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Charge Transfers in Structurally Disordered Alloys

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Structurally disordered binary alloys are investigated for which an atomic basis set is adequate. An iterative tight-binding scheme within a non-orthogonal basis and interactions among all pairs of atoms is used. The properties of the disordered systems are obtained as averages over several groups of a small number of random configurations of atoms. As the systems are structurally disordered a charge distribution is obtained for each type of atom and its average value is defined as the charge transfer. It is found that while the electrons are transferred to the atoms with higher ionization potential, as expected, they are also transferred to the larger atoms, and that both effects are almost additive. The results explain the charge transfers of several liquid alloys such as Na_xK_{1-x}, Au_xAg_{1-x}, and the gold–alkali metal alloys.

Dans ce travail nous avons étudié des alliages binaires structurellement desordonnés avec un ensemble de fonctions d'onde atomiques. Nous avons appliqué une approximation de liaisons fortes iterative avec une base non-orthogonale et nous avons consideré l'interaction entre tous les pairs d'atomes. Les proprietés des systèms desordonnés sont obtenus en prennant des moyennes sur des differentes groupes de configurations de petit nombre d'atomes distribués au hasard. Comme les systèmes sont structurellement desordonnés nous avons trouvé une distribution de charge pour chaque type d'atome. On a pris la valeur moyenne de chaque distribution comme définition de la transference de charge. Tel comme on pourrait espérer les electrons sont transferés aux atomes de plus grand potential d'ionisation mais on trouve aussi qu'ils sont transferés aux atomes plus grands et que ces deux effets sont à peu près additifs. Les résultats obtenus peuvent expliquer les phenomènes de transference de charge des alliages liquides comme Na_xK_{1-x}, Au_xAg_{1-x} aussi bien que ceux des alliages Au-metaux alcalins.

1. Introduction

In this paper we study binary alloys with structural disorder, as in the liquid and amorphous states. These are studied by a semi-empirical iterative tight-binding procedure which is basically an extension of the extended Hückel method. Information about the eigenfunctions is contained in the charge-bond order matrix whose diagonal elements are formally associated to point charges on the atoms. Recent calculations [1, 2] have shown that even in disordered systems of identical atoms the atoms acquire different charges due to the differences in the fields around them. Thus a charge distribution $n(Q)$ can be defined, that gives the number of atoms with charges between Q and $Q + dQ$.

In binary ordered alloys, there is usually a charge transfer from one type of atom to the other. If the alloys are disordered, with either compositional or structural disorder, then there appears a different charge distribution for each type of atom. Our results show that the effect of having two different atomic sizes in a random system leads to an electronic charge transfer towards the larger atoms, defined as the average of the corresponding distribution. The differences in ionization potentials

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obviously produce charge transfers to the atoms with higher ionization potentials. Thus depending on the particular alloy, these two effects can produce charge transfers in the same or in opposite directions.

2. Method

To simulate the disordered system we average the properties of interest over several random groups of a small number, N, of atoms with periodic boundary conditions. To obtain each distribution a hard core diameter $D = 1.8\ a^*$ is introduced, a^* being the average of the radius of the outer orbitals of the atoms (see Table 1). We consider

Table 1

Ionization potentials (I), first neighbour distances in the solid (d), Bohr radius of the outer s orbital (a^*), and hard core diameter (D). Note that $D \approx 1.8a^*$ and $d \approx 2a^*$

	I (eV) [9]	d (Å) [10]	a (Å) [11]	D (Å) [12]
Li	5.390	3.00	1.586	2.70
Na	5.138	3.67	1.713	3.28
K	4.339	4.54	2.162	4.06
Rb	4.176	4.87	2.287	4.31
Cs	3.898	5.24	2.518	4.73
Ag	7.574	2.88	1.286	—
Au	9.220	2.87	1.187	—

systems where an atomic basis set is adequate and take into account interactions among all pairs of orbitals in a non-orthogonal basis [2]. For the particular case of one atomic orbital per atom, for each random group of N atoms, the system of linear equations to be solved is

$$\sum_{j=1}^{N} c_{\mu j}(H_{ij} - E_\mu S_{ij}) = 0\ . \tag{1}$$

H_{ij} and S_{ij} are the Hamiltonian and overlap matrix elements, E_μ is the orbital energy, and $c_{\mu j}$ are the coefficients of the wave function. The net charge on each atom is given by

$$Q_i = 1 - 2\sum_{\mu=1}^{\mu_F}\left[\frac{(c'_{\mu i})^2}{\sum_{j=1}^{N}(c'_{\mu j})^2}\right], \tag{2}$$

where the first sum is up to the Fermi level and

$$(c'_{\mu i})^2 = \sum_{j=1}^{N} c_{\mu i}c_{\mu j}S_{ij}\ .$$

In order to take into account the intraatomic electron repulsion, calculations are performed in an iterative way introducing the dependence of both diagonal and off-diagonal matrix elements on the atomic charges. A simple dependence is the frequently used linear one,

$$H_{ii} = -I_i - Q_i(I_i - A_i) \tag{3}$$

and

$$H_{ij} = CS_{ij}\left(\frac{H_{ii} + H_{jj}}{2}\right); \tag{4}$$

I_i being the ionization potential, A_i the electron affinity of atom i, and C a parameter

with value $1 < C \leqq 2$. Iterations are continued until the charges obtained from (2) are the same as those used as input in (3) and (4).

3. Results and Discussion

We consider alloys formed by metallic atoms with one conduction electron only, which for simplicity will be taken as a 1s orbital. We generate completely random alloys, that is, systems in which the distribution of atoms in space is completely random and also the type of atom at each of these sites is random, depending only on the concentration. We further limit ourselves to alloys where we believe that the only two important effects are the difference in ionization potentials of the outer orbitals and the difference in hard cores.

As in previous work we consider two-dimensional systems. We choose several groups of N random points inside a square of length $\varrho N^{1/2}$ with periodic boundary conditions. When each new random point is generated, its distance to all previously generated sites is calculated. If any one is smaller than the sum of the corresponding hard cores this new position is rejected. We start by setting the probability of the smaller atom A to be x^*, but due to the difference in hard cores the random procedure gives a final concentration of A larger than x^*, say x, so that the final alloy is A_xB_{1-x}. In fact, in the process of placing N atoms in a square the probability of rejecting a B atom is larger than for an A atom due to its larger hard core. The length ϱ and the hard-core diameters are measured in units of the average of the corresponding values of a^*. The parameter C of (4) is $C = 2$ and all A_i in (3) are $A_i = 0$. Our unit of energy is I, the average value of the two ionization potentials for the alloys, and charges are measured in units of $|e|$. Calculations are performed with ten groups of $N = 64$ atoms as we have shown that groups of this size represent correctly the main features of the charge distribution and of the density of states [3].

We show in Table 2 results for completely random alloys with the average distance between first neighbours $\varrho = 2.5$. The real liquids have higher densities, corresponding to $\varrho \approx 2.0$, but this is only possible in the presence of local order, that we do not consider here. Column 3 shows the effect of introducing two different hard cores as compared to column 2 of identical atoms. It is evident that there is more disorder as

Table 2

Results for totally disordered alloys for ten groups with $N = 64$

D_A	1.8	1.5	1.8	1.5
D_B	1.8	2.1	1.8	2.1
I_A	1.0	1.0	1.2	1.2
I_B	1.0	1.0	0.8	0.8
x	—	0.63	0.50	0.62
$\lvert Q_A\rvert < 0.1$	64	60	60	60
$\lvert Q_B\rvert < 0.1$		59	44	44
$Q_A < 0$	46	33	70	58
$Q_B < 0$	46	61	23	35
$\bar{Q}_A$	—	0.053	−0.075	−0.041
E_u	7.1	10.0	7.83	12.6
E_l	−1.96	−2.00	−2.12	−2.29

In all calculations $\varrho = 2.5$, $C = 2$, $A = 0$, and $x^* = 0.5$. $|Q_A| < 0.1$ represents the percentage of A atoms with charges between $+0.1$ and $-0.1e$. $\bar{Q}_A$ is the average total charge of the A atoms in units of $|e|$. E_u and E_l are the upper and lower limits of the band obtained from the 640 levels. Statistical errors will possibly affect the last significant figures in this table.

the charge distribution is wider (the proportion of atoms with charges between 0.1 e and -0.1 e is smaller) and also the density of states is wider (see E_u and E_1). There is an average electronic charge transfer from the A to the B atoms, which is also evident from the difference in the percentage of negatively A and B charged atoms. This can be qualitatively understood because the larger atoms have their neighbours further away than the smaller ones thus being more isolated (having smaller interactions with neighbours). In a tight-binding scheme an almost isolated atom has a wave function nearly localized around it with energy close to the ionization potential. In the systems studied by us the ionization potentials lie always below the Fermi level and thus the isolated atom becomes negatively charged. Column 4 shows the effect of two different ionization potentials and a charge transfer towards the atom with higher ionization potential is obtained, as expected. We also note that the charge distribution for the B atoms is wider than all previous distributions. We do not know the reason for this effect. The results of column 4 would correspond to alloys like AuAg and AuLi where the difference in hard cores is negligible (see Table 1). In particular for the AuAg alloy our charge transfer $\bar{Q}_A$ compares reasonably with that calculated for the s conduction band in previous work by Gelatt and Ehrenreich [4]. This paper refers to a solid alloy only with compositional disorder while our calculations refer to liquid systems that also have structural disorder thus producing a charge distribution for each type of atom. Column 5 shows the combined effect of different hard cores and different ionization potentials. In this particular example, where the parameters are close to those for Na_xK_{1-x}, there remains a small charge transfer of magnitude and sign similar to that calculated in [5]. The charge transfer in this alloy is very small as it is a combination of two opposite effects. The density of states is the widest obtained, due to the presence of both compositional disorder and structural disorder with two different hard cores. However, it is known that this alloy presents some degree of local order [6]. For the extreme case of an ordered AB square lattice with $I_A = 1.2$ and $I_B = 0.8$ the charge transfer is only slightly larger than 0.1 e. Thus, even in a partially ordered alloy the charge transfer will be small.

We have not made calculations for very large hard cores or ionization potential differences, which would produce very large charge transfers and thus the iterative procedure would depend crucially on the type of dependence of the matrix elements on the charges. However, our analysis is also useful to qualitatively understand their behaviour. Liquid alkali metal gold alloys are examples of this type of materials and it is well known [7] that while the lithium and sodium gold alloys are metallic in the whole concentration range, the Au_xRb_{1-x} and Au_xCs_{1-x} become insulators for $x = 0.5$. The insulator character is usually attributed to the large charge transfer which makes the material ionic. We believe that the behaviour of all these gold alloys can be explained qualitatively if, apart from the effect of different hard cores and ionization potentials, the degree of local order is also considered. In fact, when there is a tendency of each type of atom to be surrounded by atoms of the other type the effect of the different hard cores becomes irrelevant: the larger atoms have their neighbours at the same distance as the smaller ones. This is the case of Au_xCs_{1-x} at equiconcentration where previous calculations [8] indicate that there is strong local order. A large charge transfer, only due to the large ionization potential difference, is thus expected. At dilute concentrations the disorder becomes important and therefore the large hard-core difference is effective and produces an opposite charge transfer (see Table 1). Thus the charge transfer is maximum at equiconcentration. In the case of AuLi there is practically no difference in the hard cores and the system seems to be completely disordered in the whole concentration range [8]. A not too large charge transfer due to the different ionization potentials is thus expected.

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