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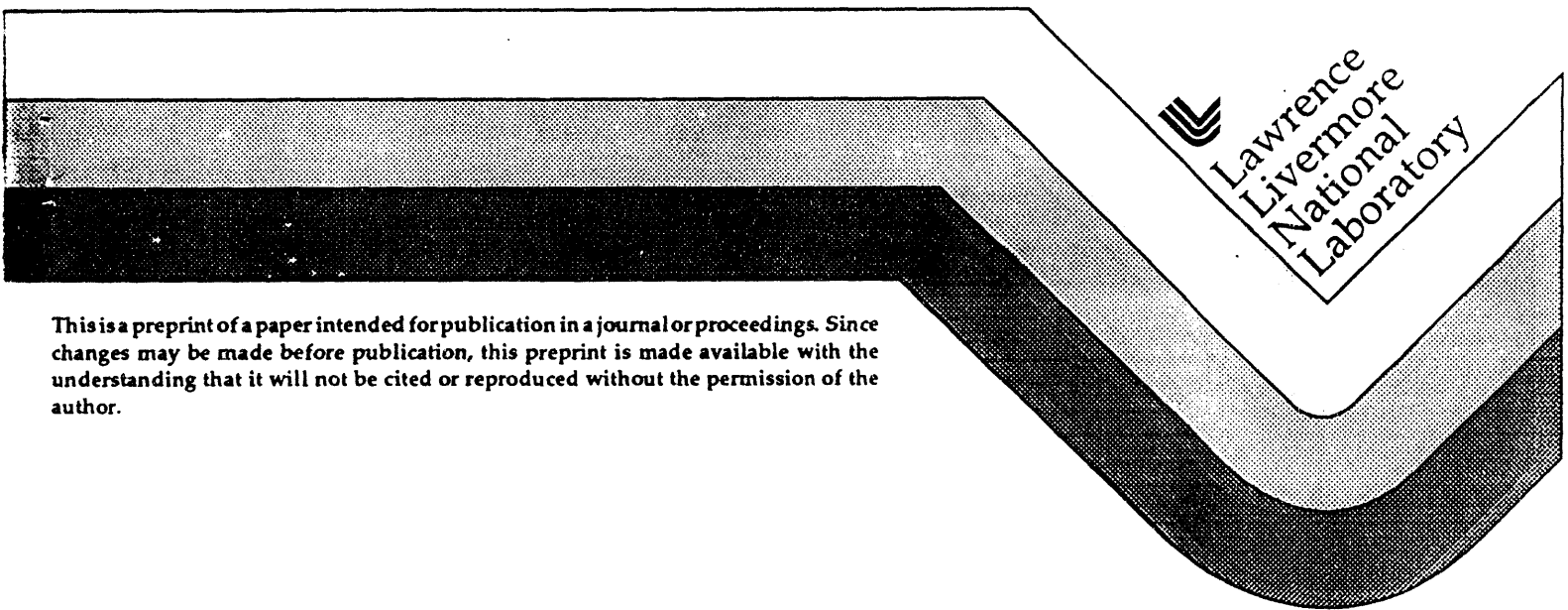
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SIMPLE AND COMPLEX PHASES IN TRANSITION
METALS**

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ELECTRONIC STRUCTURE AND STABILITY OF SIMPLE
AND COMPLEX PHASES IN TRANSITION METALS

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Abstract

Electronic factors that explain the relative stability of simple and complex phases in transition metals are examined within a realistic tight-binding model. A repulsive pairwise interaction of the Born-Mayer type is added to the band energy term. The parameters of this short-ranged repulsive term are determined by fitting the total energy to elastic properties of the bcc-based metal. The model is further simplified by introducing the Linear Green function Method. The study focuses on the properties of molybdenum, correctly predicting bcc as the stable phase.

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Introduction

The study of complex systems with realistic simulations techniques such as Molecular Dynamics or Monte Carlo has rapidly developed in the past few years. Meanwhile, the application of these methods is limited by our knowledge of the interaction potentials or forces among the atoms. To be useful the working models should be computationally efficient to treat a large number of atoms while providing a reliable representation of the structural and energetic properties of the systems under study. Methods such as the Car-Parrinello [1] scheme can treat the interatomic interactions accurately in the framework of *ab initio* density-functional theory within the local density approximation. However, to study real systems this scheme has been rather limited by the large computational effort which is required. A tight-binding approach seems to be still the most suitable method for this kind of calculations in systems with localized electrons like transition metals and their alloys, or in covalent systems (such as Si or C). The goal of the current work is to explore the applicability of such a method at different levels of approximations. After a brief description of the model, we present an application to the problem of structural stability in the case of a transition metal, namely molybdenum.

Model

We start by describing the total energy of the system per atom as the sum of two contributions,

$$E_{Tot} = E_{Band} + E_{Rep}, \quad (1)$$

where E_{Band} is the one-electron band energy calculated for a parametrized tight-binding (TB) hamiltonian, and E_{Rep} is a short-ranged repulsive energy to ensure crystal stability. The TB hamiltonian takes the usual form

$$H_o = \sum_{i\lambda} |i\lambda\rangle \epsilon_i^\lambda \langle i\lambda| + \sum_{\substack{j \\ \lambda\mu}} |i\lambda\rangle \beta_{ij}^{\lambda\mu} \langle j\mu|, \quad (2)$$

where i, j are site indices, λ, μ are orbital indices, and the ϵ and β refer to the on-site energies and hopping integrals, respectively.

The TB parameters are required to be both transferable and suitable to use in extensive Monte Carlo or Molecular Dynamics simulations. They are typically extracted from *ab initio* (or fitted to) band structure calculations. The band energy may be written as

$$E_{Band} = \int_{-\infty}^{E_F} E n(E) dE, \quad (3)$$

where E_F is the Fermi energy and $n(E)$ the density of states. This last quantity can be calculated using the familiar continued fraction expansion

$$n(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im Tr } G(E + i\epsilon) \quad (4)$$

with

$$G(z) = \langle 0 | \frac{1}{z - H} | 0 \rangle = \frac{1}{z - a_1 - \frac{b_1^2}{z - a_2 - \dots}}. \quad (5)$$

The coefficients a_n and b_n^2 , associated with the n^{th} level of continued fraction, are calculated using the recursion method [4].

The repulsive term is usually built up from a sum of two-center potentials.

$$E_{Rep} = \sum_{i < j} \Phi(r_{ij}), \quad (6)$$

where r_{ij} is the distance between atoms i and j , with $r_{ij} < r_c$ where r_c is a cut-off radius. The repulsive term is modeled via a Born-Mayer (BM) type potential,

$$\Phi(r_{ij}) = A e^{-p r_{ij}/r_o}, \quad (7)$$

where A and p are obtained by fitting the bulk modulus and the equilibrium lattice parameter, and r_o is a reference distance.

Computation and Results

We exemplify the problem with molybdenum using the TB parameters suggested in the work of Masuda *et al* [2]. The variation of the hopping integrals with distance is given by the following power-law

$$\beta(r) = \beta(r_o) \left(\frac{r_o}{r}\right)^Q, \quad (8)$$

where r_o is the first nearest neighbor distance in the bcc-based Mo lattice. The calculation is restricted to d-orbitals, and the hopping integrals extend up to the second nearest neighbor shell. The parameters are given in Table I.

Table I: TB Parameters used in the present calculation.

$dd\sigma$ (Ry)	$dd\pi$ (Ry)	$dd\delta$ (Ry)	Q
-0.08594	0.06444	-0.02402	3.57

A recursion calculation was performed to compute eleven levels (i.e., 22 exact moments of the density of states) for the continued fraction expansion of the Green function which describes the electronic properties of the bcc, fcc, and A15 crystalline structures. For this maximum number of levels of continued fraction, the band energies converge within 0.1 mRy and they will be taken as reference energies to which the results of further approximations will be compared. Keeping in mind that we want a reliable still computationally tractable method for obtaining the energetics of the system to use in MD simulations, we further study the suitability of the Linearized Green function Method (LGM). In the LGM (see [3] for an extensive study of the method) the band energy differences is expanded as a sum of "universal" functions which are defined for a convenient reference medium, multiplied by fluctuations of continued fraction coefficients (which in turn are related to the difference between the moments of the density of states).

Table II: Computed energies as defined in Eq. 1 for the three different structures, and repulsive potential parameters.

Struc.	(Energy in Ry)	Approximation	
		up to μ_6	up to μ_{22}
bcc	E_B	-0.8256	-0.8300
	E_R	0.2938	0.2962
	E_{Tot}	-0.5318	-0.5338
fcc	E_B	-0.7866	-0.7916
	E_R	0.2877	0.2901
	E_{Tot}	-0.4985	-0.5015
A15	E_B	-0.8252	-0.8363
	E_R	0.3129	0.3153
	E_{Tot}	-0.5123	-0.5210
E_R	A (Ry/at.)	0.03155	0.03178
param.	p	9.8159	9.7886

$$\Delta E_{X-Y}^{(p,q)} = \sum_{n=1}^p \phi_n \delta a_n + 2 \sum_{m=1}^q \psi_m \delta b_m, \quad (9)$$

where ϕ_n and ψ_n refer to “universal” functions, and a_i and b_i are the coefficients of the continued fraction. The quantities ϕ_n and ψ_n are calculated from the Green function elements G_{1n} which characterize the average medium. The actual expressions for these integrated quantities are

$$\phi_n(E) = -\frac{\text{Im}}{\pi} \lim_{\eta \rightarrow 0} \int_{-\infty}^E dt (t - E) G_{1n}^2(t + i\eta) \quad (10)$$

and

$$\psi_n(E) = -\frac{\text{Im}}{\pi} \lim_{\eta \rightarrow 0} \int_{-\infty}^E dt (t - E) G_{1n}(t + i\eta) G_{1n+1}(t + i\eta). \quad (11)$$

The two parameters of the repulsive term were obtained by fitting the calculated equilibrium lattice parameter and bulk modulus (of the bcc structure) to the experimental values given for Mo ($B = 1.80 \text{ Ry atom}^{-1}$). The results for the three structures are shown in Table II. We can see that the error in the approximation is about 10 mRy or less which is within the accuracy usually attributed to the determination of the elastic constants.

The next step is to use the LGM with the bcc structure taken as the reference medium. To be consistent with the previous approximation we consider $E_{X-Y}^{(3,3)}$ (see Eq. 9). Figure 1 shows the “exact” and the LGM approximation for the band energy differences between the A15 and bcc structures as a function of the d-band filling. The LGM curve follows the “exact” one qualitatively with differences of the same magnitude as in Table II.

Figures 2 (a) and (b) compare the energy differences between the three structures obtained with the LGM. Notice that, only after including the repulsive contribution does the bcc structure become more stable at the band filling value which corresponds to Mo (i.e.,

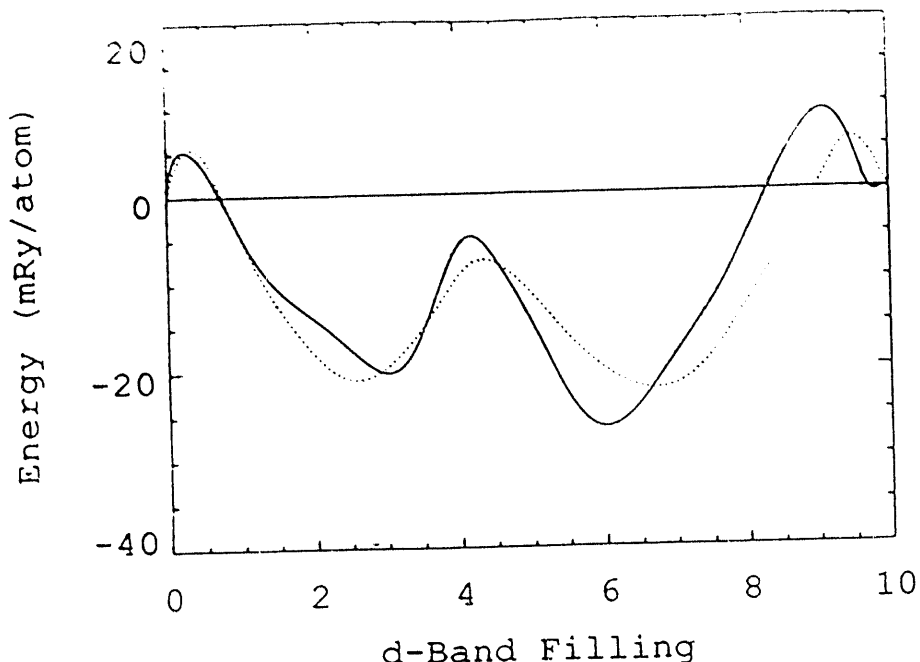


Figure 1: Band energy difference A15-bcc (Mo): full line, "exact" ; dotted line. LGM.

Table III: Shear Elastic Constant C_{44} for bcc-based Mo in $Ry\ atom^{-1}$ calculated with different approximations. The experimental value is taken from Ref. [5]

Approximation	C_{44}			Exper.
	Band contrib.	Rep. contrib.	Total	
μ_3	-1.5035	1.9948	0.49129	0.782
μ_{22}	-1.4592	1.9958	0.53664	0.782

4.4). The two parameters used in this repulsive contribution are shown in the last row of Table II.

Finally, we present in Table III the values of the calculated and experimental elastic constant C_{44} for bcc-based Mo. This allows to check the consistency of the BM potential parameters. In order to compute this quantity we need to express the total energy as a function of the lattice strain. This strain can be chosen so that the energy is an even function of the strain, and at the same time, in the case of cubic phases, preserves the volume of the unit cell [6]. The following (monoclinic) strain tensor was used in the calculation of C_{44} .

$$\epsilon = \begin{pmatrix} 0 & \frac{\eta}{2} & 0 \\ \frac{\eta}{2} & 0 & 0 \\ 0 & 0 & \frac{\eta^2}{4 - \eta^2} \end{pmatrix}. \quad (12)$$

With this strain tensor the energy can be written as

$$E(\eta) = E(-\eta) = E(0) + \frac{1}{2} C_{44} V \eta^2 \quad (13)$$

where η represents the strain and V the volume of the unit cell. We notice that the model

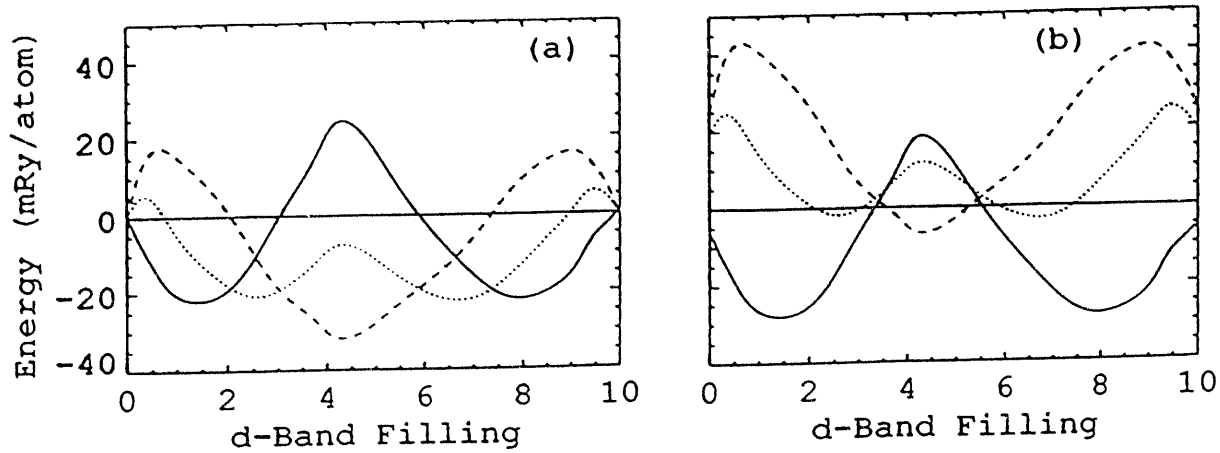


Figure 2: Band energy differences: full line, fcc-bcc; dotted line, A15-bcc; dashed line, A15-fcc: (a) band energy only, (b) total energy (band energy plus repulsive contribution). The sign convention is such that $\Delta E^{X-Y} < 0$ implies that X is more stable than Y.

underestimates the value of this elastic constant. This can be attributed to the neglect of hybridization in our TB model hamiltonian [2].

Conclusion

An application of the Linear Green function Method coupled with a Born-Mayer potential was presented to describe relative stability in transition metal systems. The need for a repulsive contribution was demonstrated in order to stabilize the ground state crystalline structure. A sixth-moment approximation of the density of states seems to be sufficient to produce physically sound results. This time efficient and simple approach is particularly suited for describing the evolution of realistic systems during a molecular dynamics simulation.

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