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A model for relaxation in intermetallic compounds

Luiz G Ferreira† and Marco A Boselli

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, UNICAMP, 13083-970
Campinas, São Paulo, Brazil

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Abstract. We use the density functional inspired model for alloying and lattice vibrations to study the relaxation of the intermetallic binary systems Ni–Al and Cu–Au. In one case the data set is made up of first-principles results for the intermetallics in their cubic form. In the other case the data set is mostly experimental. The parametrization is performed in the direct space and it resembles a parametrization for an Ising Hamiltonian, though with distance dependent pair interactions. In both cases three-body and many-body interactions were not needed, and the pair interactions did not go beyond the second-neighbour shell.

1. Introduction

In a recent paper we showed how the density functional theory could inspire the construction of a model for lattice vibrations and alloying [1]. There we derived the following energy expression (per atom)

$$E = G(\Omega, x) + \frac{1}{N^2\Omega} \sum_{\alpha, \beta} \sum_{g \neq 0} H_{\alpha\beta}(g^2) \cos(g \cdot r_{\alpha\beta}). \quad (1)$$

Here, g are reciprocal lattice vectors, N is the number of atoms in the unit cell, Ω is the volume *per atom*, α and β are atoms in the unit cell (either of species 0 or species 1, because we deal with binary systems), $r_{\alpha\beta}$ is the radius vector between them, and $G(\Omega, x)$ is an energy term dependent on the concentration x of atoms 1, and on the volume Ω . The second term in (1) is a pair interaction energy, while the first, $G(\Omega, x)$, corresponds to the background homogeneous electron gas. The latter term is able to overcome the usual objections [2] to the pair interaction model‡.

In [1] we applied the model to the Cu–Au system, performing a parametrization of the functions $H_{CuCu}(g^2)$, $H_{AuAu}(g^2)$, $H_{CuAu}(g^2)$ in the reciprocal space. The parametrization was wholly based on the experimental data for this binary system. Here we develop a direct space version of the model, putting it in close relationship to the Ising Hamiltonian, revisit the Cu–Au system, apply the model to the Ni–Al system, wholly calculated from first principles (instead of experimental data), and study the relaxation of many intermetallic compounds of both systems. This way, we intend to show that the model is almost as easy to use as the Ising Hamiltonian [3], with the added advantage of dealing with not only volume relaxations [4] but also relaxations of the most general kind.

† e-mail address: guima@ifi.unicamp.br

‡ Pure pair interaction produces $c_{12} = c_{44}$ and incompatibility between the elastic constants determined from the phonon spectrum and from strain deformations.

The problem of parametrizing model Hamiltonians to binary alloy systems is not often seen in the literature. Aside from the usual Ising Hamiltonian [3, 5, 6, 7], or its extension to volume dependent interactions [4], one seldom sees model Hamiltonian applications where general relaxations of the atomic positions are considered [8]. In principle many model Hamiltonians could be used, such as that of the embedded atom model, which is also density functional inspired [9, 10, 11, 12, 13], the pair interaction models [14, 15, 16], the multi-atom interaction models [17], and tight-binding Hamiltonians [18, 19]. In practice a parametrization that can account for the correct elastic and thermodynamic properties of the elements and their binary compounds is a difficult and challenging problem. In what follows we will show that it is possible to use the model of (1) plus either data from experiment and/or calculated from first principles, sometimes interpolated in the concentration x of one of the elements, to define a Hamiltonian able to describe the many ways of relaxation.

2. Parametrization in the direct space

For a binary system there are only three interaction functions: $H_{00}(g^2)$, $H_{11}(g^2)$, $H_{01}(g^2)$. Fourier transforming (1) and defining the interactions

$$\begin{aligned} H_0(r) &\equiv H_{00}(r) \\ H_1(r) &\equiv H_{11}(r) \\ J(r) &\equiv \frac{1}{4} [H_{00}(r) + H_{11}(r)] - \frac{1}{2} H_{01}(r) \end{aligned} \quad (2)$$

the energy per atom becomes

$$\begin{aligned} E = G(\Omega, x) &- \frac{1}{\Omega} (1-x) \int H_0(r) d^3r - \frac{1}{\Omega} x \int H_1(r) d^3r \\ &+ 4 \frac{1}{\Omega} x (1-x) \int J(r) d^3r + (1-x) \sum_{L, \alpha, r \neq 0} H_0(r)|_{r=L+r_\alpha} \\ &+ x \sum_{L, \alpha, r \neq 0} H_1(r)|_{r=L+r_\alpha} + \frac{1}{N} \sum_{\beta, L, \alpha, r \neq 0} J(r)|_{r=L+r_\alpha-r_\beta} (S_\alpha S_\beta - 1). \end{aligned} \quad (3)$$

The three integrals in the equation above come from the exclusion of $\mathbf{g} = 0$ in the sum in (1). Here we are considering a unit cell of N atoms so that the lattice vectors \mathbf{L} refer to these enlarged cells. α and β are atoms within the enlarged cell. S_α and S_β are Ising spin variables (-1 for the atom 0 and $+1$ for the atom 1).

In applying this model to any system, we expand the interactions $H_0(r)$, $H_1(r)$, $J(r)$ in cubic splines

$$H(r) = \sum_I P_I \left(1 - \frac{r}{r_I}\right)^3 \theta(r_I - r) \quad (4)$$

where θ is the step function, while the radii r_I are chosen and P_I are independent parameters for $H_0(r)$, $H_1(r)$, $J(r)$. It is good practice to have a fine grid of cut-off radii r_I between the minimum interatomic distance and a maximum which, for the simple metals, is less than the third-neighbour distance. This means that, for practical purposes, the data on the metals and their alloys can be explained by the interactions of the first and second neighbours only. So, in principle, the number of parameters P_I is infinite, while the number of data on the system is small. Thus we need a *minimum* principle restricting our freedom. As in [1] we maximize the smoothness of the splines by requiring

$$\int_0^\infty \left(\frac{d^3 H_0}{dr^3}\right)^2 dr + \int_0^\infty \left(\frac{d^3 H_1}{dr^3}\right)^2 dr + \int_0^\infty \left(\frac{d^3 J}{dr^3}\right)^2 dr = \text{minimum}. \quad (5)$$

Later we are going to modify this expression by including a least-squares fit term to part of the data set.

The function $G(\Omega, x)$ is written as

$$G(\Omega, x) = A(x) \left[\frac{\bar{\Omega}(x)}{\Omega} \right] + B(x) \left[\frac{\bar{\Omega}(x)}{\Omega} \right]^2 + C(x) \left[\frac{\bar{\Omega}(x)}{\Omega} \right]^3 \quad (6)$$

where $\bar{\Omega}(x)$ is an interpolation, for the concentration x , of the atomic volumes for some important intermetallic compounds. For example, in the case of the Cu–Au system, the atomic volumes for Cu, Cu₃Au(L1₂), CuAu(L1₀), CuAu₃(L1₂), Au are known and $\bar{\Omega}(x)$ is a polynomial interpolation of these values. The functions $A(x)$, $B(x)$, $C(x)$ are also interpolations obtained in the following way:

(i) for some important compounds Γ we choose

$$G(\Omega_\Gamma, x_\Gamma) = 0 = A(x_\Gamma) + B(x_\Gamma) + C(x_\Gamma) \quad (7)$$

because whatever value G might assume could be absorbed into the other terms of (3).

(ii) Since the atomic volume of Γ is known, and it is an equilibrium volume,

$$\begin{aligned} 0 = \Omega \left. \frac{dE_\Gamma}{d\Omega} \right|_{\Omega_\Gamma} &= -A(x_\Gamma) - 2B(x_\Gamma) - 3C(x_\Gamma) \\ &+ \frac{1}{\Omega_\Gamma} (1 - x_\Gamma) \int H_0(r) d^3r + \frac{1}{\Omega_\Gamma} x_\Gamma \int H_1(r) d^3r \\ &- 4 \frac{1}{\Omega_\Gamma} x_\Gamma (1 - x_\Gamma) \int J(r) d^3r + \frac{1 - x_\Gamma}{3} \sum_{L, \alpha, r \neq 0} [r H'_0(r)]_{r=L+r_\alpha} \\ &+ \frac{x_\Gamma}{3} \sum_{L, \alpha, r \neq 0} [r H'_1(r)]_{r=L+r_\alpha} + \frac{1}{3N_\Gamma} \sum_{\beta, L, \alpha, r \neq 0} [r J'(r)]_{r=L+r_\alpha-r_\beta} (S_\alpha S_\beta - 1). \end{aligned} \quad (8)$$

(iii) As discussed in [1], the equality of the elastic constants calculated from the phonons at $\mathbf{k} = \mathbf{0}$ and from the strain requires

$$\begin{aligned} 0 = A(x_\Gamma) + 3B(x_\Gamma) + 6C(x_\Gamma) - \frac{1}{\Omega_\Gamma} (1 - x_\Gamma) \int H_0(r) d^3r \\ - \frac{1}{\Omega_\Gamma} x_\Gamma \int H_1(r) d^3r + 4 \frac{1}{\Omega_\Gamma} x_\Gamma (1 - x_\Gamma) \int J(r) d^3r. \end{aligned} \quad (9)$$

3. The data set

The data set we use to determine the interactions $H_0(r)$, $H_1(r)$, $J(r)$, namely the P_I in (4), is made up of elastic and thermodynamic data, either measured or calculated by first principles. In most instances, the number of data available is insufficient to determine the P_I , so that the data set has to be completed with assumed values for some elastic properties. For the binary systems Cu–Au and Ni–Al, the data set is tabulated later in tables 2 and 3 and there we refer to the list of codes below.

- *Table code e.* Enthalpies of formation of the compounds

$$\Delta H_\Gamma = E_\Gamma - (1 - x_\Gamma) E_0 - x_\Gamma E_1$$

where E_0 and E_1 are the energies per atom of the elements.

• *Table code D.* The lattice vibration spectra (phonon frequencies) for the elements. The phonon frequencies are the eigenvalues of the following equation

$$M\omega^2 D_i = -2 \sum_{j,l \neq 0} \left\{ \left[\frac{\delta_{ij}}{r} H'(r) - \frac{x_i x_j}{r^3} H'(r) + \frac{x_i x_j}{r^2} H''(r) \right] e^{iK \cdot r} \right\}_{r=l} D_j \\ + 2 \sum_{j,l \neq 0} \left[\frac{\delta_{ij}}{r} H'(r) - \frac{x_i x_j}{r^3} H'(r) + \frac{x_i x_j}{r^2} H''(r) \right]_{r=l} D_j \quad (10)$$

so that the spectrum is wholly determined by the values of $rH'(r)$ and $r^2H''(r)$ at a few neighbour distances. Therefore, one first uses these derivatives as fitting parameters to the phonon spectrum and, when it comes to the alloy system, the values of the derivatives are taken as data. That is what we did with Cu and Au in the binary system Cu–Au.

• *Table code H.* For some important compounds, we set (7), (8), and (9).

• *Table code B.* For some intermetallic compounds we set the value of the bulk modulus

$$B = \frac{1-x}{9\bar{\Omega}(x)} \sum_{L,\alpha,r \neq 0} [r^2 H_0''(r) - 2r H_0'(r)]_{r=L+r_\alpha} \\ + \frac{x}{9\bar{\Omega}(x)} \sum_{L,\alpha,r \neq 0} [r^2 H_1''(r) - 2r H_1'(r)]_{r=L+r_\alpha} \\ + \frac{1}{9\bar{\Omega}(x)N} \sum_{\beta,L,\alpha,r \neq 0} [r^2 J''(r) - 2r J'(r)]_{r=L+r_\alpha-r_\beta} (S_\alpha S_\beta - 1). \quad (11)$$

• *Table code I.* When the elastic data are insufficient we also make the sound velocity isotropic for some compounds. For a cubic system, that condition would imply

$$c_{11} = c_{12} + 2c_{44}.$$

In the general case the condition is

$$(1-x) \sum_{L,\alpha,r \neq 0} \left\{ [r^2 H_0''(r) - r H_0'(r)] \frac{x^4 + y^4 + z^4 - 3x^2 y^2 - 3x^2 z^2 - 3y^2 z^2}{r^4} \right\}_{r=L+r_\alpha} \\ + x \sum_{L,\alpha,r \neq 0} \left\{ [r^2 H_1''(r) - r H_1'(r)] \frac{x^4 + y^4 + z^4 - 3x^2 y^2 - 3x^2 z^2 - 3y^2 z^2}{r^4} \right\}_{r=L+r_\alpha} \\ + \frac{1}{N} \sum_{\beta,L,\alpha,r \neq 0} \left\{ [r^2 J''(r) - r J'(r)] \frac{x^4 + y^4 + z^4 - 3x^2 y^2 - 3x^2 z^2 - 3y^2 z^2}{r^4} \right\}_{r=L+r_\alpha-r_\beta} \\ \times (S_\alpha S_\beta - 1) = 0. \quad (12)$$

• *Table code C.* Also when the data set is small, it is practical to set the elastic constants (or their averages) linear with composition, namely the three equations

$$\frac{1}{N\bar{\Omega}(x)} \sum_{\beta,L,\alpha,r \neq 0} [r H_{\alpha\beta}'(r)]_{r=L+r_\alpha-r_\beta} = \frac{1-x}{\bar{\Omega}_0} \sum_{l,r \neq 0} [r H_{00}'(r)]_{r=l} \\ + \frac{x}{\bar{\Omega}_1} \sum_{l,r \neq 0} [r H_{11}'(r)]_{r=l} \quad (13)$$

$$\frac{1}{N\bar{\Omega}(x)} \sum_{\beta,L,\alpha,r \neq 0} \left\{ \frac{x^2 y^2 + x^2 z^2 + y^2 z^2}{r^3} [r H_{\alpha\beta}''(r) - H_{\alpha\beta}'(r)] \right\}_{r=L+r_\alpha-r_\beta}$$

$$\begin{aligned}
 &= \frac{1-x}{\bar{\Omega}_0} \sum_{l,r \neq 0} \left\{ \frac{x^2 y^2 + x^2 z^2 + y^2 z^2}{r^3} [r H''_{00}(r) - H'_{00}(r)] \right\}_{r=l} \\
 &+ \frac{x}{\bar{\Omega}_1} \sum_{l,r \neq 0} \left\{ \frac{x^2 y^2 + x^2 z^2 + y^2 z^2}{r^3} [r H''_{11}(r) - H'_{11}(r)] \right\}_{r=l} \tag{14}
 \end{aligned}$$

$$\begin{aligned}
 &\frac{1}{N\bar{\Omega}(x)} \sum_{\beta, L, \alpha, r \neq 0} \left\{ \frac{x^4 + y^4 + z^4}{r^3} [r H''_{\alpha\beta}(r) - H'_{\alpha\beta}(r)] \right\}_{r=L+r_\alpha-r_\beta} \\
 &= \frac{1-x}{\bar{\Omega}_0} \sum_{l,r \neq 0} \left\{ \frac{x^4 + y^4 + z^4}{r^3} [r H''_{00}(r) - H'_{00}(r)] \right\}_{r=l} \\
 &+ \frac{x}{\bar{\Omega}_1} \sum_{l,r \neq 0} \left\{ \frac{x^4 + y^4 + z^4}{r^3} [r H''_{11}(r) - H'_{11}(r)] \right\}_{r=l} . \tag{15}
 \end{aligned}$$

In these equations L is a lattice vector for the compound, which has an enlarged cell, and l is a lattice vector of the elements.

4. The intermetallic compounds and their configurations of atoms

In the case of Cu–Au and Ni–Al we applied the model to the configurations of table 1. Some have standard notations, but most of them (those with notations in quotation marks) do not. The list of configurations based on the FCC lattice is all the possible configurations with up to four atoms per cell [20]. The arrangement of atoms for most configurations can be readily understood because the unit vectors are tabulated and they are superlattices with a certain alternation of planes along the given directions. Only three of the configurations in the table are not superlattices. For these we show the arrangement of atoms in figure 1.

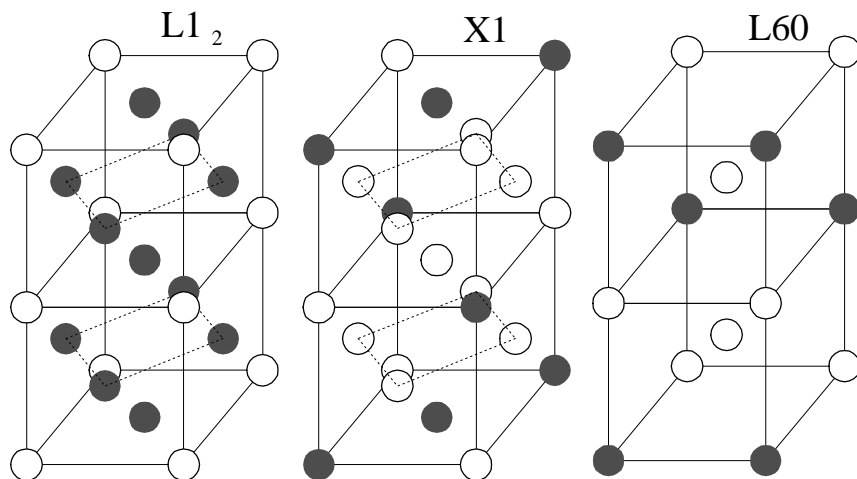


Figure 1. Arrangements of atoms in configurations that are not superlattices.

5. The Ni–Al binary system

5.1. Fitting

In this case we use the calculated (LMTO) first-principles results of [21]. The data set consists of 22 enthalpies of formation plus the bulk moduli of FCC Ni and Al. All the intermetallic compounds were calculated by LMTO in their perfect cubic (FCC or BCC) arrangement of atoms. The bulk moduli of the compounds, though necessarily calculated, were not published. We know only that they are positive, otherwise it would be impossible to calculate the enthalpy.

To apply the model, the data set has to be completed with elastic data, as in table 2. The compounds with codes H were used to define the atomic volume $\bar{\Omega}(x)$ function of composition, and the function $G(\Omega, x)$ through (7), (8), (9). The bulk moduli (codes B (11)) were set equal to the calculated values for Ni(FCC) and Al(FCC); for the compounds we set them equal to the value linearly interpolated in x . For some compounds we also set the isotropic sound velocity condition (code I (12)).

The calculated enthalpies of formation (code e) were fitted by the model in the following way. We complete the maximum spline smoothness condition (5) with a least-squares error term as in the equation below.

$$\sum_{\Gamma} (\Delta H_{\Gamma, fit} - \Delta H_{\Gamma, LMTO})^2 + \beta \left\{ \int_0^{\infty} \left(\frac{d^3 H_0}{dr^3} \right)^2 dr + \int_0^{\infty} \left(\frac{d^3 H_1}{dr^3} \right)^2 dr + \int_0^{\infty} \left(\frac{d^3 J}{dr^3} \right)^2 dr \right\} = \min. \quad (16)$$

β is chosen so that all compounds have positive bulk moduli. The value of β is not critical and can be taken in a broad range. This handling of the enthalpies, instead of setting them equal to the LMTO values, renders the whole fitting process easier. This process is based on the assumption that the LMTO calculated enthalpies do not have a precision much better than 1.0 kcal g⁻¹/atom, and that they contain a residual atomic interaction beyond the second neighbour, which is outside the range of our splines (equation (4)). Table 2 compares the LMTO enthalpies with those resulting from the fit. The standard deviation depends on the value assumed for β .

In figure 2 we plot the interactions $H_0(r)$, $H_1(r)$, $J(r)$ as functions of distance. For comparison, we quote the first- and second-neighbour distances in the elements.

5.2. Relaxation

In [21] the enthalpy data set was analysed by means of an Ising Hamiltonian extending to the fourth neighbour. Here we do not reach the third neighbour but our interactions $H_0(r)$, $H_1(r)$, $J(r)$ depend on the distance. That permits us to study how the many configurations relax by moving the atoms out of their ideal cubic positions. For each configuration, the relaxation had the most general form

$$\mathbf{a}_i \rightarrow \bar{\mathbf{E}} \cdot \mathbf{a}_i \quad \mathbf{r}_\alpha \rightarrow \bar{\mathbf{E}} \cdot (\mathbf{r}_\alpha + \delta \mathbf{r}_\alpha) \quad (17)$$

that is, the unit vectors \mathbf{a}_i are deformed by a general six-component strain tensor $\bar{\mathbf{E}}$ and the atoms within a cell are displaced arbitrarily by $\delta \mathbf{r}_\alpha$.

The resulting enthalpies after relaxation are given in the last column of table 2. There are some interesting features to be observed in that column. The configuration L1₀, originally so similar to configuration '40', relaxes into the CsCl configuration B₂. The configuration

Table 1. The configurations studied.

	Unit vectors	Superlattice	along
BCC			
DO ₃	(200), (20 $\bar{2}$), (02 $\bar{2}$)	[AAAB]	2/a (111)
L ₆₀	(200), (022), (0 $\bar{2}$ 2)		see figure 1
C ₁₁ b	(200), (020), (113)	[AAB]	2/a (001)
B ₂	(200), (020), (002)	[AB]	2/a (001)
'A1'	($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}\bar{1}$), (220)	[AB]	2/a (110)
B ₁₁	(200), (020), (004)	[AABB]	2/a (001)
B ₃₂	(220), (2 $\bar{2}$ 0), (20 $\bar{2}$)	[AABB]	2/a (111)
FCC			
L ₁₂	(200), (020), (002)		see figure 1
DO ₂₂	(200), (002), ($\bar{1}\bar{2}\bar{1}$)	[AAAB]	2/a (210)
'V1'	($\bar{1}\bar{1}\bar{0}$), ($\bar{1}0\bar{1}$), (233)	[AAAB]	1/a (111)
'W1'	($\bar{1}\bar{1}\bar{0}$), (112), ($\bar{1}\bar{2}\bar{1}$)	[AAAB]	1/a (113)
'X1'	(110), ($\bar{1}\bar{1}\bar{2}$), ($\bar{1}\bar{1}\bar{2}$)		see figure 1
'Y1'	($\bar{1}\bar{1}\bar{0}$), (002), (220)	[AAAB]	2/a (110)
'Z1'	($\bar{1}\bar{1}\bar{0}$), (110), (004)	[AAAB]	2/a (001)
' α '	($\bar{1}\bar{1}\bar{0}$), ($\bar{1}0\bar{1}$), (222)	[AAB]	1/a (111)
' β '	($\bar{1}\bar{1}\bar{0}$), (110), (103)	[AAB]	2/a (001)
' γ '	($\bar{1}\bar{1}\bar{0}$), (002), (121)	[AAB]	2/a (110)
L ₁₀	(110), ($\bar{1}\bar{1}\bar{0}$), (002)	[AB]	2/a (001)
L ₁₁	($\bar{1}\bar{1}\bar{0}$), ($\bar{1}0\bar{1}$), (211)	[AB]	1/a (111)
'40'	(200), (002), ($\bar{1}\bar{2}\bar{1}$)	[AABB]	2/a (210)
'V2'	($\bar{1}\bar{1}\bar{0}$), ($\bar{1}0\bar{1}$), (233)	[AABB]	1/a (111)
'W2'	($\bar{1}\bar{1}\bar{0}$), (112), ($\bar{1}\bar{2}\bar{1}$)	[AABB]	1/a (113)
'Y2'	($\bar{1}\bar{1}\bar{0}$), (002), (220)	[AABB]	2/a (110)
'Z2'	($\bar{1}\bar{1}\bar{0}$), (110), (004)	[AAAB]	2/a (001)

'A1', never observed in nature, also relaxes into B₂, and the configurations L₆₀ relax into the configurations L₁₂ with the same composition. Another feature to be observed is that, after relaxation, the compounds Ni₂Al in the configurations C₁₁b and ' β ' attain an enthalpy value slightly below the interpolated value of the enthalpies of NiAl(B₂) and Ni₃Al(L₁₂). That opens the possibility of ground state configurations with compositions between those of the two compounds, a well known occurrence [22].

We must mention that we also studied the volume relaxations, that is the simple relaxation where $\delta r_\alpha = 0$ and $\bar{E} = (1 + \varepsilon)\bar{I}$. That is the kind of relaxation that one considers when using the Connolly–Williams description [4]. The enthalpy shift because of this relaxation was very small; in the extreme case of 'Z2' it was only 1.0 kcal g⁻¹/atom. This means that the equilibrium volume of all configurations never deviates much from the interpolated function $\bar{\Omega}(x)$.

6. The Cu–Au binary system

6.1. Fitting

The data set in this case was mostly experimental. For the elements we fitted the phonon spectrum adjusting the first and second derivatives of the interaction according to (10). The results of this fit are in figures 3 and 4. The experimental frequencies are from [23] and [24]. The derivatives of the interactions entered the fitting process as data and mean the table code D in table 3. The experimental atomic volumes of the configurations with

Table 2. Enthalpies are in kcal g⁻¹/atom = 0.0434 eV/atom.

Compound	Code	LMTO	Fit	Relaxation
Ni(FCC)	BIH	0.00	0.00	0.00
Al(FCC)	BIH	0.00	0.00	0.00
NiAl(L1 ₀ cubic)	BIe	-13.38	-13.73	-17.63 (B ₂)
Ni ₃ Al(L1 ₂)	BIeH	-11.62	-11.70	-11.70
NiAl ₃ (L1 ₂)	BIeH	-5.37	-5.86	-5.86
Ni ₂ Al ₂ ('Z2')	Be	-2.54	-2.38	-6.46
Ni ₂ Al ₂ ('40')	Be	-13.70	-13.69	-14.60
NiAl(L1 ₁)	BIe	-8.19	-7.95	-14.88
NiAl ₂ ('β')	BIe	-5.40	-4.89	-8.77
Ni ₂ Al('β')	BIe	-8.10	-8.12	-13.76
NiAl ₃ (DO ₂₂)	e	-5.47	-5.79	-5.81
Ni ₃ Al(DO ₂₂)	e	-10.98	-11.65	-11.65
Ni (bcc)	BIe	0.69	0.15	0.14
Al (bcc)	BIe	1.27	1.34	1.34
NiAl (B ₂)	BIeH	-18.15	-17.63	-17.63
Ni ₃ Al(DO ₃)	BIe	-11.30	-11.21	-11.21
NiAl ₃ (DO ₃)	BIe	-3.83	-4.15	-4.19
NiAl('A1')	BIe	-8.83	-7.93	-17.63 (B ₂)
Ni ₂ Al ₂ (B ₁₁)	Be	-4.77	-5.96	-15.14
Ni ₂ Al ₂ (B ₃₂)	Be	-10.35	-10.49	-10.65
Ni ₃ Al(L ₆₀)	Ie	-10.35	-9.44	-11.70 (L1 ₂)
NiAl ₃ (L ₆₀)	Ie	-4.04	-3.89	-5.86 (L1 ₂)
Ni ₂ Al(C ₁₁ b)	Be	-11.62	-11.85	-13.77
NiAl ₂ (C ₁₁ b)	Be	-8.14	-7.94	-9.76
Standard deviation			0.65	

code H define the function $\bar{\Omega}(x)$ and the function $G(\Omega, x)$. Experimental values for the enthalpy are known for only three configurations [22]. Another important datum is the ratio $c/a = 0.91$ for the equilibrium configuration L1₀.

The experimental data described above was clearly insufficient to define the interactions. Ideally we would like to have the phonon spectrum for some compounds, that would define the derivatives of the interaction $J(r)$. Lacking this information, we completed the data by assuming linearity of the elastic constants with x (configurations with code C in table 3) and by importing from a first-principles LAPW calculation the enthalpy differences [21] $\Delta H_{Cu_2Au_2('Z2')} - \Delta H_{Cu_3Au(L1_2)}$ and $\Delta H_{CuAu(L1_1)} - \Delta H_{Cu_3Au(L1_2)}$. The LAPW enthalpies, after a shift such that Cu₃Au(L1₂) coincides with experiment, are quoted in table 3 in the column 'Shift LAPW'.

As in (16), the assumed enthalpies (experimental or shifted LAPW for 'Z2' and L1₁) were introduced into the variational expression itself (code e)

$$\sum_{\Gamma} (\Delta H_{\Gamma, fit} - \Delta H_{\Gamma, assumed})^2 + \beta \left\{ \int_0^{\infty} \left(\frac{d^3 H_0}{dr^3} \right)^2 dr + \int_0^{\infty} \left(\frac{d^3 H_1}{dr^3} \right)^2 dr + \int_0^{\infty} \left(\frac{d^3 J}{dr^3} \right)^2 dr \right\} = \min. \quad (18)$$

In the present case the value of β is not important at all because, the number of enthalpies to be fitted being small, the least-squares error term is almost equal to zero.

Figure 5 gives a plot of the interactions for the Cu–Au system. It is interesting to

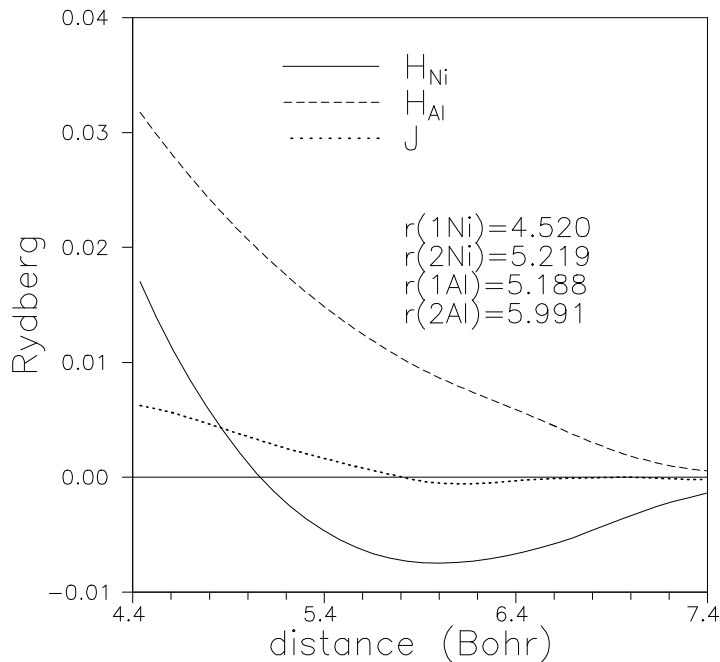


Figure 2. Pair interaction functions for Ni–Al. First- and second-neighbour distances in the elements are given.

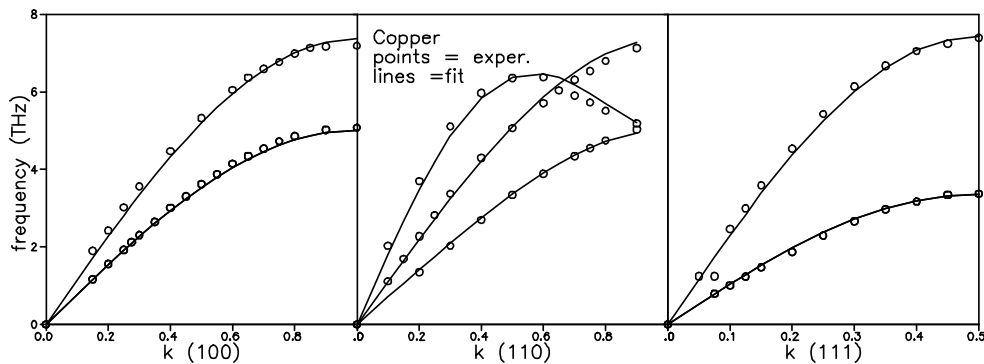


Figure 3. Phonon frequencies of copper along the symmetry directions.

observe that the asymmetry between the two $L1_2$ configurations (Cu_3Au and $CuAu_3$) is brought about by the distance dependence of the pair interactions, not by the three-body interactions, as in the Ising model [25].

6.2. Relaxation

We studied the relaxation of all configurations of atoms with up to four atoms per cell. By relaxing only the volume, the enthalpies practically undergo no change, again implying that the interpolated atomic volume $\bar{\Omega}(x)$ is very near the equilibrium volumes for all

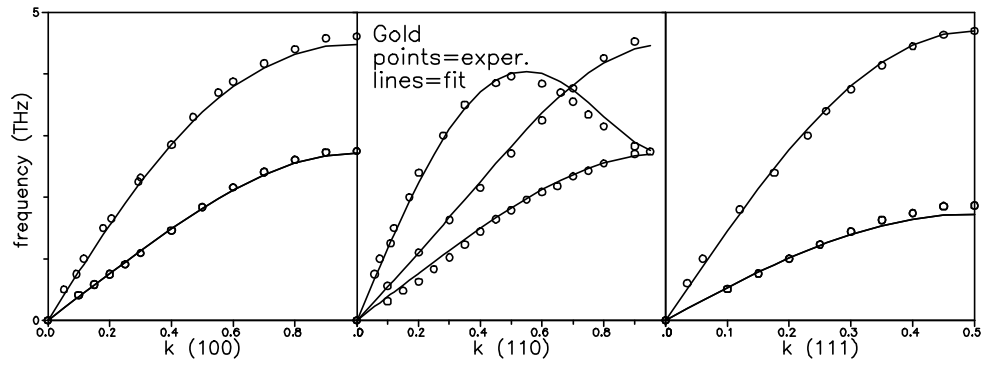


Figure 4. Phonon frequencies of gold along the symmetry directions.

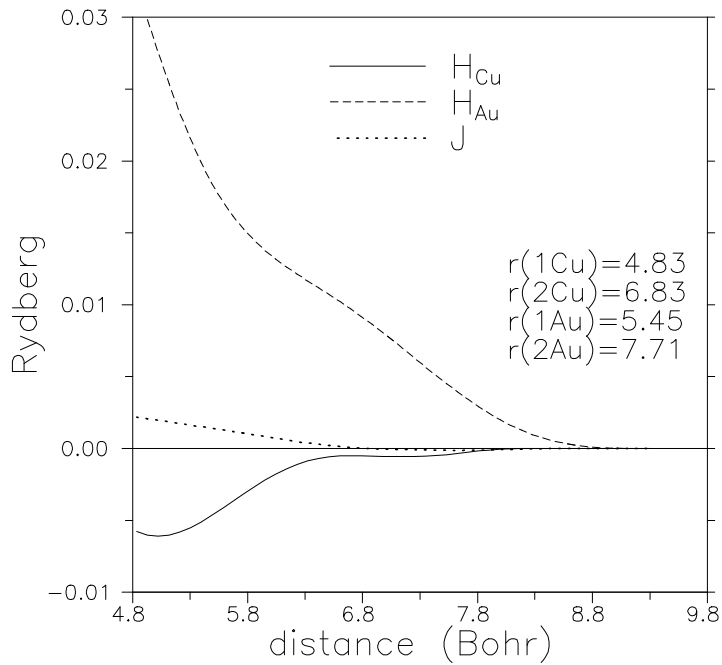


Figure 5. Pair interaction functions for Cu–Au. First- and second-neighbour distances for the elements are given.

configurations. The effect of full relaxation according to (17) is presented in table 4. The relaxation has usually a small energetic effect, but there are configurations, such as CuAu_3 ('Z1') and CuAu_2 (' β' '), where it cannot be neglected.

7. Conclusions

The model presented in [1], here adapted to the direct space, was shown able to handle the energetics of a simple metal binary system. The model leads directly to pair interactions plus a homogeneous electron gas term and in no way suffers from the maladies commonly

Table 3. Fitting for the system Cu–Au. Enthalpies are in kcal g⁻¹/atom.

Compound	Codes	Exp.	Shift LAPW	Fit
Cu(FCC)	DH	0.00	0.00	0.00
Cu ₃ Au(L1 ₂)	eCH	-1.71	-1.71	-1.71
Cu ₃ Au(DO ₂₂)	C		-1.61	-1.66
Cu ₂ Au('β')	C		+0.48	+0.30
CuAu(L1 ₀ cubic)	CH		-1.67	-1.90
CuAu(L1 ₀ c/a = 0.91)	eC	-2.10	-2.33	-2.10
CuAu(L1 ₁)	e		+0.67	+0.67
CuAu('40')	C		-1.25	-1.79
CuAu('Z2')	e		+2.68	+2.68
CuAu ₂ ('β')	C		+0.17	+0.36
CuAu ₃ (L1 ₂)	eCH	-1.37	-1.27	-1.37
CuAu ₃ (DO ₂₂)	C		-1.11	-1.31
Au(FCC)	DH	0.00	0.00	0.00

Table 4. Enthalpies are in kcal g⁻¹/atom = 0.0434 eV/atom.

	Cubic	Relaxation		Cubic	Relaxation
Cu ₃ Au(L1 ₂)	-1.71	-1.71	CuAu ₃ (L1 ₂)	-1.37	-1.37
Cu ₃ Au(DO ₂₂)	-1.66	-1.66	CuAu ₃ (DO ₂₂)	-1.31	-1.31
Cu ₃ Au('V1')	+1.96	+1.81	CuAu ₃ ('V1')	+2.00	+1.86
Cu ₃ Au('W1')	-0.39	-0.43	CuAu ₃ ('W1')	-0.12	-0.17
Cu ₃ Au('X1')	-0.39	-0.41	CuAu ₃ ('X1')	-0.12	-0.15
Cu ₃ Au('Y1')	-0.44	-0.49	CuAu ₃ ('Y1')	-0.18	-0.24
Cu ₃ Au('Z1')	+0.69	+0.53	CuAu ₃ ('Z1')	+0.82	-0.12
Cu ₂ Au('α')	+1.97	+1.79	CuAu ₂ ('α')	+1.97	+1.79
Cu ₂ Au('β')	+0.30	+0.10	CuAu ₂ ('β')	+0.36	-0.84
Cu ₂ Au('γ')	-1.17	-1.21	CuAu ₂ ('γ')	-1.01	-1.06
CuAu(L1 ₀)	-1.90	-2.10	Cu ₂ Au ₂ ('W2')	-0.61	-0.81
CuAu(L1 ₁)	+0.67	+0.49	Cu ₂ Au ₂ ('Y2')	+0.56	+0.37
Cu ₂ Au ₂ ('40')	-1.79	-1.81	Cu ₂ Au ₂ ('Z2')	+2.68	+2.43
Cu ₂ Au ₂ ('V2')	+3.85	+3.65			

attributed to the pair interaction models. The model was shown to describe simultaneously vibrations, elastic constants, and alloying. In this sense, the model is far superior to the Ising Hamiltonian frequently used to describe alloy systems. In finding the parameters, the combination of cubic splines with a minimum principle related to the smoothness of the interaction functions was proven to be effective. Frequently we found that the data set available, either from experiment or from first-principles calculations, was insufficient and had to be completed by simple recipes like linearity with composition. Of course these assumptions are never too far from reality. Ideally, a good data set would include the phonon spectrum not only of the elements but of some intermetallic compounds as well. Such knowledge would permit us to find the pair interaction functions without making extra assumptions.

Before closing we should warn the reader about two points. The first is that the model has been applied to metal systems with short-range interactions. For longer-range interactions, the parametrization of the interaction functions would be more complicated

because one would have to go to the third neighbour or beyond. The second point is that, as the theory of [1] stands, there is no room for ionic materials. Ionicity would be obtained only if we had included in the Hamiltonian a term linear in the electronic density. That would modify the formulation to some extent.

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