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From the Hückel model to effective-medium theory

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Abstract. The energy of an atom as a function of all topographically different configurations of its nearest neighbours in the whole range of coordination in the FCC lattice is calculated using a simple Hückel Hamiltonian. The result follows closely the square-root dependence of the coordination number. The implications of this result in the effective-medium theory of metals are discussed.

1. Introduction

The approximate 'embedded-atom' (EAM [1] and related methods [2, 3]) or 'effective-medium' (EMT) [4–6] schemes have made available a new way of modelling the energetics of metals in a form suitable for computer simulation of finite-temperature phenomena. They overcome the difficulties inherent in classical pair potentials of describing the many-atom features of electronic cohesion, which manifest themselves in defect energies, elastic properties and in the surface structure [7]. All the recent models [1–5] can be written in a common form having two principally different constituents in the total energy E of a metallic system of N atoms:

$$E = \sum_{i=1}^{N} F(\rho_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i} V(r_{ij}) \qquad (1)$$

where F is a non-linear cohesive function depending on a local quantity ρ_i at the atomic site i and V has the form of a classical pair potential. The derivation and interpretation of the two parts in the total energy expression vary considerably from one model to another. For example, in the EAM-related model of Finnis and Sinclair [2], $F \propto \sqrt{\rho}$, and ρ is interpreted as a sum of squares of overlap integrals. In EMT [5], on the other hand, F is interpreted as the energy change when an atom is embedded in a homogeneous electron gas having an uniform density of ρ. This reflects in a way the possibility of dividing the metallic 'bonding' into the d–d interaction part, or s–d or s–p hybridization parts among transition, noble and simple metals [8–12].

The purpose of this work is to introduce a simple model where we can compare the effective-medium results with the exact results calculated within the same model. For that purpose we use the nearest-neighbour Hückel Hamiltonian and the method of moments. The energy of an atom is calculated as a function of all topographically different configurations of its nearest neighbours in the whole range of coordination in the FCC lattice. The weighted, averaged energy curve is shown to follow closely

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the square-root dependence of coordination, which is predicted by the tight-binding theory. As our model system is best suited to describing s-type one-electron states of a real metal, this calculation introduces a new way of approximating the error made in the omitting of the one-electron energy term in the effective-medium theory. Furthermore, we can estimate the effect of more distant neighbours in the defect energies.

We continue by describing briefly our calculational method in section 2 and discussing the results in section 3. Conclusions are made in section 4.

2. Model and method

We consider the simplest possible case of crystal binding in the tight-binding theory: one s-type orbital per lattice site forming an s band. The interaction between lattice sites is determined via the nearest-neighbour Hückel Hamiltonian:

$$\begin{aligned} &H = \sum_{i,j} h_{ij} |i\rangle\langle j| \qquad \langle i|j\rangle = \delta_{ij} \\ &h_{ij} = -1 \qquad \text{when } i, j \text{ are nearest neighbours} \\ &h_{ij} = 0 \qquad \text{elsewhere.} \end{aligned} \tag{2}$$

With this model Hamiltonian it is easy to calculate the moments $\mu_i^{(n)}$ of the local density of states $g_i(\epsilon)$ [8]:

$$\mu_i^{(n)} = \int_{-\infty}^{\infty} \epsilon^n g_i(\epsilon)\,\mathrm{d}\epsilon = \langle i|H^n|i\rangle = \sum_j \sum_k \ldots \langle i|H|j\rangle\langle j|H|k\rangle\langle k|H \ldots H|i\rangle. \tag{3}$$

Graphically the calculation of $\mu^{(n)}$ involves n linked steps via nearest neighbours in the lattice starting and ending at site i. We have constructed the local density of states of its moments up to $\mu^{(8)}$ by using a polynomial expansion

$$g_i(\epsilon) = A_1(\epsilon - \epsilon_{\min})^{1/2} + \sum_{m=2}^{9} A_m(\epsilon - \epsilon_{\min})^m \tag{4}$$

where $\epsilon_{\min}$ is the bottom of the band. While our method is not capable of extracting the fine structure of $g(\epsilon)$ of $\mu^{(n)}$, it is adequate for producing the energy of an atom, defined as

$$F_i = \int_{\epsilon_{\min}}^{\epsilon_F} \epsilon g_i(\epsilon)\,\mathrm{d}\epsilon \tag{5}$$

where ϵ_F is the Fermi energy of the system. The total energy of the system is then

$$E = \sum_i F_i. \tag{6}$$

If F_i depends only on the coordination number of the atom i we recover the first term in (1) and the pair potential term is not needed. For simplicity, we make the calculations non-self-consistently by keeping the Fermi energy in (5) fixed at its bulk value in all situations.

3. Results and discussion

The cohesive energy per atom in an ideal FCC lattice is shown in figure 1 as a function of the order of the moment expansion (4) used in the calculation of the local density of states. We see that when going beyond the third moment the cohesive energy per atom changes by less than one per cent. This validates to some extent the wide use of the second-moment approximation in describing of the cohesive band energy in the tight-binding theory [2, 10] and also shows that our polynomial expansion (4) is adequate for the present calculation, where only the cohesive energy (being an *average* property of the band) is of interest Note that in our FCC case the local density of states is asymmetric. Previously it has been shown [13] that the cohesive energy for a symmetric band (such as in SC or BCC) can be obtained within a few per cent using the first four moments of the local density of states.

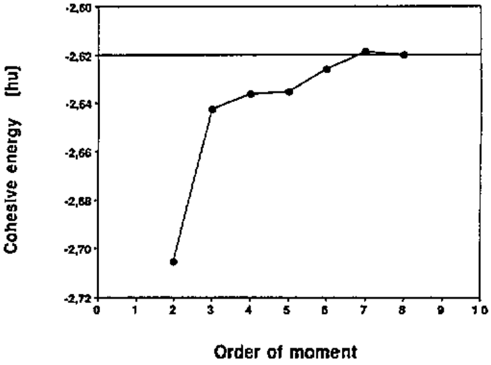

Figure 1. The energy per atom (HU) in a perfect FCC lattice as a function of the order of the moment expansion. The exact value for an FCC lattice is −2.62 HU.

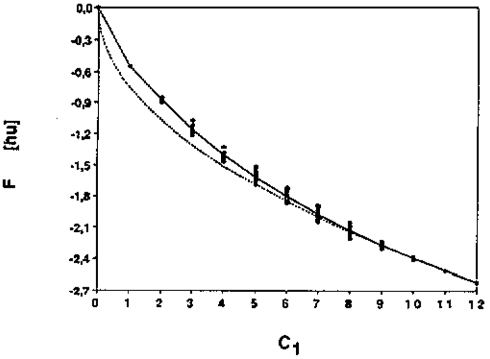

Figure 2. The energy F of an atom as a function of all topographically different configurations of its nearest neighbours in the whole coordination range $1 \leqslant C_1 \leqslant 12$ in the FCC lattice (dots). The solid curve is the weighted, averaged $F(C_1)$ and the dashed curve is a one-parameter fit $F = -(2.62/\sqrt{12})\sqrt{C_1}$.

The main result of this paper is presented in figure 2, which shows the energy of an atom in an FCC lattice as a function of all topographically different configurations of its nearest neighbours in the whole coordination range $1 \leqslant C_1 \leqslant 12$. The number of different possibilities for making vacancies in the vicinity of an atom in the FCC lattice for different values of C_1 are tabulated in table 1. Figure 2 clearly shows a smooth, non-linear, *many-atom* dependence of C_1, which is in fact not very far from the simple one-parameter fit to the square-root function, shown also in the same figure.

The deviation of the points around the weighted, averaged $F(C_1)$ curve in figure 2 is maximal (about 5%) at around $C_1 = 6$, as would be expected from table 1. In the present model, this deviation can be regarded as a measure of intrinsic directionality bonding effects. It must be noted, however, that at low coordination our system is quite unrealistic. In the limit of $C_1 = 1$, the system consists of an atom having only one other atom within the nearest-neighbour radius, beyond which there exists an ideal FCC lattice.

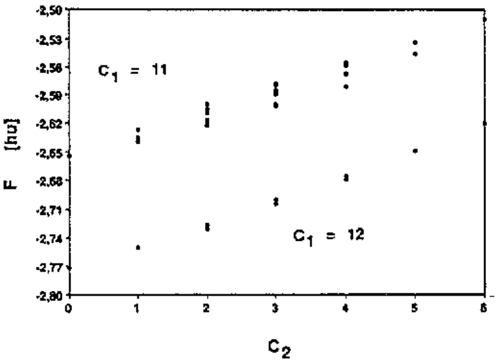

Figure 3. The energy F of an atom when C_1 is fixed at 11 or 12 and C_2 is varied from 1 to 6 in a FCC lattice.

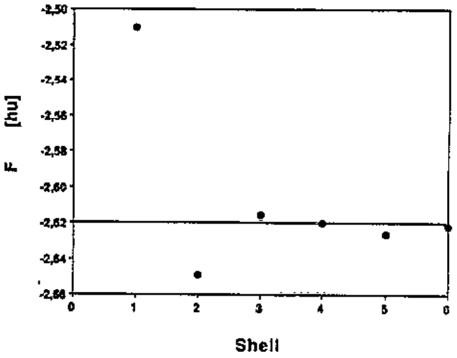

Figure 4. The effect of a vacancy on the energy of the first six neighbouring shells in the FCC lattice. The (negative of) the bulk cohesive energy −2.62 HU is shown for comparison.

We can study the effect of the next-nearest neighbours on the cohesive energy by fixing C_1 and varying C_2 from 1 to 6 in FCC lattice. We have done this for $C_1 = 11, 12$ and the results are shown in figure 3. The proportional effect of the next-nearest neighbours on the cohesive energy is seen to be of the same order of magnitude (5%) as the effect arising from the directionality in the nearest-neighbour bonds.

Table 1. The number N of topographically different ways to place the nearest neighbours around an atom in the FCC lattice. The second column shows N in the case where C_1 is varied from 1 to 12, and the fourth and the fifth columns show N in the cases where C_2 is varied from 1 to 6 and C_1 is fixed to 12 and 11, respectively. The situation is symmetric with respect to $C_1 = 6$ and $C_2 = 3$.

C_1	N	C_2	$N(C_1 = 12)$	$N\ (C_1 = 11)$
1	1	1	1	3
2	4	2	2	7
3	9	3	2	8
4	16			
5	24			
6	28			

The results in figures 2 and 3 show that the total energy in the Hückel model mainly depends on the coordination numbers of atoms. This gives further support to the EAM/EMT methods. In particular, the results indicate that the sum over the one-electron eigenvalues in the effective-medium theory can be incorporated in the cohesive function [1, 4, 5] and that the error made in doing so is small in most cases. However, the variation of the energy with topology becomes important in small clusters [14] where the effects of discrete one-electron energy levels have to be explicitly included in the effective-medium theory.

For calculating defect energies we parametrize the cohesive energy function in

Table 2. Defect energies calculated using the Hückel model in the FCC lattice. σ_{111}, σ_{100} and σ_{110} are the surface energies for the three basic faces of FCC, $\sigma_{110}^{\mathrm{MR}}$ is the surface energy for an (1 × 2) missing-row reconstructed (110) face and E_{VF} is the vacancy formation energy. The surface energies are given in Hückel units × a^{-2} (a is the FCC lattice parameter). For comparison, the cohesive energy per atom E_{coh} is also given. The 'exact' results are obtained by direct lattice summations involving moments up to $\mu^{(8)}$. The second and the third columns show the results from the parametrized model (7) taking into consideration the changes in C_1 and C_1, C_2, respectively. The 'exact' vacancy formation energy has been calculated by taking into consideration the energy changes around the vacancy up to the sixth shell (see figure 4).

	Exact	$E = A\sqrt{C_1}$	$E = A\sqrt{C_1} + BC_2$
σ_{111} (HU a^{-2})	0.76	0.81	0.64
σ_{100} (HU a^{-2})	1.00	0.96	0.76
σ_{110} (HU a^{-2})	1.01	1.03	0.89
$\sigma_{110}^{\mathrm{MR}}$ (HU a^{-2})	0.98	1.02	0.85
E_{VF} (HU)	1.08	1.34	1.19
E_{coh} (HU)	2.62	2.62	2.62

the FCC lattice in terms of the number of nearest and next-nearest neighbours as

$$F(C_1, C_2) = A\sqrt{C_1} + BC_2 \tag{7}$$

where $A = -0.756$, $B = 0.025$ and C_1, C_2 are the corresponding coordination numbers. Equation (7) gives the energy in Hückel units (HU), which are defined by fixing the nearest-neighbour interaction energy as unity in (2). In Hückel units, the cohesive energy per atom in a perfect FCC lattice is 2.62. The linear coefficient B is determined from the data shown in figure 3. We have calculated (table 2) the vacancy formation energy, the surface energy for (100), (110) and (111) faces of the FCC lattice, as well as the energy for the (1 × 2) missing-row reconstructed (110) surface. For comparison we have given also the 'exact' values calculated directly using moments up to $\mu^{(8)}$. It is seen that the simple $\sqrt{C_1}$ dependence gives the surface energies quite well but overestimates the vacancy formation energy by 25%. The inclusion of the next-nearest neighbours brings the vacancy formation energy nearer to the 'exact' value, but makes the surface energies worse. This may reflect the fact that our parametrization (7), made on the basis of near-bulk coordination, is not adequate for describing energetics of surface atoms. Another interpretation would be that the total energy is not easily separable into parts arising from the nearest, next-nearest etc contributions [8]. In fact, our model may lead to 'Friedel oscillations' in surface energies if more and more distant neighbours were to be included, as illustrated in figure 4 for the vacancy formation energy.

Our model stabilizes the (1 × 2) missing-row reconstructed (110) surface with respect to the unreconstructed (110). For the $\sqrt{C_1}$ model this is not a surprise, since the reconstruction energy has been shown to be proportional to the negative of the curvature in the cohesive function and is then always negative in EAM/EMT models with only nearest-neighbour interactions [15]. The inclusion of the next-nearest neighbours does not make the situation more realistic, as in our expression (7) the energy *rises* as a function of increasing C_2, which leads to the negative formation energy for the step in the (1 × 2)(110) surface [15].

4. Conclusions

The energy of an atom as a function of all topographically different configurations of its nearest neighbours in the FCC lattice has been calculated using a simple Hückel Hamiltonian and the method of moments. The calculation leads to a non-linear energy function, where the leading term can be described well by the $\sqrt{C_1}$ dependence from the second-moment approximation in the tight-binding theory. The present model allows the estimation of the effects arising from the one-electron energy levels in the cohesive energy as well as the effects from more distant neighbours to the defect energies.

Acknowledgments

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