

Phase stability in Ni-Ti alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 7895

(<http://iopscience.iop.org/0953-8984/3/40/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 11/05/2010 at 12:35

Please note that [terms and conditions apply](#).

Phase stability in Ni–Ti alloys

D H Le, C Colinet, P Hicter and A Pasturel

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, ENSEEG, BP 75, 38402, Saint-Martin-d'Hères, France

Received 7 March 1991, in final form 3 June 1991

Abstract. A tight-binding bond model is used for a quantitative study of electronic interactions in nickel–titanium compounds. The model is not an *ab initio* calculation, but it requires only the data on the elemental properties of pure metal constituents that are readily available in the literature. Combined with an extended cluster Bethe lattice method (CBLM) for FCC- and BCC-based solid solutions and the B2 phase, and the recursion method for NiTi₂ and Ni₃Ti stoichiometric compounds, this approach allows the energy of formation of these alloys to be calculated and the chemical trends in the ordering effects to be analysed.

1. Introduction

In recent years, materials based on Ni and Ti have been extensively studied for their promising practical applications. Around the equiatomic composition, Ni–Ti alloys exhibit interesting shape memory effects and corrosion resistance. Their expanding use in nickel-based superalloys and the possibility of creating amorphous phases are other interesting properties. To obtain a quantitative understanding of these properties, the underlying thermodynamic properties have to be known with respect to composition and temperature or, in other terms, the study of the alloy properties depends critically on a knowledge of the relevant phase diagrams. A fundamental explanation of the formation of phases is a difficult task because the necessary calculations must combine, at a high level of accuracy, both quantum mechanical and statistical thermodynamical contributions. Recently, tight-binding (TB) calculations in conjunction with the cluster variational method (CVM) [1–6] have shown that quantitatively reasonable phase diagrams displaying either a miscibility gap like that of the Cr–Mo system or the ordered intermetallic compounds like the Ti–Rh system can be obtained. The computational scheme used in these studies is summarized as follows.

(i) The CVM is a reliable statistical thermodynamical model developed to calculate temperature–composition diagrams; this method has the advantage of incorporating both short- and long-range order (SRO and LRO) in the description of the thermodynamic behaviour of binary and multicomponent alloys. The CVM requires, as input, interaction parameters that determine the ordering, or clustering, reactions.

(ii) The interactions are then obtained numerically by means of electronic structure calculations: two rather different procedures have been used to obtain these interactions; the starting point for one is the ordered state while for the other is the disordered state.

In the first approach, the total energy is assumed to be written as a sum of configuration-independent many-body interaction potentials multiplied by the multisite correlation functions [7]. The sum runs over all the cluster types but in practice it requires the existence of a maximum cluster beyond which the many-body interactions are supposed to be negligible. In the second approach, the idea is to use the completely disordered state as the one described by the coherent-potential approximation (CPA) as an appropriate reference medium [8]. The effective cluster interactions are calculated by the embedded-cluster method [9] or by the generalized perturbation method (GPM) [10] using a perturbative treatment about the completely disordered state. In this case the ordering energies can be written as an expression in terms of concentration-dependent l th-order effective cluster interactions. These calculations can be carried out either in the KKR-CPA [10] or tight-binding [11] schemes. At this level of approximation an alternative method of describing short-range order in alloys has been proposed by Robbins and Falicov [12]. Despite the fact that their approach relies on a topological approximation, the Bethe lattice, it has the great advantage of including SRO explicitly in the calculation of the electronic spectrum and internal energy. Off-diagonal disorder and self-consistent effects of charge transfer are taken into account, contributions that have been shown to be of consequence in the variation of energy with SRO [13]. In what follows we compare the TB-CBLM and TB-CPA-GPM methods for the Ni-Ti system. The quantities compared are the total energy of the random alloy, the first nearest-neighbour interactions for FCC-based phases and the first- and second-nearest-neighbour interactions for BCC-based phases. To make this study complete we have used the recursion method to calculate the total energies of the two complex NiTi₂ and Ni₃Ti compounds and compared the values thus obtained with those provided by the TB-CBLM or TB-CPA-GPM methods for fictitious FCC or BCC-based compounds. In section 2 we present a brief review of the theory used in our calculations and our results are discussed in section 3.

2. Theory

2.1. Total energy and the tight-binding Hamiltonian

In general the total energy can be written as the sum of two terms,

$$E_T = E_{\text{rep}} + E_{\text{bond}} \quad (1)$$

where the labels imply that the division has been made in such a way that around the equilibrium volume the first contribution is repulsive and the second attractive. In a tight-binding model [14] it is generally assumed that the repulsive energy is well described by an empirical pair potential

$$E_{\text{rep}} = \frac{1}{2}N \sum_{\substack{i,j \\ i \neq j}} \phi(r_{ij}) \quad (2)$$

where the attractive contribution stems from the quantum mechanical bonding between the atoms. Within the tight-binding approximation this term is given by

$$E_{\text{bond}} = E_{1e} - E_{e-e}^{\text{intra}} - E_{e-e}^{\text{inter}} + E_{\text{ion-ion}} \quad (3)$$

The first term represents the sum of the one-electron energies, the second and third

terms the double-counting corrections for the electron–electron interaction, which has been counted twice in the first term. The last term stands for the interionic Coulomb interactions.

The one-electron total energy (E_{1e}) is given simply by integrating the density of electronic state $N(E)$ multiplied by the energy E up to the Fermi energy E_F :

$$E_{1e} = \int_{-\infty}^{E_F} EN(E) dE. \quad (4)$$

In this paper the electrons are described by the following one-electron TB Hamiltonian:

$$H_{1e} = \sum_{i,\lambda} \varepsilon_{i\lambda} |i\lambda\rangle\langle i\lambda| + \sum_{i\lambda,j\mu} \beta_{i\lambda,j\mu} |i\lambda\rangle\langle j\mu| \quad (5)$$

where $|i\lambda\rangle$ represents an orbital λ centred at site i . We consider in equation (5) five atomic d orbitals per lattice site ($\lambda = 1.5$), these orbitals being chosen such that they verify the orthogonality relationship. Accordingly, the contributions of the s and p electrons to the total energy are neglected. It is known that these contributions, via their hybridization with the d states, have to be taken into account to explain the cohesive properties of the transition metals, in particular at the beginning or at the end of a transition-metal series [15], which is the case for titanium and nickel. However, retaining the d part is sufficient to explain the strong negative values of the alloying formation energies in the Ni–Ti system [16]. At the end of the calculation we have neglected the contributions arising from magnetic interactions.

The on-site and hopping energies, that is $\varepsilon_{i\lambda}^0$ and $\beta_{i\lambda,j\mu}$ are assumed to depend only on the species of atom at the relevant sites and, in the case of the hopping parameters, the relative positions of the sites:

$$\begin{aligned} \beta_{i\lambda,j\mu} &= \beta_{i\lambda,j\mu}(r) \\ \varepsilon_{i\lambda} &= \varepsilon_{i\lambda}^0 + Y_{i\lambda} \end{aligned} \quad (6)$$

where I denotes the species I at site i ; $Y_{i\lambda}$ is the mean effective Coulomb potential seen by the λ orbital on a type- I atom in a given alloy; it is calculated in two parts, an intrasite contribution (the effective direct exchange energy) $Y_{i\lambda}^{\text{intra}}$ and an intersite contribution (the effective Madelung energy), which is taken to be the same for all orbitals.

The values of ε_i^0 used in this study are listed in table 1. They have been calculated [16] for relativistic atoms in the configuration $s^1 d^{Z_i-1}$ where Z_i is the number of valence electrons. This configuration is close to the $s^{1.3} d^{Z_i-1.3}$ configuration predicted by band structure calculations [17] and we have taken the number of d electrons to be equal to $Z_i - 1.3$ in our calculations.

The hopping integrals $\beta_{i\lambda,j\mu}$ are obtained using the Slater–Koster [18] parametrization scheme. The Slater–Koster parameters depend on the atomic species located at sites i and j and on the distance between sites i and j . The Slater–Koster parameters between like species are taken from Harrison [19] who has fitted the band widths (W_i) of the pure metals predicted by Andersen and Jepsen [20]. These band widths are also given in table 1. The spatial dependence of the hopping integrals has also been chosen using Harrison's prescription. This means that nearest- and next-nearest-neighbour hopping are included for BCC-based superstructures while only nearest-neighbour interactions are taken into account for the other close-packed cubic or hexagonal structures studied in this paper. The expression for the Slater–Koster parameters between unlike atoms can be calculated using the Shiba approximation [21].

Table 1. Tight-binding parameters for the Ni-Ti system, where $U = 3$ eV and $V = 0.4$ eV.

	Ti	Ni
N_d	2.7	8.7
W_d (eV)	6.08	3.78
ϵ_d^0 (eV)	0	-2.83

The intra atomic electron-electron energy can be approximated by [22]:

$$E_{e-e}^{\text{intra}} = \frac{1}{2}U[x_A n_A^2 + x_B n_B^2] \quad (7)$$

where n_A is the number of d electrons per A atom, x_A is the concentration of A atoms and U represents the effective intrasite Coulomb interactions.

To evaluate the intersite electron-electron interaction we assume that d electrons are distributed around the atoms spherically. The following expression is then obtained:

$$E_{e-e}^{\text{inter}} = \frac{e^2}{N} \sum_{i,j} \frac{n_i n_j}{2\omega r_{ij}} \quad (8)$$

where ω is the dielectric constant of the medium, N is the total number of lattice sites and r_{ij} is the distance between sites i and j ; $|e|n_i$ is the valence of the species on site i .

The Coulomb ion-ion interaction is given by a similar expression,

$$E_{\text{ion-ion}}^{\text{inter}} = \frac{e^2}{N} \sum_{i,j} \frac{Z_i Z_j}{2\omega r_{ij}} \quad (9)$$

where $|e|Z_i$ is the charge of an ion on site i .

The net contribution of the two last terms to the total energy largely cancels out and can be written as [23],

$$E_{\text{ion-ion}}^{\text{inter}} - E_{e-e}^{\text{inter}} = -V_2^Z \sum_l x_l \sum_j P_{lj} (n_l n_j - n_l^0 n_j^0) \quad (10)$$

where V denotes the nearest-neighbour contribution to the average intersite potential per transferred electron; $\Delta n_l = n_l - n_l^0$ is the charge transfer to species l and Z is the coordination number. P_{lj} describes the pair probabilities and n_l^0 is the valence of the species l that have no alloying effect.

We can also use a decomposition other than equation (3) [24], which is easier to analyse but with the additional assumption that the charge transfer does not vary strongly with SRO; it has been shown that this assumption is checked for binary transition metal alloys [24]. In this case, E_{bond} is given by

$$E_{\text{bond}} = \int_{-\infty}^{E_F} E \bar{N}(E) dE + V_2^Z x_l x_j \sigma_{\text{WC}} (\Delta n_l - \Delta n_j)^2 \quad (11)$$

where σ_{WC} is the Warren-Cowley SRO parameter and $\int_{-\infty}^{E_F} E \bar{N}(E) dE$ is the variation of the sum of one-electron energies that one would obtain by taking into account the variation with SRO of the kinetic Hamiltonian

$$\sum_{i\lambda j\mu} \beta_{i\lambda j\mu} |i\lambda\rangle \langle j\mu|$$

but not that of $\epsilon_{i\lambda}$.

The calculation of $\int_{-\infty}^{E_F} E \tilde{N}(E) dE$ and its evolution with SRO now depends on the assumption made in obtaining $N(E)$, either the TB-CPA-GPM approach, or the TB-CBLM approach.

The energies of central interest in our study are the energies of formation, ΔE_f , which is given by

$$\Delta E_f = E_T(\text{alloy/struct}, x) - xE_T^A - (1-x)E_T^B \quad (12)$$

where $E_T(\text{alloy/struct}, x)$ denotes the total energy of the alloy AB at a concentration x of species A. The relative energy of stability is

$$\Delta E_{\text{stab}} = E_T(\text{alloy/struct 1}, x) - E_T(\text{alloy/struct 2}, x). \quad (13)$$

The best way to obtain such quantities is to use equation (1) for the definition of E_T , that is to add E_{rep} to E_{bond} and to use the structural energy difference theorem [25]. This approach has been used by Pettifor and co-workers to study the structural stability of the pd-bonded AB compound [26] and the sp-bonded elements [27]. The structural energy difference theorem, as a generalization of the frozen-potential theorem [28] allows the study of the relative stability of structures that may be characterized by very different local coordination numbers and hence different nearest-neighbour bond lengths. However, it requires a knowledge of the pairwise repulsive potential $\phi(r_{ij})$. For d-band metals experience suggests a pair interaction of the form C/R_{ij}^m with $m = 8-10$ [29], but little is known about the exact values of the exponent and of the prefactors. In fact, E_{rep} has been neglected in our study for the following reasons. (i) It has been shown that this contribution may be neglected in the ΔE_f calculations, the energy of formation being mainly the result of strong d-d interactions for Ni-Ti alloys [16]. (ii) For structural stability, we have only competition between close-packed structures in the Ni-Ti system, based on BCC, FCC or HCP lattices, which are not too different concerning their local environments. The relative stability energy has then been given only by comparing the bond energies of the two structures. In this approximation, for a given structure, the nearest-neighbour distance is kept constant on going from pure metals to compounds.

2.2. The electronic density of states in the alloy

The one-electron contribution to the total energy is related to the local density of states which can be obtained itself from the single-particle Green function:

$$N_i(E) = -\pi^{-1} \text{Im}[G_{ii}(E)] \quad (14)$$

where $G_{ii}(E)$ is the projected Green function on site i :

$$G_{ii}(E) = \sum_{\lambda=1,5} \langle i\lambda | G(E) | i\lambda \rangle. \quad (15)$$

For a compound, to calculate the Green function on site i , we have used the recursion method [30], which consists in constructing from the basis of the five atomic d orbitals $\{|i\lambda\rangle\}$ a new orthogonal basis $\{|\xi_k\rangle, k = 1, \dots\}$, where the tight-binding Hamiltonian matrix is tridiagonal. If $|\xi_1\rangle$ is made equal to $|i\lambda\rangle$, then the Green function of this Hamiltonian is given by the continued fraction

$$\langle i\lambda | G(z) | i\lambda \rangle = \frac{1}{z - a_1 - \frac{b_1^2}{z - a_2 - \frac{b_2^2}{z - a_3 - \dots}}} \quad (16)$$

where $\{a_n\}$ and $\{b_n\}$ are the matrix elements.

The coefficients a_n and b_n^2 are calculated up to a given step n_0 and the local density of states is calculated using the Nex Gaussian quadrature method [31]. We repeat these calculations for all the non-equivalent sites of the studied compound and the electronic density of states of the compound is given by the sum of these local densities of states.

For solid solutions, the configuration-averaged Green function at arbitrary concentration and arbitrary SRO is required; two methods can be used to obtain such a quantity, that is the CBLM [23] or the CPA-GPM [11].

In the coherent-potential approximation, CPA, only completely disordered alloys can be studied, the projected average Green function of an i atom being calculated using the identity:

$$\bar{G}_{ii}(E) = [W_R/W_i] G_{00}^+(E - \sigma) [1 + t_i G_{00}^+(E - \sigma)] \quad (17)$$

where $G^+(z - \sigma)$ is the Green operator that corresponds to the CPA Hamiltonian,

$$\sum_{i,\lambda} \sigma |i\lambda\rangle \langle i\lambda| + \sum_{i,\lambda,j,\mu} \beta_{(R\lambda,R\mu)} |i\lambda\rangle \langle j\mu|$$

and $G^+(z)$ is the Green function of the pure reference metal R (defined by $\varepsilon_R^0 = 0$ and W_R or $\beta_{R\lambda,R\mu}$). The potential σ is determined self-consistently by the condition on the scattering operators:

$$\langle t \rangle = \sum_i x_i t_i = 0 \quad (18)$$

where

$$t_i = \Delta\varepsilon_i / [1 - \Delta\varepsilon_i G_{00}^+(E - \sigma)] \quad \Delta\varepsilon_i = \varepsilon_i - \sigma \quad (19)$$

with

$$G_{00}^+(z) = \frac{1}{z} \sum_{\lambda} \langle 0\lambda | G^+(z) | 0\lambda \rangle. \quad (20)$$

To analyse the ordering effects in solid solutions it is necessary to use the GPM, the ordering energy being expressed in terms of pair and many-body interactions using a perturbation expansion of the random CPA energy in concentration fluctuations [11],

$$E_{\text{ord}} = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{Tr} \sum_{p=2}^{\infty} [G^+(E - \sigma) T_d]^p 1/p \quad (21)$$

where T_d is the diagonal part of the scattering matrix and p is the order of the cluster expansion. It has been shown that for binary transition-metal alloys [32], the contributions of the triplet and larger cluster interactions to the ordering energy are small compared with that of the pairs, so we shall retain only the pair interactions in the following calculation.

The other method of calculating the configuration-averaged Green function is the CBLM; in its simplest version, a simple single-atom cluster, the real lattice is replaced by

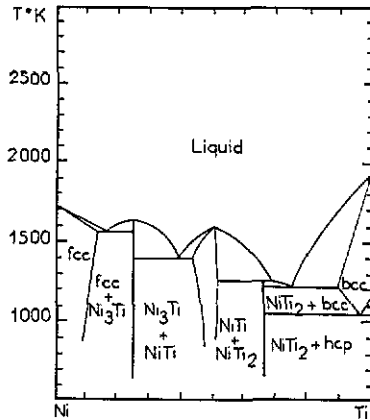


Figure 1. Experimental phase diagram of the Ni-Ti system [34].

a Bethe lattice, the coordination number and the near distribution of the nearest neighbours being reproduced exactly. The mean Green function of atom I on site i is given by [33]:

$$G_I(z) = \left(z - H_{0I} - \sum_{R_{K,J}} P_{JI} T_{JI}^+(R_K) G_J(z, R_K) T_{JI}(R_K) \right)^{-1} \quad (22)$$

and

$$G_J(z, R_K) = \left(z - H_{0I} - \sum_{J, R_L (\neq -R_K)} P_{JI} T_{JI}^+(R_L) G_J(z, R_L) T_{JI}(R_L) \right)^{-1} \quad (23)$$

where $T_{JI}(R_K)$ is the transfer matrix from an atom I to an atom J in the direction R_K and $G_J(z, R_K)$ is the mean Green function of a J atom located on the auxiliary Bethe lattice, which is obtained from the initial Bethe lattice by removing the bond in the direction $-R_K$. H_{0I} is the Hamiltonian without hybridization and SRO appears in the definition of the pair probabilities [33]. The one-electron contribution to the total energy is also calculated as a function of SRO and the one-electron contribution to the effective pair interactions is obtained from its dependence [2, 5].

In what follows both approaches will be compared for the Ni-Ti system and the origin of SRO in FCC- and BCC-based solid solutions will be analysed in terms of electronic interactions.

3. Discussion and results

The Ni-Ti phase diagram displayed in figure 1 [34] is characterized by a liquid phase, a FCC (A1) phase at the Ni-rich end, a BCC (A2) phase at the Ti-rich end for high temperature; two stoichiometric compounds NiTi₂ and Ni₃Ti, and one intermediate phase with a variable range of solubility of NiTi.

3.1. Energies of formation of compounds

As a first step, we have calculated the energies of formation of the three intermediate phases observed in the equilibrium phase diagram. In the bericht structure notation,

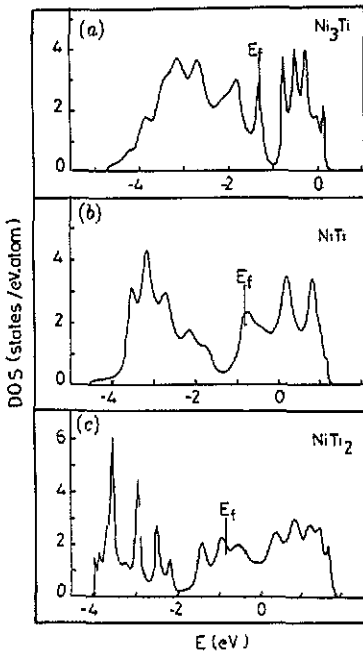


Figure 2. Electronic densities of states of Ni₃Ti, compounds: (a), Ni₃Ti; (b), NiTi; (c), NiTi₂.

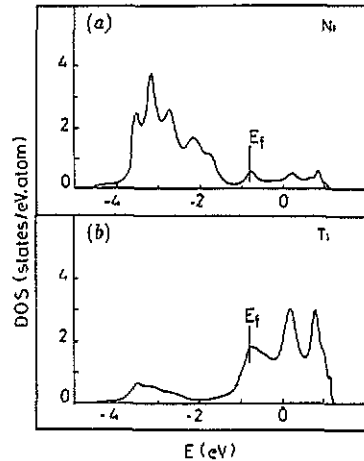


Figure 3. Partial densities of states of NiTi compounds: (a), d states of Ni; (b), d states of Ti.

these phases are called the DO₂₄ (Ni₃Ti), B2 (NiTi) and E9₃ (NiTi₂) phases. The DO₂₄ hexagonal and the E9₃ cubic phases are found experimentally to be stoichiometric compounds and are treated as such in the present work using the recursion method. The cubic B2 phase is reported from experiments to be stable over a large concentration range and will be treated as such using the CBLM or GPM-CPA approaches.

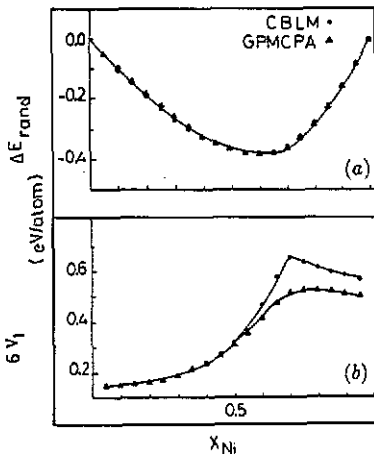
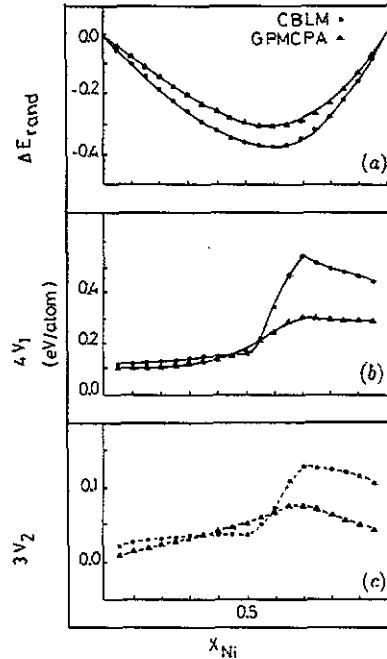
To calculate the energies of these three compounds we have used the tight-binding Hamiltonian described previously, coupled with the recursion method with 15 exact steps of the continued fraction; the self consistency of charge transfer is taken into account via the electron–electron and ion–ion interactions as described in section 2.1. In figure 2 the electronic densities of states of the three compounds are presented. They are characterized by a two-peak structure and the occurrence of a pseudogap; the lower energy states are mainly the d states of nickel while the upper energy states are the d states of the titanium as can be seen in figure 3 from the partial densities of states in the NiTi compound. For the energies of formation we obtain -46.4 kJ/atom, -47.0 kJ/atom and -35.0 kJ/atom, respectively, for the compounds Ni₃Ti, NiTi and NiTi₂. In table 2, the comparison with the experimental values obtained by different authors [35, 36] shows that our calculated values are slightly more negative than the experimental ones; the experimental asymmetry is also well reproduced by our calculations, the Ni₃Ti compound displaying practically the same energy of formation as the NiTi compound.

3.2. Effective pair interactions and disordered alloys

We have seen that the energy of formation of a solid solution with SRO can be written as a sum of the energy of formation of the random alloy ΔE_{rand} and an ordering energy ΔE_{ord} .

Table 2. Calculated and experimental energies of formation of the compounds Ni₃Ti, NiTi and NiTi₂.

Compound	ΔE_{cal} (kJ)	ΔE_{exp} (kJ)	Ref
Ni ₃ Ti	-46.4	-35	[35]
		-43	[36]
NiTi	-47.0	-34	[35]
		-34	[36]
NiTi ₂	-35.0	-27	[35]
		-29	[36]

**Figure 4.** Concentration dependence of (a) E_{rand} and (b) $6V_1$ for FCC-based structures.**Figure 5.** Concentration dependences of E_{rand} , $4V_1$ and $3V_2$ for BCC-based structures.

To calculate these two contributions, two approaches can be adopted, either TB-GPM-CPA or TB-CBLM as has been shown in section 2.2. We have kept only pair interactions to describe the ordering contribution to the energy, first-nearest-neighbour interactions have been retained for FCC-based phases, whereas first- and second-nearest-neighbour interactions have been considered for BCC-based phases.

3.2.1. FCC-based structures. In figure 4(a), we have represented the concentration dependence of the calculated energy of mixing $E_{\text{rand}}(x)$ for the completely random FCC solid solution using both the TB-CBLM and TB-CPA approaches ($x = x_{\text{Ni}}$). The agreement between the two sets of calculations is very good, the greater the coordination number Z , the better the Bethe lattice approximation. We see that $E_{\text{rand}}(x)$ displays negative

values at all concentrations and its minimum is shifted towards the Ni-rich part. This behaviour shows that the microscopic interactions that lead to the occurrence of stable compounds in this region are already present in the random solid solution. For all the compositions the charge transfer comes from the Ti d band to the Ni d band; however, it is small as, for instance, the value obtained for the equiatomic composition $\Delta n_{\text{Ni}} = 0.14$ electrons/atom. This result indicates that the self-consistent contribution from ionic bonding to the formation energies of these alloys is small. In the same way the effective pair interactions (EPI) display a strong concentration dependence (see figure 4(b)). Their large positive value at the Ni-rich end is consistent with the very strong ordering tendency in Ni_3Ti , which remains ordered up to its melting point. On the other hand, at the Ti-rich end, the value of the effective pair interaction drops rapidly, which is consistent with the fact that the ordered NiTi_2 compound has a complex structure. For both methods, the effective pair interactions are directly proportional to the ordering energy [5, 11]. As the ordering energy is more sensitive to the details of the electronic density of states than E_{rand} , it is not surprising that we find a larger difference for V_1 than for E_{rand} between the two sets of results. We shall see that this comparison for BCC solid solutions will be still more difficult to do.

3.2.2. BCC-based structures. For BCC-based structures we have also represented the concentration dependence of the calculated energy of mixing $E_{\text{rand}}(x)$ using the TB-CBLM and TB-CPA approaches; the agreement between the two sets of calculations is worse than for the FCC-based structures but it is still satisfying. This results from the fact that, on the one hand, the BCC structure is more sensitive to the Bethe lattice approximation and, on the other hand, the treatment of the off-diagonal disorder in CPA is also more difficult. As for FCC-based structures, $E_{\text{rand}}(x)$ displays an asymmetrical behaviour and first-nearest-neighbour interactions with a very strong concentration dependence (see figure 5). For second-nearest-neighbour interactions the same behaviour is obtained, that is a smoother variation as a function of composition for the CPA results; let us mention that the contribution of the second nearest neighbours to the ordering energy is much smaller than that of the first nearest neighbours. Once more, the charge transfer is small, $\Delta n_{\text{Ni}} = 0.135$ electrons/atom for $x = 0.5$ and very similar to that obtained for the FCC lattice.

3.2.3. Ground states at zero temperature. We have seen in the previous section that TB-GPM-CPA and TB-CBLM give practically the same results concerning the energy of the random alloy and the effective pair interactions. To study the complete phase diagram TB-CBLM has the advantage that it can also be used to study CSRO in liquid phases by using a scalar approximation [6, 24, 33]. In this section we first present the results using the TB-CBLM method to obtain the phase diagram, that is ground states at zero temperature.

For the FCC lattice, taking into account the values of EPI, the structures to be adopted by the alloy will be L1_2 structure for $x = 0.25$ and 0.75 , and the L1_0 structure for $x = 0.5$. For the BCC lattice the structure will be DO_3 for $x = 0.25$ and 0.75 , and B2 for $x = 0.5$. We have reported in table 3 the energies of these different compounds at $T = 0$ K. For $x = 0.25$, no compound exists and one can see that the L1_2 and DO_3 structures display the same weak energy of formation. For $x = 0.33$, we do not have ground states with the BCC or FCC structures but, nevertheless, calculations have been made for these two structures with the maximum ordering. In each case, the value obtained for the energy of formation displays a more positive value than the one obtained by recursion for the

Table 3. Calculated energies of formation for the BCC and FCC superstructures using the TB-CBLM method.

x_{Ni}	ΔE_{real} (kJ)		
	FCC	BCC	Compounds
0.25	-19.3 (L1 ₂)	-19.3 (DO ₃)	—
0.33	-27.7	-29.4	-35 (E9 ₃)
0.50	-40.8 (L1 ₀)	-45.0 (B2)	-47 (B2)
		-37.1 (B32)	
0.75	-44.8 (L1 ₂)	-44.6 (DO ₃)	-46.4 (DO ₂₄)

E9₃ phase. For $x = 0.5$, we find that the B2 structure is more stable than the L1₀ structure or the B32 structure. For $x = 0.75$, the L1₂ and DO₃ structures display a more positive value than that obtained by the recursion method for the DO₂₄ structure, in complete agreement with the experimental observations. However, this difference is small and to know if it is significant we have performed a calculation based on the recursion method for the L1₂ compound. We obtain -44.9 kJ, in complete agreement with the value provided by the CBLM method.

4. Conclusions

In this paper we have shown that a model tight-binding Hamiltonian is able to reproduce the experimental energies of formation found in the Ni-Ti system. The large interaction between the d states of Ni and the d states of Ti is the main factor governing the electronic structure of these compounds leading to a strong short-range order on the Ni-rich side. To extract effective pair interactions we have used either TB-CBLM or TB-GPM-CPA, the energy of formation of the alloy being represented by a non-local term describing the energy of the random alloy and by an ordering term given these concentration-dependent effective pair interactions. At $T = 0$ K we have obtained that for $x = 0.5$ the B2 structure is more stable than the L1₀ or B32 structures while for $x = 0.75$ the DO₂₄ structure is more stable than the L1₂ or DO₃ structures. For $x = 0.33$, the complex cubic structure E9₃ is predicted to be more stable with regard to a mixture of the NiTi B2 and the Ti HCP phases, since its calculated formation energy is above the line connecting the formation energies of the Ti HCP and NiTi B2 phases. All these results are in good agreement with the experimental observations. The complete determination of the phase diagram by combining the tetrahedron approximation of the CVM and the concentration-dependent EPI obtained in this way will be presented in a forthcoming paper.

References

- [1] Sigli C, Kosugi M and Sanchez J M 1986 *Phys. Rev. Lett.* **57** 253
- [2] Hawkins R, Robbins M O and Sanchez J M 1986 *Phys. Rev. B* **33** 4782
- [3] Sluiter M, Turchi P, Fu Zezhong and de Fontaine D 1988 *Phys. Rev. Lett.* **60** 716
- [4] Sigli C and Sanchez J M 1988 *Acta Metall.* **36** 367
- [5] Colinet C, Bessoud A and Pasturel A 1988 *J. Phys. F: Met. Phys.* **48** 903

- [6] Colinet C and Pasturel A 1991 *J. Phys.: Condens. Matter* submitted
- [7] Connolly J W D and Williams A R 1983 *Phys. Rev. B* **27** 5169
- [8] Velicky B, Kirkpatrick S and Ehrenreich H 1968 *Phys. Rev.* **175** 747
- [9] Ducastelle F and Gautier F 1976 *J. Phys. F: Met. Phys.* **6** 2039
- [10] Turchi P, Stocks G M, Butler W H, Nicholson D M and Gonis A 1988 *Phys. Rev. B* **37** 5982
- [11] Ducastelle F 1989 *Alloy Phase Stability, Nato ASI series E; Applied Sciences* vol 163, Ed G A Stocks and A Gonis (Kluwer) p 293
- [12] Robbins M O and Falicov L M 1982 *Phys. Rev. B* **25** 2343
- [13] Colinet C and Pasturel A 1989 *Physica B + C* **159** 275
- [14] Ducastelle F 1970 *J. Physique* **31** 1055
- [15] Gelatt C D, Ehrenreich H and Watson R E 1977 *Phys. Rev. B* **15** 1613
- [16] Pasturel A, Colinet C and Hicter P 1985 *Calphad* **9** 349
- [17] Papaconstantopoulos D 1986 *Handbook of the Band Structure of Elemental Solids* (New York: Plenum)
- [18] Slater J C and Koster G F 1954 *Phys. Rev.* **94** 1498
- [19] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco, CA: W H Freeman) pp 476-550
- [20] Andersen O K and Jepsen O 1977 *Physica* **91** B 317
- [21] Shiba H 1971 *Prog. Theor. Phys.* **46** 77
- [22] Gautier F, Van der Rest J and Brouers F 1975 *J. Phys. F: Met. Phys.* **5** 1884
- [23] Robbins M O and Falicov L M 1984 *Phys. Rev. B* **29** 1333
- [24] Mayou D and Pasturel A 1989 *J. Phys.: Condens. Matter* **1** 9685
- [25] Pettifor D G 1986 *J. Phys. C: Solid State Phys.* **19** 285
- [26] Pettifor D G and Podloucky R 1986 *J. Phys. C: Solid State Phys.* **19** 315
- [27] Cressoni J C and Pettifor D G 1991 *J. Phys.: Condens. Matter* **3** 495
- [28] Pettifor D G and Varma C M 1979 *J. Phys. C: Solid State Phys.* **12** L253
- [29] Pettifor D G 1983 *Physical Metallurgy* ed R W Cahn and P Haasen (Amsterdam: North-Holland) ch 3
- [30] Haydock R 1980 *Solid State Physics* vol 35, ed H Ehrenreich, D Turnbull and F Seitz (New York: Academic) p 215
- [31] Nex C M M 1984 *Comput. Phys. Commun.* **34** 101
- [32] Bieber A, Gautier F, Treglia G and Ducastelle F 1981 *Solid State Commun.* **39** 149
- [33] Mayou D, Nguyen Manh D, Pasturel A and Cyrot-Lackmann F 1986 *Phys. Rev. B* **33** 3384
- [34] Hultgren R, Desai P D, Hawkins D T, Gleiser M and Kelley K K 1973 *Selected Values of the Thermodynamic Properties of Binary Alloys* (Metals Park, OH: ASM)
- [35] Kubaschewski O 1958 *Trans. Faraday Soc.* **54** 814
- [36] Gachon J C, Notin M and Hertz J 1981 *Thermochim. Acta* **48** 155