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Transferable tight-binding parameters for ferromagnetic and paramagnetic iron

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Abstract

We construct transferable tight-binding (TB) parameters for ferromagnetic and paramagnetic iron by fitting the total energy and the electronic band structure to three prototype crystal structures of Fe (BCC, both ferromagnetic and paramagnetic; and FCC, paramagnetic only) calculated by the general-potential linearized augmented plane wave (LAPW) method. We use these TB parameters to calculate the total energy and other properties of Fe in various other crystal structures, which we compare with independent LAPW results. The agreement between LAPW and TB results is very good, suggesting a realistic parametric physical description in the tight-binding approximation for any structure of Fe.

Keywords: Magnetism; Band structure; Total energy; Tight binding

1. Introduction

The Naval Research Laboratory (NRL) group has implemented a tight-binding total energy method (NRL-TB) which uses parameters which are transferable between structures [1–4]. The method has been tested for a large number of elemental systems, including alkaline earth, transition, and noble metals; semiconductors [5], and the early IIIb elements of the periodic table [6]. The transferability of the method is shown by its ability to calculate elastic constants which are in good agreement with experiment [7] and first-principles theoretical values [3,8]; by the calculation of surface energies, which improve upon the values found by the embedded atom method [9,10] and are comparable to first-principles results [11]; the determination of phonon frequencies [1] in agreement with experiment; and the calculation of vacancy formation energies, also in good agreement with the experiment [3]. In addition, the method determines the correct ground state of the HCP transition metals [3] and α-Manganese [2], even though these structures were not included in the database which was used to determine the parameters.

Due to the success of the NRL-TB method and because it is three orders of magnitude faster than first-principles all-electron methods based on

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self-consistent density functional theory, it is desirable to extend it to ferromagnetic systems as well. In this work we construct transferable spin-polarized tight-binding parameters for ferromagnetic iron, whose averages describe paramagnetic iron as well.

2. Theory

The success and speed of the NRL-TB depend on two facts [1,3]: (i) The fitted value of the charge density-dependent part of the total energy expression within the density functional theory can be absorbed as a structure-dependent shift to the eigenvalues ε_i and the chemical potential μ. (ii) The two-center Slater–Koster [SK] [12] parameters can be described in terms of functions of the internuclear distance, which are independent of any specific geometric structure.

Thus, the total energy is written as

$$E[n(\boldsymbol{r})] = \sum_{i;s=1,2} f\left(\frac{\mu-\varepsilon_{is}}{T}\right)\varepsilon_{is} + F[n(\boldsymbol{r})] = \sum_{i;s=1,2} f\left(\frac{\mu'-\varepsilon'_{is}}{T}\right)\varepsilon'_{is}, \tag{2.1}$$

where $f(x) = 1/(1+\mathrm{e}^x)$, $T = 5$ mRy and

$$\varepsilon'_{is} = \varepsilon_{is} + V_0; \quad \mu' = \mu + V_0; \quad V_0 = F[n(\boldsymbol{r})]/N_\mathrm{e} \tag{2.2}$$

with

$$N_\mathrm{e} = \sum_{i;s=1,2} f\left(\frac{\mu-\varepsilon_{is}}{T}\right)\varepsilon_{is} \tag{2.3}$$

being the number of electrons, i counts the states, and $s = 1,2$ counts the spin. The two-center, non-orthogonal tight-binding calculation uses on-site, hopping and overlap parameters. The on-site SK parameters for atom I in a ferromagnetic structure are expressed as

$$h^I_{ls} = \sum_{n=0}^{3} b^I_{lns}\, \varrho_{Is}^{2n/3}; \quad l = \mathrm{s,p,d_{e_g}, d_{t_{2g}}}, \tag{2.4}$$

where

$$\varrho_{Is} = \sum_{J\neq I} \mathrm{e}^{-\lambda^2_{\tilde{I}\tilde{J}s}R_{IJ}} f\left(\frac{R_{IJ}-R_0}{r_\mathrm{c}}\right); \quad R_0 = 15\mu_\mathrm{B}; \quad r_\mathrm{c} = 0.5\mu_\mathrm{B}, \tag{2.5}$$

ϱ_{Is} describes the density of the neighboring atoms [3], R_{IJ} is the inter-nuclear distance between atoms I and J, $\tilde{I}(\tilde{J})$ denotes the type of atom on the site $I(J)$ and $\lambda_{\tilde{I}\tilde{J}s}$ is a transferable parameter depending on the atom types, while b^I_{lns} are the on-site parameters.

We define *paramagnetic* on-site parameters by the spin average of (2.4). For ferromagnetic structures it is possible, in principle, to introduce spin-polarized hopping and overlap parameters. However, we found it sufficient to use spin-independent parameters for these integrals, and to use the same values for both the ferromagnetic and paramagnetic cases. These integrals have the form

$$P_\gamma(R) = \left(\sum_{n=0}^{2} c_{\gamma n}R^n\right)\mathrm{e}^{-g_\gamma^2 R} f\left(\frac{R-R_0}{r_\mathrm{c}}\right), \tag{2.6}$$

where γ indicates the type of interaction (e.g. ssσ, pdπ, etc.) This form has been proven efficient and transferable to any structure. The TB parameters are $c_{\gamma n}$ and g_γ, R is the interatomic distance, and R_0 and r_c are as in (2.5).

For a monatomic material we thus have 40 hopping parameters, 40 overlap, 13 on-site spin-up, and 13 on-site spin-down parameters, for a total of 106 independent parameters. It should be emphasized here that we use the term "parameters" for historical reasons. These so-called parameters are not empirically fitted to experiment but they are representations of integrals that serve the purpose of transforming the LAPW results to a tight-binding formalism.

3. Results and discussion

The first-principles calculations were performed with the general-potential linearized augmented plane wave method (LAPW) [13,14] using a generalized gradient approximation (GGA) for exchange and correlation [15]. The fit for Fe was performed using six (6) paramagnetic BCC structures with

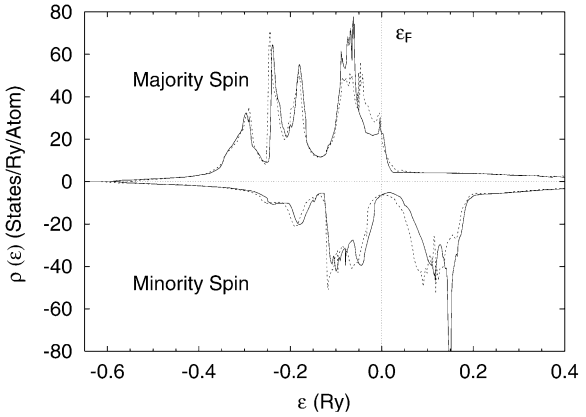

Fig. 1. Electronic density of states for BCC iron at the lattice constant $a = 5.40$ a.u. The solid lines represent the results of first-principles, full-potential LAPW calculations using the Perdew–Wang 1991 GGA. The dashed lines represent our tight-binding results. The graphs have been adjusted to have a common Fermi level, at zero.

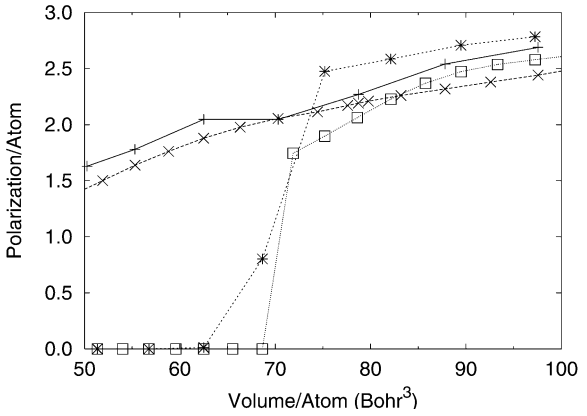

Fig. 2. Spin polarization of BCC and FCC iron as a function of volume, using full-potential LAPW and TB calculations. The solid line with the + symbols represents the LAPW result for the BCC phase. The dashed line with the × symbols represents the TB result for the BCC phase. The dotted line with the ∗ symbols represents the LAPW FCC phase. Lastly, the finely dotted line with the □ symbols represents the TB FCC phase.

lattice constants from 4.9 to 5.9 a.u., five (5) ferromagnetic BCC structures with lattice constants from 4.8 to 5.6 a.u., and five (5) paramagnetic FCC structures with lattice constants from 6.1 to 6.9 a.u. In Fig. 1, we show a comparison of LAPW and TB densities of states for both majority and minority spins. It is clear that the TB does a good job reproducing the LAPW results. In Fig. 2, we show the magnetization as a function of volume. As expected, there is good agreement for the BCC band structure which was fitted. However, our Hamiltonian is also able to reproduce the magnetization in the ferromagnetic FCC structure that was not fitted; it even correctly shows the collapse of magnetism for small volumes.

In Fig. 3, we show the total energy of Fe for the ferromagnetic and paramagnetic phases of the FCC and BCC structures. The TB results reproduce the LAPW total energies correctly showing the ferromagnetic BCC structure as the ground state and next in the sequence the two FCC phases and the BCC paramagnetic above them all. It should be stressed that the FCC ferromagnetic phase was not fitted and is in good agreement with our independent LAPW calculations for this phase. Finally, as explained in Section 2, the average of our on-site TB parameters and the same hopping and overlap

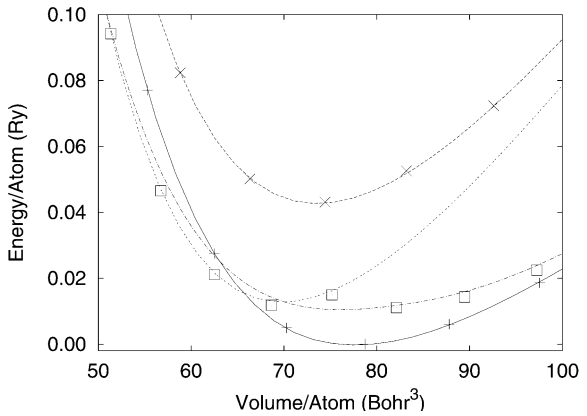

Fig. 3. The total energy of iron in the BCC and FCC structures. The + symbols represent the LAPW calculation for BCC ferromagnetic iron. The □ symbols represent the LAPW calculation for FCC ferromagnetic iron. The × symbols represent the LAPW calculation for the spin-restricted (paramagnetic) BCC phase. The lines represent the corresponding tight-binding calculations.

parameters were used to describe the paramagnetic phase. Using these parameters we calculated the paramagnetic equation of state, and compared with independent LAPW calculations, for the BCC,

Table 1
Bulk modulus and the elastic constants (in GPa) of ferromagnetic BCC iron at the experimental lattice constant

	TB	LAPW	Exp. [7]
B	138	150	173
C_{11}	223	226	237
C_{12}	95	112	141
C_{44}	78		69

FCC, HCP and SC structures. The agreement between TB and LAPW for structures that were not fitted is very good.

We have also calculated the bulk modulus and the elastic constants at the experimental lattice constant of ferromagnetic iron using both the NRL-TB and the LAPW method. The LAPW calculations of the structures from which C_{11}, C_{12} and C_{44} were derived were not included in the database and so the TB results are a measure of the transferability of our tight-binding parameters. Table 1 compares our results with first-principles calculations and experiment. Both LAPW and TB results for the elastic constant C_{12} are significantly lower than experiment although C_{11} and C_{44} show satisfactory agreement.

4. Conclusions

We have extended the NRL tight-binding method to treat ferromagnetic structures. By fitting the total energy and the band structure of a few prototype structures (in the present work for iron: FCC paramagnetic, BCC paramagnetic and BCC ferromagnetic) at various lattice constants we obtain spin-polarized transferable tight-binding parameters appropriate to ferromagnetic structures, which, when averaged over the two spins, yield transferable parameters for the paramagnetic structures.

The method was tested for Fe, at various lattice constants, against first-principles results for various other crystal structures which were not included in the fitting procedure, and by calculating the equation of state, the bulk modulus and elastic constants of the BCC phase. The agreement for all structures is quite satisfactory. This indicates that our transferable parameters provide a realistic TB description for any structure of iron, and can be used for efficiently performing large-scale calculations of both basic and practical industrial interest.

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