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## LETTER TO THE EDITOR

# Interatomic forces and atomic structure of liquid $\text{Al}_{80}\text{Mn}_{20}$ alloys

L Do Phuong, D Nguyen Manh† and A Pasturel

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, UA 29 CNRS, ENSEEG BP75, 38402 Saint Martin d'Hères, France

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**Abstract.** A tight-binding-bond approach to interatomic forces in disordered aluminium-transition-metal (Al-M) alloys is presented. The bond order is calculated on a Bethe lattice reference system, well adapted to topologically disordered alloys. It is shown that the bond order depends strongly on the strength of the *pd* hybridization in the Al-M alloy, leading to non-additive potentials with a strong preference for the formation of pairs of unlike atoms and short bond distances in the Al-M pairs. This is illustrated by studying the structural properties of liquid  $\text{Al}_{80}\text{Mn}_{20}$  alloy using molecular-dynamics simulations and by comparing our results with the available experimental ones.

The principal goal in materials science is understanding the relationship between the structures and properties of materials. For perfect crystals, knowledge of the position of only a few atoms within the unit cell is sufficient to deduce many material properties. In liquids, the problem is more difficult due to the lack of long-range order in the liquid state. On the other hand, with the development of simulation techniques in the past two decades, there have been many studies of the properties of various liquid systems. However, an accurate simulation of the properties of transition metals and of their alloys is still a challenging problem since bonding is not well described by currently available pair and embedded-atom potentials. In this paper, we present a new approach to interatomic forces in transition-metal alloys and apply it to liquid  $\text{Al}_{80}\text{Mn}_{20}$  alloy. This approach is based on the bond-order concept [1, 2] in which the actual atomic environment is replaced by Bethe lattice. This allows for an explicit expression of the bond order as a function of the interatomic distance and leads to an expression for the interatomic forces in terms of strongly non-additive pair forces. Within the framework of the tight-binding Hückel theory, the quantum-mechanical bond energy in a given pair of atoms *i* and *j* is written in the chemically intuitive form

$$U_{\text{bond}}(i, j) = \sum_{\alpha, \beta} \Phi_{\alpha(i), \beta(j)}^{\text{bond}} = 2 \sum_{\alpha, \beta} H_{i\alpha, j\beta} \Theta_{j\beta, i\alpha} \quad (1)$$

where  $H_{i\alpha, j\beta}$  is the Slater-Koster bond integral matrix linking the orbitals  $\alpha$  and  $\beta$  on sites *i* and *j* together.  $\Theta$  is the corresponding bond-order matrix whose elements give the difference between the number of electrons in the bonding  $1/\sqrt{2}|i\alpha + j\beta\rangle$  and anti-bonding  $1/\sqrt{2}|i\alpha - j\beta\rangle$  states. Bond-order potentials are similar to the embedding potentials in that the bond in a given pair of atoms is considered as embedded in and depending on the local

† Permanent address: Department of Physics, Polytechnic University of Hanoi, Viet Nam.

atomic environment. Thus (1) represents only formally a pair interaction and depends via the bond order on many-atom effects.

This bond order can be expressed in terms of the integral over the imaginary part of the off-diagonal Green function:

$$\Theta_{i\alpha,j\beta} = -\frac{2}{\pi} \text{Im} \int^{E_F} G_{i\alpha,j\beta}(E) dE. \quad (2)$$

To calculate such a quantity, we have used the cluster Bethe lattice reference system (CBLM) [3]. Then, it is clear that the many-body expansion in the bond order depends on the size of the cluster embedded in the Bethe lattice. If the cluster is chosen to be the lattice site, a very rapid convergence of the many-body expansion is obtained. Moreover, as this approximation is exact up to the fourth moment, it gives bond potentials which are based on a better many-body expansion than the classical ones used.

As in this paper we are dealing with liquid alloys, we present the derivation of the bond potentials within the lattice site approximation.

In this case, the bond order can be written as

$$\Theta_{i\alpha,j\beta} = -\frac{1}{\pi} n_\alpha n_\beta \text{Im} \int^{E_F} \left[ h_{\alpha(i),\beta(j)} G_{\alpha(i)}(E) G'_{\beta(j)}(E) \right] dE \quad (3)$$

where  $n_\alpha$  and  $n_\beta$  are the degeneracies of orbital subspaces  $\alpha$  and  $\beta$  respectively and  $h_{\alpha(i),\beta(j)}$  are the hopping energies between a state of subspace  $\alpha$  of atom  $i$  and a state of subspace  $\beta$  of atom  $j$ .  $G_{\alpha(i)}$  is the Green function of atom  $i$  in the subspace  $\alpha$  as given by the CBLM formalism:

$$G_{\alpha(i)}(z) = \left( z - E_{\alpha(i)} - Z \sum_{\beta(j)} p_{ij} n_\beta T_{\alpha(i),\beta(j)}^2 G'_{\beta(j)}(z) \right)^{-1} \quad (4)$$

where  $Z$  is the coordination number and  $p_{ij}$  the pair probability.  $T_{\alpha(i),\beta(j)}^2$  is the mean square of the matrix element between a state of subspace  $\alpha$  of atom  $i$  and a state of subspace  $\beta$  of atom  $j$  [4] and the Green function  $G'_{\beta(j)}$  can be defined by

$$G'_{\beta(j)}(z) = \left( z - E_{\alpha(i)} - (Z - 1) \sum_{\gamma(k)} p_{jk} n_\gamma T_{\beta(j),\gamma(k)}^2 G_{\gamma(k)}(z) \right)^{-1}. \quad (5)$$

The advantage of (3) is that it allow us to estimate the different orbital contributions in the bond energy, and in particular to treat the effect of hybridization explicitly. Assuming that the distance dependence of the bond order is negligible against that of the transfer integral [1], we obtain

$$\Phi_{\alpha(i),\beta(j)}^{\text{bond}} = 2h_{\alpha\beta}(r_{ij})\Theta_{i\alpha,j\beta} \quad (6)$$

with the distance dependence of the hopping integral. Here the average integrals are evaluated according to Harrison's power law [5] ( $h_{\alpha\beta}(r_{ij}) = h_{\alpha\beta}(1)/r_{ij}^n$ ,  $n = 2$  for s and p orbitals,  $n = 5$  for d orbitals). An especially attractive feature of this bond-energy representation is that the electronic forces on the atoms are simply obtained by taking derivations of the tight-binding hopping-matrix elements. However, the strength of the interaction is proportional to  $\Theta$ , which is influenced not only by the local environment

around atom  $i$  but by more distant atoms. Although this model is relatively simple, it includes in a natural way the non-local many-body effects.

The repulsive part of the binding energy is assumed to be given by a sum over pair potentials [6]

$$U_{\text{rep}} = \frac{1}{2N} \sum_{i,j \neq i} \Phi_{ij}^{\text{rep}}(r_{ij}) \quad (7)$$

with

$$\Phi_{ij}^{\text{rep}}(r_{ij}) = \sum_{\alpha,\beta} \Phi_{\alpha(i)\beta(j)}^{\text{rep}}(r_{ij}) = \frac{1}{2} \sum_{\alpha,\beta} \left( \frac{C_{\alpha(i)} C_{\beta(j)}}{r_{ij}^{m_{\alpha} + m_{\beta}}} \right)^{1/2} \quad (8)$$

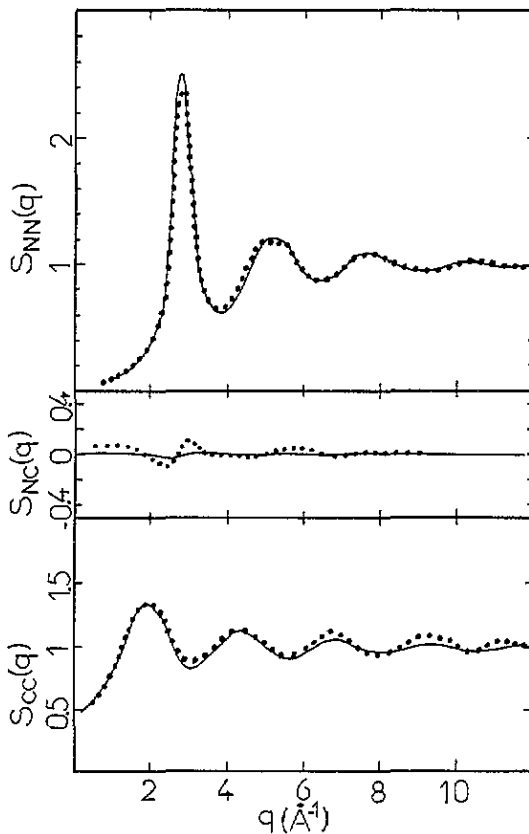


Figure 1. Comparison between theoretical and experimental Bhatia-Thornton partial structures for liquid  $\text{Al}_{30}\text{Mn}_{20}$ : —, simulation; ·····, [9].

For s-s and p-p interactions, the repulsive pair interaction may be modelled as  $\Phi_{\alpha,\alpha}^{\text{rep}}(r_{ij}) = C_{\alpha,\alpha}/r_{ij}^4$  while for d-d interactions, a stronger power-law dependence  $C_{d,d}/r_{ij}^{10}$  is chosen [5].  $C_{\alpha,\alpha}$  ( $\alpha = s, p,$  or  $d$  orbitals) are the only parameters of the model; they are determined from knowledge of the experimental atomic volume and bulk modulus of the pure metals. To treat the alloying effect, i.e. the A-B interactions, we have to

determine the attractive and the repulsive parts of the heteroatomic bond potential. The parametrization of the repulsive pair interaction is still performed using (8) with the same  $C_{\alpha(A)}$  and  $C_{\beta(B)}$  values. To obtain the  $h_{A\alpha,B\beta}$  hopping integrals (that is,  $(ss\sigma)_{AB}$ ,  $(sp\sigma)_{AB}$ ,  $(sd\sigma)_{AB}$ ,  $(pd\sigma)_{AB}$ , and  $(pd\pi)_{AB}$ ), we use the geometrical average of the hopping integrals given in table 1, which is reasonable in the case of the studied alloys. Consequently, no parameters are introduced to describe the alloy properties. At the end, the usual dependence for both hopping integrals and repulsive terms has been modified using the rescaling method proposed by Goodwin *et al* [7]. This method is known for generating improved tight-binding parameters which are both transferable and suitable for extensive molecular-dynamics simulations. The two scaling parameters of the scaling smoothed step-function, i.e.  $r_c$  and  $n_c$ , have been chosen in such a way that the step is positioned between the first- and the second-nearest neighbours in the FCC lattice and that the interactions become zero at  $L/2$ , where  $L$  is the linear dimension of the molecular-dynamics cell.

Table 1. Tight-binding and repulsive parameters for Al and Mn (eV).

	$ss\sigma$	$dd\sigma$	$dd\pi$	$dd\delta$	$sd\sigma$	$pp\sigma$	$pp\pi$	$sp\sigma$	$C_{ss}$	$C_{dd}$	$C_{pp}$
Al	-0.52	—	—	—	—	1.20	-0.31	0.71	0.30	—	0.30
Mn	-1.33	-0.65	0.32	0.00	-1.15	—	—	—	1.64	0.14	—

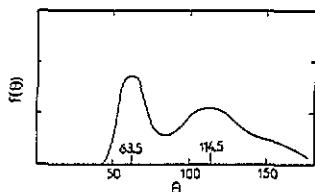


Figure 2. Calculated bond-angle distributions: —, liquid  $Al_{80}Mn_{20}$ .

The discovery of quasicrystalline phases in Al-Mn alloys [8] has generated a renewal of interest in the possible occurrence of icosahedral order in liquid alloys. Experimental study of topological and chemical short-range order in liquid  $Al_{80}Mn_{20}$  alloy, through the accurate determination of the partial pair correlation functions by neutron diffraction, has shown the existence of a well defined topological order [9]. More particularly, it extends more than  $10 \text{ \AA}$ , characterized by a distribution of the first-neighbour Mn-Mn distances centred at  $2.89 \text{ \AA}$ , which is quite different from the nearest-neighbour distance at  $2.67 \text{ \AA}$  in pure liquid Mn, and by moderate chemical-ordering effects. It is important therefore to know whether our interactions are able to reproduce such differences. Consequently, the molecular-dynamics simulations of liquid  $Al_{80}Mn_{20}$  alloy were performed at constant volume and constant temperature. We consider a system of 691 Al atoms and 173 Mn atoms in a cubic box with periodic boundary conditions such that the densities of the two systems are equal to the experimental ones. The initial atomic positions are randomly chosen. The Newtonian equations of motion were solved using the Verlet algorithm with a time increment of  $3 \times 10^{-15} \text{ s}$ . Typical runs took 40 000–50 000 steps for melting and equilibration and about as many for production. The Bhatia-Thornton partial structure factors (PSFs) shown in figure 1 are based on averages of over 50 independent configurations taken at intervals

of 100 time steps. They are perfectly in phase with the experimental curves and, more particularly, reproduce the experimental height of the first and second peaks of  $S_{NN}(q)$ . The theoretical results presented here allow us to point out clues that indicate icosahedral order in the  $S_{NN}(q)$  function of liquid  $\text{Al}_{80}\text{Mn}_{20}$ , as already used in the experimental study [9, 10]. These arguments are the following. (i) The height and the shape of the first peak ( $S_{NN}(q_1) = 2.45$  with  $q_1 = 2.85 \text{ \AA}^{-1}$ ) can be attributed to a variation of the spatial extent  $\xi$  of topological ordering.  $\xi$  is estimated from the breadth of the first peak of  $S_{NN}(q)$  using the Scherrer particle-broadening equation  $2\pi/\Delta q_{NN}$  [9, 10]. The value of  $\xi$  found for  $\text{Al}_{80}\text{Mn}_{20}$  is 10  $\text{\AA}$ , emphasizing a specific topological short-range order. (ii) The shape of the second peak of  $S_{NN}(q)$ , which displays a flat top, is suggestive of local icosahedral order according to Sachdev and Nelson [11]. Another interesting feature is the height ratio between the second and the first peak; this is equal to 0.49, which is similar to the value obtained by using a Landau description of short-range icosahedral order [12].

The first and second oscillations of the two functions  $S_{cc}(q)$  are comparable in amplitude with experimental data. The spatial extent of chemical ordering deduced from the breadth of the first peak is about half that of topological ordering. All these results are confirmed by an analysis of the atomic arrangements between Al and transition-metal atoms in the first shell. The experimental distribution of the first Mn–Mn distances is centred at 2.89  $\text{\AA}$ , while the theoretical value is equal to 2.86  $\text{\AA}$ . We note that the nearest distances are 2.67  $\text{\AA}$  in pure liquid Mn [13], and then suggest different local structural arrangements. This is also supported by the first Al–Al distances, significantly shorter than Mn–Mn contacts in  $\text{Al}_{80}\text{Mn}_{20}$ . Experimental data give  $r_{\text{AlAl}} = 2.74 \text{ \AA}$  for  $\text{Al}_{80}\text{Mn}_{20}$  while theoretical analysis gives 2.76  $\text{\AA}$ . The distributions of the first heteroatomic pairs are centred at 2.54  $\text{\AA}$  for experiments and 2.55  $\text{\AA}$  for calculations, which correspond to short distances in comparison with Mn–Mn and Al–Al contacts.

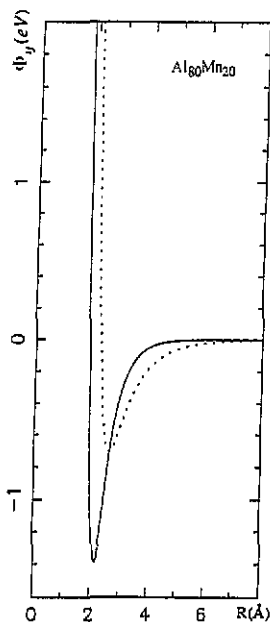


Figure 3. Mn–Al tight-binding bond potentials (eV): ..... , total; —, pd contribution.

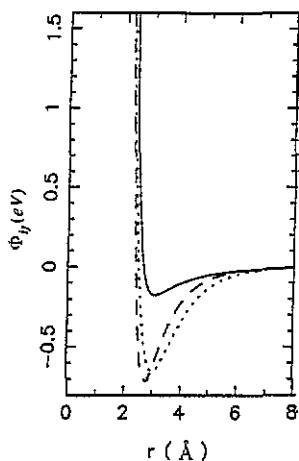


Figure 4. Tight-binding bond potentials (eV): —, Mn–Mn interaction; ---, Mn–Al interaction; ..... , Al–Al interaction.

Such local symmetry can be also confirmed by the bond-angle distribution functions (see figure 2). For  $\text{Al}_{80}\text{Mn}_{20}$ , the calculated distribution shows a prominent peak near  $63^\circ$  and a broad maximum near  $115^\circ$ , very close to the icosahedral bond angles of  $\theta = 63.5^\circ$  and  $\theta = 116.5^\circ$ . This peculiar structural behaviour may now be traced back to the variation of the interatomic forces and of the electronic structure. For liquid  $\text{Al}_{80}\text{Mn}_{20}$  alloy, figure 3 compares the total Al–Mn tight-binding bond potential with the partial one obtained by using the pd contribution only. We can see that the pd hybridization is very strong and represents the major part of the heteroatomic bond potential, leading to a strong interaction between Al and Mn atoms for both liquids. As shown in figure 4 this is reflected in a strong non-additivity of the bond potentials and the consequence is the formation of pairs of unlike atoms and short bond distances in the Al–Mn pairs. However, an important feature is that the Mn–Mn interaction is found to be very small in comparison with Al–Al or Al–Mn interactions. It can be thought that it is the peculiar behaviour of Mn–Mn interactions which can explain the topological ordering in  $\text{Al}_{80}\text{Mn}_{20}$  liquid alloy.

In conclusion, we have developed a new interatomic force field for liquid transition-metal–aluminium alloys which we believe contains an important improvement: the dependence of the pair interaction on the bond order determined by the strength of the pd hybridization. We have shown that applications to simulations of  $\text{Al}_{80}\text{Mn}_{20}$  liquid alloy are very promising. This will allow the study of the structure–property relationship of these materials at a level of detail not previously possible.

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