

The functional dependence of the cohesive energy on coordination in transition-metal systems

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

1994 J. Phys.: Condens. Matter 6 3939

(<http://iopscience.iop.org/0953-8984/6/21/018>)

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 12/05/2010 at 18:29

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

The functional dependence of the cohesive energy on coordination in transition-metal systems

J Guevara, M Weissmann and A M Llois

Departamento de Física, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, 1429 Buenos Aires, Argentina

Received 1 December 1993, in final form 28 February 1994

Abstract. The energy of an atom as a function of its coordination number has been calculated within the tight-binding model for added vacancies in FCC and BCC lattices considering s and d orbitals. We show that the dispersion due to the different possible topologies of nearest-neighbour vacancies is larger when d bands are replaced by five degenerate s bands in simplified models. We also show that when calculations are performed going beyond the second moment the cohesive band energy follows approximately a square-root dependence with coordination for s bands but that for d bands it has a different dependence.

Besides the case of a bulk atom with different numbers of nearest-neighbour vacancies, the cases of surfaces and lattices containing uniformly distributed vacancies have also been considered.

1. Introduction

During the last decade different approaches to approximate the total energy of metallic systems have been introduced in order to obtain suitable potentials for computer simulations [1, 2, 3, 4, 5]. In a recent paper Hakkinen *et al* [6] have compared the results obtained by one of these approximate methods, the effective-medium theory, with exact results for the band energies, calculated within the same simple model, namely the nearest-neighbour s-type tight-binding Hamiltonian for half filling. In that work the covalent bond energy (band energy) of an atom, E_c , was calculated by the moments method as a function of all topographically different configurations of its nearest-neighbour vacancies in the whole range of coordination for the FCC lattice. The weighted, averaged energy curve was shown to follow closely a square-root dependence of coordination predicted by the tight-binding theory in the second-moment approximation.

We are interested in transition-metal systems whose properties are to a considerable degree dominated by d-band electrons. It is assumed, especially when doing molecular dynamics in the second-moment approximation, that d bands can be replaced by five degenerate s bands and thereafter we can take for the covalent bond energy of an atom a square-root dependence of the second moment of the local density of states (effective coordination number). In this contribution we go beyond the s-band model, take into account the symmetry of the d orbitals and consider different band fillings in order to calculate E_c as a function of coordination number, for both FCC and BCC lattices. We use the recursion method [7] to perform the calculations. We show that when local charge neutrality is required E_c shows an approximate square-root dependence for the s band, but for d bands $E_c = AC_1^n$ with n approximately $\frac{2}{3}$ and C_1 the number of nearest neighbours left

when vacancies are introduced in the nearest-neighbour shell and only nearest-neighbour interactions are considered. As we shall see C_1 is actually the effective coordination number, which is proportional to the second moment of the local density of states

By the same method we study the covalent bond energy for surface atoms with different coordination and finally a lattice which contains uniformly distributed vacancies.

The situations considered in this paper are very simple (and quite unphysical) as the number of neighbours changes but there is no relaxation in the structure. We do this to be able to compare J approximations with 'exact' tight-binding results.

2. Method of calculation

We consider s- or d-band tight-binding Hamiltonians of the form

$$H = \sum_{i,m} \epsilon_i^m c_i^{\dagger m} c_i^m + \sum_{i,j,m,m'} t_{ij}^{mm'} c_i^{\dagger m} c_j^{m'} \quad (1)$$

where $c_i^{\dagger m}$ (c_i^m) is the creation (annihilation) operator of an electron state on lattice site i , m denotes the band and $t_{ij}^{mm'}$ are the hopping elements of the Hamiltonian. ϵ_i^m are the site energies. In almost all cases only nearest-neighbour interactions are considered. Due to screening effects we expect charge transfers among atoms in metallic systems to be very small. Actually, *ab initio* calculations show that transition-metal atoms in configurations of lower coordination than in the bulk, i.e. surfaces, have nearly the same d-band occupations as in the perfect bulk. In a first approach we can take this into account by requiring local charge neutrality. The Hamiltonian is then solved iteratively by shifting the diagonal elements corresponding to the atom for which the covalent bond energy is being calculated, that is

$$\epsilon_i^m = \epsilon_{i0}^m + \alpha. \quad (2)$$

By local charge neutrality we mean that the parameter α , independent of orbital symmetry, is adjusted so that there is no atom-to-atom charge transfer, within an error of $10^{-4}e$.

The covalent bond energy of the i th atom is given by [4]

$$E_c(i) = \sum_m \int_{-\infty}^{E_F} (E - \epsilon_i^m) n_i^m(E) dE \quad (3)$$

where $n_i^m(E)$ is the local density of states on the m th orbital of the i th atom. To obtain $n_i^m(E)$ we used the recursion method within the Green-function formalism. In all cases four levels (eight moments) of the recurrence expansion were considered ensuring a convergence error of less than 0.05% in the bulk covalent bond energy independent of band filling. We used the standard quadratic termination for the continued fraction expansion with the final coefficients equal to the limiting ones of the bulk material. The values used for the nearest-neighbour two-centre integrals are $ss\sigma = -W/16$ for s bands, $dd\sigma = -W/8$, $dd\pi = W/16$, $dd\delta = 0$ for FCC d bands and $dd\sigma = -W/6.5$, $dd\pi = W/13$ and $dd\delta = 0$ for BCC d bands, W being the bandwidth.

3. Results and discussion

We calculated the covalent bond energy for an atom as a function of coordination and band filling for FCC and BCC structures considering three situations. The first case was that of

a bulk atom with nearest-neighbour vacancies in the corresponding lattice structure and considering all topographically different configurations for a given coordination number as in [6]. The second case was that of a surface atom for different surface orientations, which implies different coordination. In this situation there is only one possible topology for each coordination. For these two cases the Fermi level of the system is the bulk Fermi level. The third case was a system consisting of atoms and randomly distributed vacancies, a 'hole net' for three different hole concentrations. In this last case the Fermi level is not the bulk one and it is obtained self-consistently.

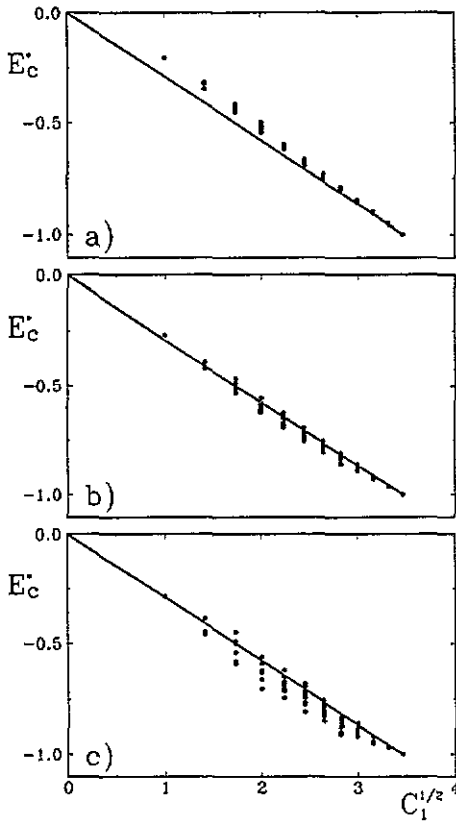


Figure 1. Covalent bond energies, E_c^* , versus $C_1^{1/2}$ for the FCC structure, one s orbital per atom and different band fillings, η , with local charge neutrality. The E_c^* are normalized to the corresponding bulk value, and C_1 is the number of nearest neighbours. (a) $\eta = 0.6$; (b) $\eta = 0.5$; (c) $\eta = 1.4$.

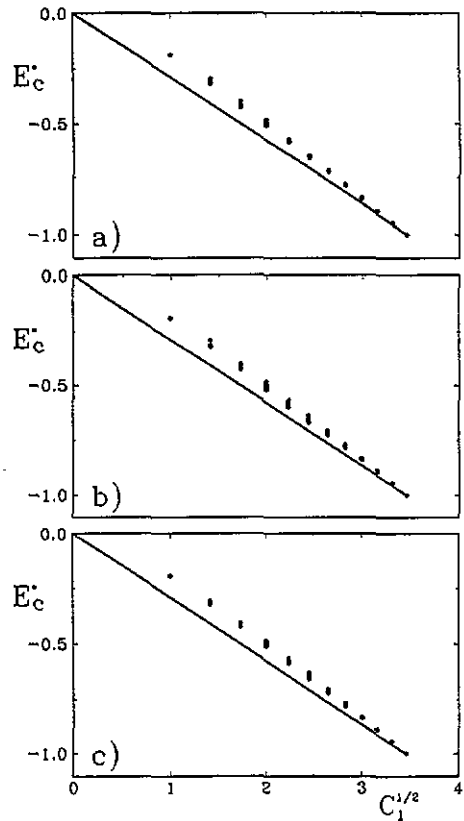


Figure 2. Same as figure 1 but for d orbitals. (a) $\eta = 3$; (b) $\eta = 5$; (c) $\eta = 7$.

In figure 1 we show E_c^* versus $\sqrt{C_1}$ (E_c^* is the covalent bond energy normalized to the corresponding bulk one) for the first case of a bulk atom in an FCC lattice considering only one s orbital per atom and different band fillings. If the band is not half filled, local charge neutrality is required. We find an approximately linear dependence, as in [6]. In figure 2 we show the results for the same case as figure 1 but considering d bands instead of s bands. It is clearly seen that the dispersion is smaller when d-orbital symmetries are

taken into account. When local charge neutrality is imposed it is always possible to fit a linear dependence of E_c versus $\sqrt{C_1}$, but E_c does not go to zero for $C_1 = 0$ as it should within the tight-binding model with nearest-neighbour interactions. Looking for a better fit we found that E_c follows, for d bands, an approximately $C_1^{2/3}$ dependence, independently of band filling. In figure 3 we show the results obtained for the FCC structure and the same band fillings as in figure 2 but plotting now E_c^* versus $C_1^{2/3}$.

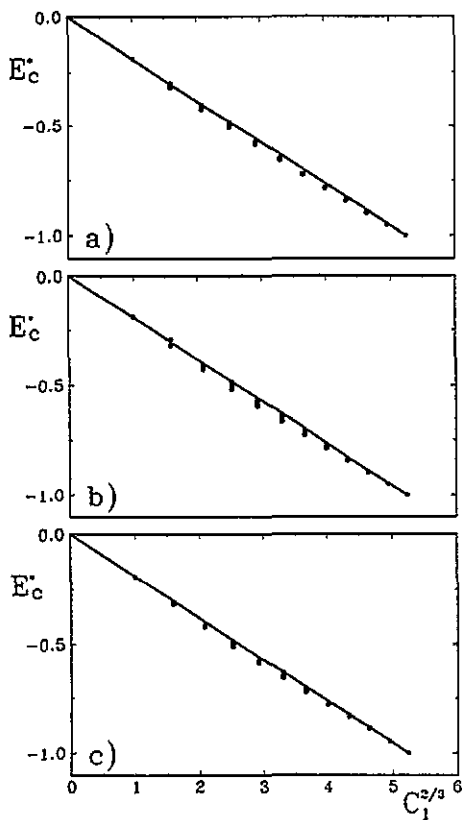


Figure 3. Same as figure 2 but plotting E_c^* versus $C_1^{2/3}$.

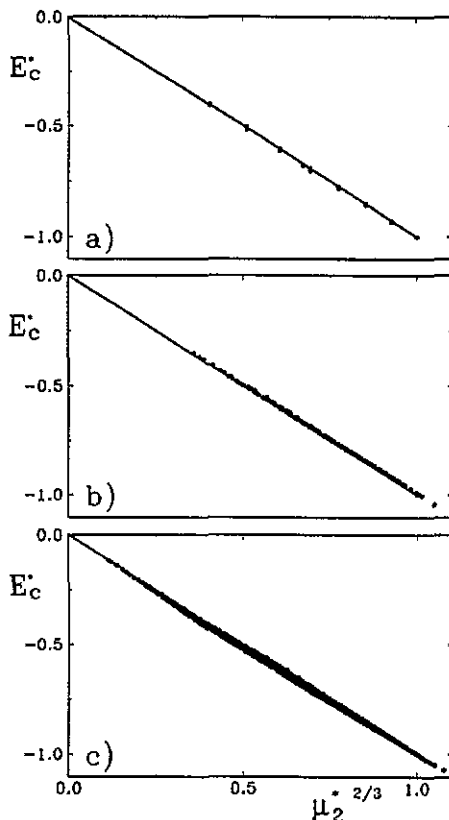


Figure 4. E_c^* versus $\mu_2^{*2/3}$, the second moment of the local density of states normalized to the corresponding bulk one. (a) BCC lattice with first- and second-neighbour interactions and $\eta = 3$. (b) The same example but with the central atom moved from its lattice site. In units of the lattice parameter $\Delta x = 0.02$, $\Delta y = 0.05$ and $\Delta z = -0.03$. (c) FCC lattice with the central atom moved from its lattice site. $\Delta x = 0.05$, $\Delta y = 0.02$ and $\Delta z = -0.03$, and $\eta = 7$. In (b) and (c) the different topologies are not degenerate and the figures show 256 and 4096 points respectively.

Results for the BCC structure with only nearest-neighbour interactions are very similar to the ones shown here for FCC systems and are therefore not shown. In this case the dispersion is smaller due to the fact that odd moments are zero in the BCC structure. However, for the BCC structure the second-neighbour interactions are known to be significant and it is

interesting to show here that in this case E_c is proportional to $\mu_2^{2/3}$ (the second moment of the local density of states)

$$\mu_2(i) = \sum_m \int_{-\infty}^{+\infty} (E - \epsilon_i^m)^2 n_i^m(E) dE. \quad (4)$$

Therefore for more general plots of the kind of figures 1–3 C_1 should be considered as the effective coordination number within the given model and replaced by μ_2 . In figure 4(a) we show E_c^* versus $\mu_2^{*2/3}$ (μ_2^* is the second moment normalized to the corresponding bulk one) for the BCC structure and a band filling of three electrons considering nearest- and next-nearest-neighbour interactions (but only first-neighbour vacancies as before) and find a very good fit. The second-neighbour two-centre integrals are related to the already given first-neighbour ones by an r^{-5} dependence with distance [8].

To make the dependence of E_c on μ_2 even more evident we moved the central atom away from its lattice site and therefore changed the distances to all its neighbours, again using the r^{-5} law for the integrals. Figure 4(b) shows the results obtained for the same example as figure 4(a), which are quite surprising. Finally, figure 4(c) shows another example, the FCC structure with a band filling of seven electrons and the central atom moved. The $\mu_2^{*2/3}$ dependence is also clearly evident.

For the second case studied, we calculated E_c for an atom in the three surface orientations (110), (100) and (111) of an FCC structure, with values for C_1 equal to 7, 8 and 9 and d bands. Even if the environment of the atom studied is very different in surface and bulk cases, these energies fall within the dispersion obtained for the corresponding coordination number in the bulk calculation with nearest-neighbour vacancies. This naturally implies that the contribution of first neighbours is the most important. The effect of moments higher than the second one, which involve further neighbours, is responsible for the dispersion in energy.

For the 'hole net' we considered an FCC lattice with a variable number of holes inside a cell of 32 sites and d orbitals. The holes were randomly distributed and the cell periodically repeated. For each hole concentration the values of E_c for each atom of the cell were obtained for only one configuration of the vacancies. For the three concentrations and different band fillings considered we obtained again that $E_c = AC_1^{2/3}$. In figure 5 we show an example of E_c^* versus $C_1^{2/3}$ for the 12/32-hole net with a band filling of three electrons per atom and local charge neutrality.

In conclusion, we have shown that for a more realistic study of transition-metal systems taking into account the symmetry of the relevant d orbitals, a $\frac{2}{3}$ power of the effective coordination number or second moment for the cohesive bond energy fits better the multi-atom interactions than the square-root dependence suggested by the second-moment approximation, the latter being appropriate for s-orbital interactions. The validity of this dependence has been tested for different situations: (a) a fixed value of the Fermi level, (b) a non-bulk value for the Fermi level, (c) interactions beyond first-nearest-neighbour ones. The particular power-law dependence of E_c (the attractive part of the total energy) will show up when studying the dynamics of these systems, for instance melting, diffusion and relaxation processes. Molecular-dynamics calculations using this dependence will be attempted. It may be possible to improve potentials for computer simulations of transition-metal systems without computing moments higher than the second ones but taking into account the symmetry of the orbitals which mainly contribute to the band energy.

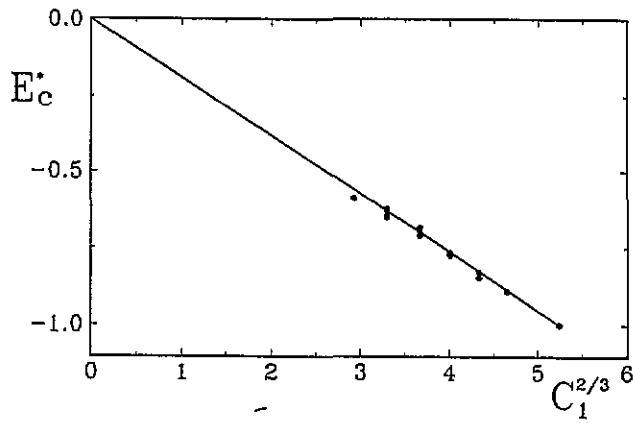


Figure 5. E_c^* versus $C_1^{2/3}$ for the 12/32-hole net with the FCC structure, d orbitals, local charge neutrality and $\eta = 3$.

Acknowledgments

We acknowledge grants from Fundaci3n Sauber3n and Consejo Nacional de Investigaciones Cientificas y T3cnicas (CONICET) for partial support of this work.

References

- [1] Jacobsen K W, Norskov J K and Puska M J 1987 *Phys. Rev. B* **35** 7423
- [2] Daw M S and Baskes M I 1984 *Phys. Rev. B* **29** 6443
- [3] Finnis M W and Sinclair J E 1984 *Phil. Mag.* **A 50** 45
- [4] Sutton A P, Finnis M W, Pettifor D G and Ohta Y 1988 *J. Phys. C: Solid State Phys.* **21** 35
- [5] Ercolessi F, Tosatti E and Parrinello M 1986 *Phys. Rev. Lett.* **57** 719
- [6] H3kkinen H, Mansikka-aho J and Manninen M 1991 *J. Phys.: Condens. Matter* **3** 7757
- [7] Haydock R 1980 *Solid State Physics* vol 35, ed F Seitz, H Ehrenreich and D Turnbull (New York: Academic)
- [8] Harrison W A and Froyen S 1980 *Phys. Rev. B* **21** 3214