd–Al system for instance. In this paper, we present the calculation of the electronic structure of Ni–Al compounds and then study the hybridisation effects and their consequences for electronic and thermodynamic properties. We focus our attention on this system since the determination of enthalpies of formation represents the first step towards a microscopic calculation of phase diagram [7], and that NiAl system can be considered as the prototype-phase diagram to perform such calculations [2].

## 2. Model

### 2.1. Internal energy calculation

The main assumptions of the model used by Nguyen Manh *et al* [4, 5] to calculate the electronic properties of T–Al compounds are briefly reviewed here. We choose as the Hamiltonian a tight-binding Hartree model with inter- and intra-site electron–electron Coulomb interactions, neglecting the magnetic interactions:

$$H = \sum_{i\mu} E_{i\mu} |i\mu\rangle\langle i\mu| + \sum_{i\mu, j\nu} t_{i\mu, j\nu} |i\mu\rangle\langle j\nu| - H_{ee} + H_{ion-ion} \quad (1)$$

The first two terms represent the one-electron Hamiltonian,  $H_{1e}$  incorporating the effective potential from the ions and other valence electrons.  $H_{ee}$  is a correction for double counting the electron–electron interaction in  $H_{1e}$  and  $H_{ion-ion}$  represents the ion–ion interaction. In this expression,  $|i\mu\rangle$  is the ket for the orbital  $\mu$  on site  $i$ , the on-site and hopping energies  $E_{i\mu}$  and  $t_{i\mu, j\nu}$  give respectively the effective atomic energy of the  $\mu$  orbital on site  $i$  and its coupling to the orbital  $\nu$  on site  $j$ .

The density of states (D.O.S.) which is one quantity of interest for our calculations is given by:

$$N(E) = \sum_{i\mu} N_{i\mu}(E) \quad (2)$$

where the local density of states  $N_{i\mu}(E)$  is given in terms of configurationally averaged diagonal Green function  $G_{i\mu, i\mu}(E)$ :

$$N_{i\mu}(E) = -\frac{1}{\pi} \text{Im}[\langle G_{i\mu, i\mu}(E) \rangle] \quad (3)$$

$\langle G_{i\mu, i\mu}(E) \rangle$  is evaluated with using the alloy Cluster Bethe lattice method (C.B.L.M.) The two main assumptions of this method are to use an effective environment determined self-consistently by the pair probabilities and the application of the Bethe Lattice approximation. In our previous treatment, we evaluated the configurational average by using three parameters that characterise the alloy; that is the composition  $x$ , the coordination number  $Z$  and the chemical short range order parameter  $\sigma$ . The pair probabilities,  $y_{ij}$ , defined as the ratio of the number of  $ij$  pairs to the total number of pairs in the solution are related to the S.R.O. parameter in the following way:

$$\begin{aligned} y_{ii} &= x_i[x_i + (1 - x_i)\sigma] & \text{for } i \text{ and } j \\ y_{ij} &= x_i x_j (1 - \sigma) & \text{for } i \neq j \end{aligned} \quad (4)$$

Assuming that  $N_{i\mu}(E)$  is obtained for a given set of parameters (for more details see [4]), the total internal energy  $E_T$  can be written in terms of the occupation  $n_i$ , and the total density of states,  $N(E)$ .

$$\begin{aligned} E_T &= \int^{E_F} N(E) \cdot E \cdot dE - \frac{1}{2} \sum_{\substack{i \\ \mu, \nu}} x_i U_{\mu, \nu} \langle n_{i\mu} \rangle \langle n_{i\nu} \rangle \\ &\quad - \frac{1}{2} \cdot V \sum_i \sum_j y_{ij} [n_i \cdot n_j - n_i^0 \cdot n_j^0] \end{aligned} \quad (5)$$

where  $\langle n_{i\mu} \rangle = \int^{E_F} N_{i\mu}(E) dE$

$$n_i = \sum_{\mu} \langle n_{i\mu} \rangle \quad (6)$$

$U_{\mu, \nu}$  is the effective intrasite Coulomb interaction and  $V$  the nearest-neighbour Coulomb

interaction,  $n_i^0$  is the number of electrons of pure  $i$  metal. The last two terms in equation (5) represent the electron–electron and ion–ion interactions as shown by Robbins and Falicov (8).

## 2.2. Electronic parameters

The calculation of the internal energy of Ni–Al compounds includes the five d-like and one s-like orbitals for Ni metal and the three p-like and one s-like orbitals for Al metal.

The off-diagonal Hamiltonian matrix elements or hopping energies  $t_{i\beta,j\gamma}$  are assumed to depend only on the atomic species at the relevant sites, on the relative positions of the sites and the character of the orbitals  $\beta$  and  $\gamma$ . Nearest and next-nearest neighbour hopping were included for BCC structure while only nearest neighbour interactions are taken into account for FCC structure. The hopping energies between like species were evaluated from Harrison's Solid State Table [9].

Hopping energies between different species  $t_{A\beta,B\gamma}$  were calculated using [9].

$$t_{A\beta,B\gamma} = [t_{A\beta,A\beta} \times t_{B\gamma,B\gamma}]^{1/2} \quad (7)$$

For the on-site energies, we use the atomic on-site energies given by Herman and Skillman [10]; for transition metals, the values were calculated for one transition atom with the  $d^{n+1}s$  configuration [11]; the values of  $E_s^{\text{Ni}}$ ,  $E_d^{\text{Ni}}$ ,  $E_s^{\text{Al}}$ ,  $E_p^{\text{Al}}$  are equal to  $-0.76$ ,  $-2.27$ ,  $-2.94$  and  $2.27$  eV respectively (the zero of energy has been taken equal to  $1/2(E_{\text{Ni}}^d + E_{\text{Al}}^p)$ ).

The only remaining elemental parameters are the Coulomb energies. They were taken to be  $U_{ss} = 0.50$  eV,  $U_{sd} = 0.75$  eV,  $U_{dd} = 1.6$  eV and  $V = 0.25$  eV with the additional assumption that for Al metal,  $U_{ss} = U_{pp}$ . These values are consistent with previous estimates [4, 5].

From this set of tight-binding parameters, we can thus calculate the internal energy of the respective compounds and their heats of formation which is the energy difference between the compound and the weighted sum of the constituents.

## 3. Results and discussion

The solid part of the Ni–Al phase diagram is characterised by a noncongruently melting compound  $\text{Al}_3\text{Ni}$  and three intermediate phases with variable range of solubilities. In the commonly used structure notation, these phases are called the  $\text{D0}_{20}$  ( $\text{Al}_3\text{Ni}$ ),  $\text{D5}_{13}$  ( $\text{Al}_3\text{Ni}_2$ ),  $\text{B2}$  ( $\text{AlNi}$ ) and  $\text{L1}_2$  ( $\text{AlNi}_3$ ) phases [12]. Although  $\text{Al}_3\text{Ni}$  and  $\text{Al}_3\text{Ni}_2$  compounds do not display cubic symmetry, we have chosen to calculate their heats of formation with hypothetical cubic structures to keep simplicity in our microscopic analysis.

### 3.1. Alloy densities of states

As a first step, we have calculated the DOS of the different alloys as shown in figure 1. The overall shape of the electronic density of states of  $\text{Ni}_3\text{Al}$  and  $\text{NiAl}$  compounds is in complete agreement with more sophisticated band-structure calculations for the corresponding compounds [13, 14]. One can see that the density of states of these compounds is characterised by the occurrence of a pseudogap at the top of the d band; the peak located just below this pseudogap is due to the very weakly coupled d states while the strong mixing d–sp is characterised by the lower energy peak and by the group

of states which lies above the pseudogap. Such a mixing gives an alloy density of states which is very dissimilar to that in pure metals. To study the influence of the covalent bonding on the DOS shape, we have reported in figure 1*b* the calculated density of states of a disordered BCC-type NiAl alloy and compared it with the one of the B<sub>2</sub> phase. The evolution of the DOS is very important, the local chemical environment being responsible of the creation of structures in the DOS. More particularly, we find that the occurrence of the pseudogap is directly related to this high degree of short range order. Thus the DOS of these compounds can be divided into three parts:

- (i) at the lower energies the bonding hybrids which are more tightly bound than either of the states from which they are formed;
- (ii) near the centre, the non-bonding states;
- (iii) at the top of the band the antibonding hybrids.

This peculiar shape allows us to give a qualitative interpretation of the stability of these compounds. The strong hybridisation creates a well-separated bonding and antibonding region by the occurrence of the pseudogap. Obviously, the stability of the compound depends on the position of the Fermi level. From figure 1, it is expected that NiAl compound, in which the Fermi level is located in the pseudogap, is the most stable compound since the valence electrons fill all the bonding states and leave all the antibonding states empty.

### 3.2. Energies of formation

NiAl compounds are characterised by exceptionally negative thermodynamic data of mixing and the rigid-band approach already explains the main features of this strong non-ideal mixing behaviour [2]. To demonstrate that our calculations can also give quantitative informations about the thermodynamic behaviour of NiAl compounds, we compare in figure 2 calculated energies of formation with experimental results. It can be seen that the agreement with the experimental results is very satisfactory although our calculated results lead to a more asymmetric  $\Delta E_f$  curve than the experimental one. This difference is mainly due to the fact that calculations have been performed for NiAl<sub>3</sub> and Ni<sub>2</sub>Al<sub>3</sub> with cubic symmetry while these two compounds exhibit D0<sub>20</sub> and D5<sub>13</sub> structures respectively. We find that the minimum in  $\Delta E_f$  occurs at  $x = 0.5$  which is in complete agreement with our above discussion on the alloy densities of states.

As discussed in the introduction, these energies of formation can be considered as the starting point of phenomenological treatment of alloy phase equilibrium by means of the Cluster Variation Method [15]. To extract effective pair interactions, which are the basic energetic parameters in the calculation of phase diagrams, it is more convenient to write the internal energy as a sum of non local energy term (associated with the random alloy) plus a strictly local ordering energy contribution [16, 17]. Thus we write the energy of alloy formation  $\Delta E_f$  as:

$$\Delta E_f = E_{\text{rand}}(x) + E_{\text{ord}}(x, \sigma) \quad (8)$$

where  $E_{\text{rand}}(x) = \Delta E_f(x, 0)$  is the heat of formation of the random alloy and where the ordering energy  $E_{\text{ord}}$  takes into account the contribution due to the short range order.

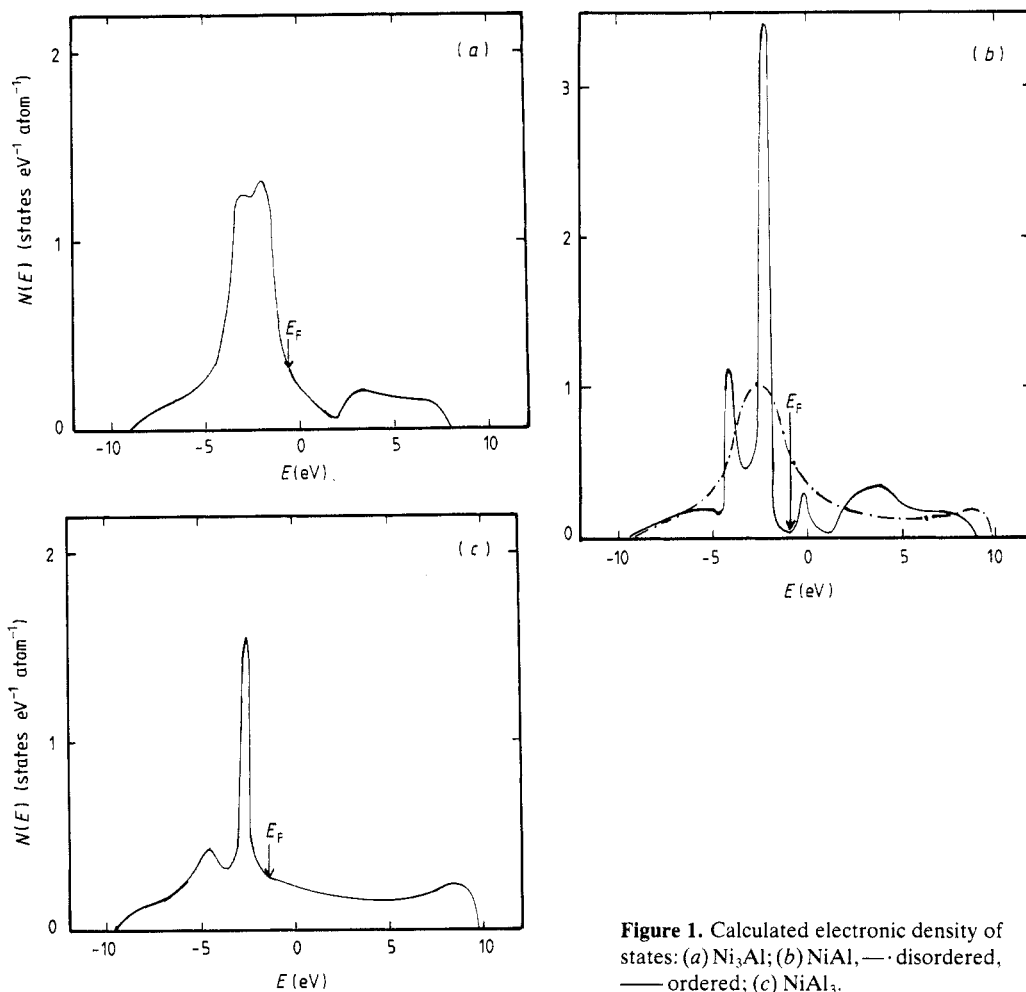


Figure 1. Calculated electronic density of states: (a) Ni<sub>3</sub>Al; (b) NiAl, —·— disordered, — ordered; (c) NiAl<sub>3</sub>.

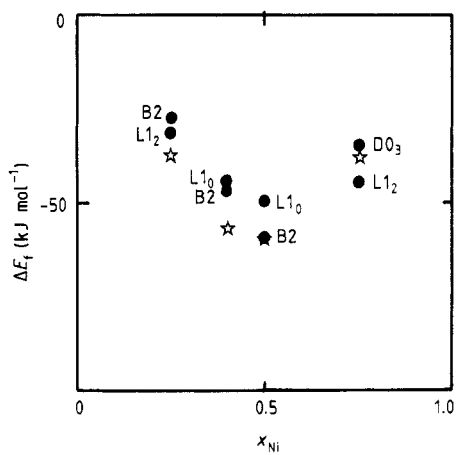
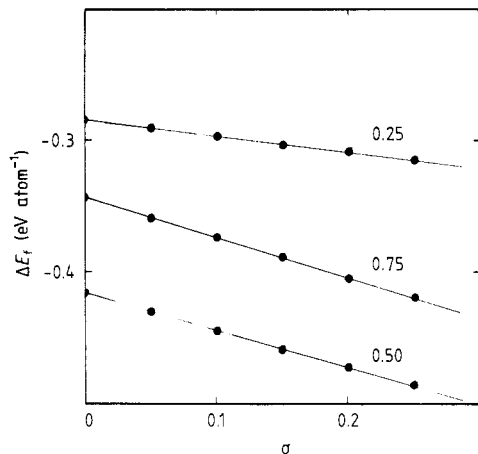


Figure 2. Comparison between experimental (\*) and calculated heats of formation in NiAl system.



**Figure 3.**  $\Delta E_f$  as a function of CSRO parameter for FCC based structures.

$E_{\text{rand}}$  is a function only of the point correlation function  $\xi_1 = x_A - x_B$  [18]. As previously used [19, 20],  $E_{\text{rand}}$  can be expressed by the following expression:

$$E_{\text{rand}}(x) = (A_0 + B_0 \xi_1)(1 - \xi_1^2) \quad (9)$$

In terms of effective pair interactions, the ordering energy is written:

$$E_{\text{ord}} = \frac{1}{2} \sum_k z_k V_k (\xi_2^{(k)} - \xi_1^2) \quad (10)$$

where  $z_k$ ,  $V_k$  and  $\xi_2^{(k)}$  are respectively the coordination number, effective pair interaction and pair correlation function for  $k$ th nearest neighbour.

**3.2.1. FCC based structures.** For FCC based structures the values of  $\Delta E_f$  have been plotted as a function of  $\sigma$  on figure 3. For each composition a linear variation of  $\Delta E_f$  as a function of  $\sigma$  is observed and consequently,  $E_{\text{ord}}$  can be written as:

$$E_{\text{ord}} = 4x(1-x)z/2 \times V_1 \times \sigma \quad (11)$$

In figure 4, we have represented the concentration dependence of the calculated enthalpy of mixing  $E_{\text{rand}}(x)$  for the completely random FCC solid solution and the concentration dependence of  $Z/2 \times V_1$ . We see that  $E_{\text{rand}}(x)$  displays negative values at all concentration and its minimum is shifted towards the Ni-rich part. This behaviour shows that the microscopic interactions which lead to the occurrence of stable compounds in this region are already present in the random solid solution. In the same way, the effective pair interactions EPI display a strong concentration dependence. Its large positive value at the Ni-rich end is consistent with the very strong ordering tendency in  $\text{Ni}_3\text{Al}$  which remains ordered up to its melting point. On the other hand, at the Al-rich end the value of the effective pair interaction drops rapidly which is consistent with the fact that ordered  $\text{Al}_3\text{Ni}$  phase cannot have the  $\text{Cu}_3\text{Au}$  structure. It is also interesting to compare the EPI values obtained here to those obtained by Carlsson [21] using a supercell total energy approach or the ones obtained from a fit to the Ni-rich part of the Ni–Al phase diagram based on empirical Lennard Jones potentials [22]. At 75% Ni, the EPI value obtained from the empirical fit is 0.31 eV while it is 0.34 eV from Carlsson calculation; we see that our value which is equal to 0.29 eV is in fair agreement with the other determinations. For the other compositions, we find 0.19 eV and 0.11 eV for 50%

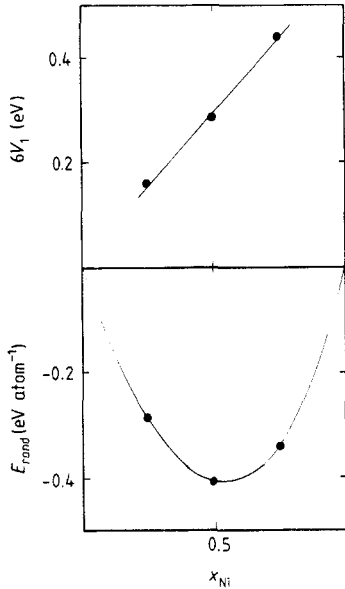


Figure 4. Concentration dependence of  $E_{rand}$  and  $6V_1$  for FCC based structures.

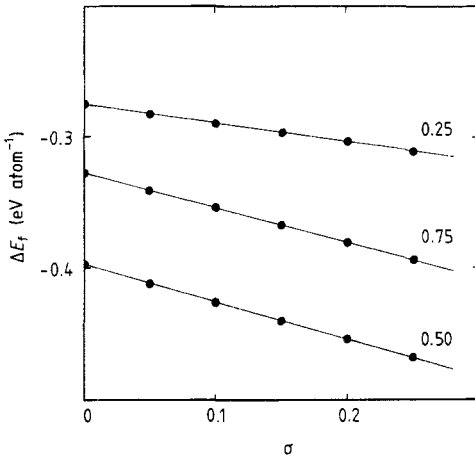


Figure 5.  $\Delta E_f$  as a function of CSRO parameter for BCC based structure.

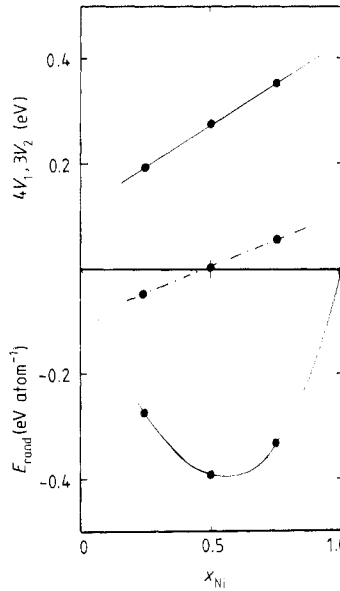
Ni and 25% Ni respectively while the matching method gives 0.29 eV and 0.15 eV. The difference between the two sets of calculated values is bigger in this composition range even if the concentration dependence is similar in both cases.

3.2.2. *BCC based structures.* For BCC based structures, pair interactions are kept between first and second nearest neighbours. Thus  $E_{ord}$  can be written as:

$$E_{ord} = 4x(1 - x)[z_1/2 V_1 \sigma_1 + z_2/2 V_2 \sigma_2] \quad (12)$$

We have checked that this formulation was in agreement with the evolution of the calculated  $E_{ord}$  as a function of  $\sigma_1$  or  $\sigma_2$ . For instance, we have plotted in figure 5 the evolution of  $\Delta E_f$  as a function of  $\sigma_1$  with  $\sigma_2 = 0$ , and we can see that this evolution is





**Figure 6.** Concentration dependence of  $E_{\text{rand}}$ ,  $4V_1$  (—) and  $3V_2$  (·-·) for BCC based structures.

**Table 1.** Calculated and experimental energies of formation in kJ at  $T = 0$  K, referred to pure Ni and Al FCC. The superstructures are indicated in parenthesis.

$x_{\text{Ni}}$	$\Delta H_f$ (kJ)	$\Delta H_f$ (kJ)	$\Delta H_f$ (kJ)
	calculated	calculated	
	FCC	BCC	experimental
0.25	-31.14 (L1 <sub>2</sub> )	-23.68 (B2)	-37.66
0.40	-42.15 (L1 <sub>0</sub> )	-44.41 (B2)	-56.48
0.50	-49.68 (L1 <sub>0</sub> )	-58.31 (B2)	-58.78
0.75	-43.38 (L1 <sub>2</sub> )	-34.15 (D0 <sub>3</sub> )	-37.76

effectively linear as a function of short range parameter. In figure 6, we have also represented the concentration dependence of  $E_{\text{rand}}$ ,  $z1/2V_1$  and  $z2/2V_2$ . As for FCC based structures,  $E_{\text{rand}}(x)$  displays an asymmetrical behaviour and  $z1/2V_1$  a very strong concentration dependence; let us also mention the peculiar behaviour of  $V_2$  which displays negative values in the Al-rich part and becomes positive in the Ni-rich end.

**3.2.3. Ground states at zero temperature.** In the use of FCC lattice, taking into account the values of EPI, the structures which will be adopted by the alloy will be L1<sub>2</sub> structure for  $x = 0.25$  and  $0.75$  and L1<sub>0</sub> structure for  $x = 0.5$ . For BCC lattice, the structure will be B2 for  $x = 0.25$  and  $x = 0.50$  and D0<sub>3</sub> for  $x = 0.75$  since  $V_2$  is positive at this composition.

We have reported in table 1 the energies of formation of these different compounds at  $T = 0$  K. For  $x = 0.25$ , one can see that the L1<sub>2</sub> structure is more stable than B2 but the comparison with the experimental result show that both structures are less stable than the experimental one, i.e. D0<sub>20</sub>. For  $x = 0.4$ , we don't have ground states with BCC or FCC structure but nevertheless calculations have been made for these two structures with the maximum ordering. In each case, the obtained value for the energy of formation is bigger than the experimental one which is in agreement with the fact that Al<sub>3</sub>Ni<sub>2</sub>

displays  $D5_{13}$  structure. For  $x = 0.5$  and  $x = 0.75$  we find that B2 and  $L1_2$  structures are stable as in the experimental phase diagram.

#### 4. Conclusion

In this paper, we have shown that a model tight-binding Hamiltonian is able to reproduce the experimental energies of formation found in Ni–Al system. The large mixing between the d states of the transition metal and the sp states of Aluminium and the resulting strong short range order are the main factors governing the electronic structure of these compounds. To extract effective pair interactions, we have used that alloy energy of formation could be represented well by a function consisting of a non local term describing the energy of the random alloy and an ordering term given by concentration-dependent effective pair interactions. The so generated EPI are similar in character to those obtained by the matching method. The most important feature is the concentration dependence of the EPI thus obtained. Its manifestation on the phase diagram determination via the tetrahedron approximation of the CVM will be presented in a forthcoming paper.

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