Application of a tight-binding total-energy method for FeAl

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Abstract
The Naval Research Laboratory tight-binding (TB) method accurately describes
the electronic and mechanical properties of many elemental systems, including
semiconductors, simple metals, and transition metals. We report an extension
of the method to an intermetallic compound, $Fe_x Al_{1-x}$. We found a set of
non-orthogonal TB parameters which reproduced the electronic structure and
total energy versus volume of a set of first-principles linearized augmented-
plane-wave (LAPW) calculations for the B1 (NaCl), B2 (CsCl), $D0_3$ ($Fe_3 Al$),
$C11_b$ ($MoSi_2$), and B32 (NaTl) structures. Structural properties, such as lattice
constants and bulk moduli, and electronic properties, such as the densities of
states and energy bands, are reproduced well. In addition, quantities that were
not fitted, such as elastic constants, are found to be in very good agreement with
independent LAPW calculations.

1. Introduction

Numerous technological applications require the use of intermetallic alloys. New materials
can be made relatively easily by changing the stoichiometry of the intermetallic alloys and
their crystal structures. One goal of this research is to find an alloy which remains strong
at high temperatures yet ductile at low temperatures. Of particular interest are the transition
metal aluminides, e.g. FeAl, NiAl, and CoAl, which are resistant to corrosion and oxidation,
have interesting magnetic properties [1], and are used as high-temperature structural materials
and soft magnetic materials. First-principles calculations can be used as an aid in developing
new alloys of this type. In particular, we can calculate quantities such as elastic constants [2]
and phonon frequencies [3, 4] for these materials. First-principles determination of other
properties, e.g. surface interface energies and dislocation energies, are at best at the cutting
edge of computational physics. An approximate method which retains the physics of the

problem but which can handle larger systems, e.g. of the order of 1000 atoms, is desirable. The tight-binding (TB) method developed at the Naval Research Laboratory (NRL) [3, 5] is ideal for this type of calculation, as it maps first-principles electronic structure and total-energy information onto a set of two-centre spd-orbital Slater–Koster [6] parameters, reducing the basis set size from approximately 100 orbitals per atom for a full-potential calculation to 9 orbitals/atom, with a corresponding increase in computational speed and a reduction of computational memory.

In this paper we develop and test a set of TB parameters for the Fe–Al system. As we shall see, the TB parametrization reproduces the electronic structure and energetics determined from a database of first-principles calculations of several different crystal structures over a wide range of pressures at several compositions $Fe_x Al_{1-x}$. The parameters may thus be used for further study in this system, including large-scale TB molecular dynamics simulations (TBMD) [4].

Slater and Koster [6] introduced the tight-binding method as an interpolation scheme to facilitate the analysis of band structures and densities of states. The development of this approach has continued and now includes total-energy data [7]. This is a very useful method because of its computational efficiency; it is now possible to treat a system containing thousands of atoms with accuracy comparable to that of first-principles LDA calculations [8]. There are two philosophies in the practice of TB theory. The first one aims for simplicity, using a minimal number of orbitals and consequently a small number of parameters, which are only required to approximate some band-structure features. This is a useful approach for understanding general trends and to provide a simple physical picture of various phenomena. The other category incorporates a more realistic number of relevant orbitals and hence employs a large number of TB parameters, which are fitted to very closely reproduce the first-principles band structure and total energy. The current approach [3,5], developed at the NRL, is representative of this second category of TB Hamiltonians. Physical properties such as the equilibrium lattice constant, bulk modulus and other elastic constants, vacancy formation energies, surface energies, and phonon spectra were found to be in good agreement with experiment for a variety of materials ranging from transition metals [5, 7, 9], sp^3 trivalent metals (Al, Ga, and In) [10], and elemental semiconductors [8, 11, 12], as well as magnetic materials [13, 14] and chemisorption [15]. Here we use this NRL-TB method to develop the phase-transferable TB parameters for the FeAl compound. Section 2 briefly describes the method used, and section 3 describes our results.

2. Method

A brief description of the method follows. The total energy of the NRL-TB method is expressed as

$$E[n(r)] = \sum_{n}^{occ} \varepsilon'_n, \tag{1}$$

where the sum is over the occupied states and the eigenvalues are shifted to include the non-band-structure energy appearing in the density functional theory (DFT) formalism:

$$\varepsilon'_n = \varepsilon_n + F[n(r)]/N_e, \tag{2}$$

where N_e is the number of electrons in the calculation. This avoids the necessity of choosing an arbitrary shift of energy for the band-structure term and the usual pair-potential term, simplifying the numerical fitting process. The detailed justification is explained elsewhere [5].

There are three types of parameter in the fit: the on-site terms, which depend on the local environment and represent the energy required to put an electron in a specific atomic shell,

the hopping parameters, which represent the energy required for the electron to move between atoms, and overlap parameters, detailing the non-orthogonality of the TB orbitals. In all three cases we must determine pairwise interactions between atoms of the same type as well as those between atoms of different species. This involves an expansion of our original work [5, 7], which only described monatomic systems.

The environmental dependence of the on-site parameters is controlled by a set of atomic-like densities:

$$\rho(i, \tilde{j}) = \sum_{j \in \tilde{j}} \exp[-\lambda_{\tilde{i}\tilde{j}}^2 |\boldsymbol{R_i} - \boldsymbol{R_j}|] \mathcal{F}(|\boldsymbol{R_i} - \boldsymbol{R_j}|), \tag{3}$$

where the ith atom is of type $\tilde{i}$, the jth atom is of type $\tilde{j}$, $\rho(i, \tilde{j})$ is the density on atom i due to atoms of type $\tilde{j}$, and $\lambda_{\tilde{i}\tilde{j}}$ is a fitting constant to be determined. The cut-off function $\mathcal{F}$ takes the form

$$\mathcal{F}(R) = \theta(R_c - R)/\{1 + \exp[(R - R_c)/L_c + 5]\}, \tag{4}$$

where θ is the step function. For FeAl, we take $R_c = 16.5$ Bohr and $L_c = 0.5$ Bohr for all interactions.

The on-site terms themselves are polynomial functions of $\rho^{2/3}$:

$$h_\ell(i) = a_\ell(\tilde{i}) + \sum_{\tilde{j}} [b_\ell(\tilde{i}, \tilde{j})\rho(i, \tilde{j})^{2/3} + c_\ell(\tilde{i}, \tilde{j})\rho(i, \tilde{j})^{4/3} + d_\ell(\tilde{i}, \tilde{j})\rho(i, \tilde{j})^2], \tag{5}$$

where the sum is over all atom types in the system. In general we use $\ell = $ s, p, d. However, in systems with essentially cubic symmetry it is convenient to split the d on-site terms into t_{2g} and e_g components. We take this approach for the current parametrization of FeAl.

The two-centre Slater–Koster hopping integrals are determined using an exponentially damped polynomial, and depend only on the atomic species and the distance between the atoms:

$$H_{\ell\ell'\mu}(i, j; R) = [A_{\ell\ell'\mu}(\tilde{i}, \tilde{j}) + B_{\ell\ell'\mu}(\tilde{i}, \tilde{j})R + C_{\ell\ell'\mu}(\tilde{i}, \tilde{j})R^2] \exp[-D_{\ell\ell'\mu}^2(\tilde{i}, \tilde{j})R]\mathcal{F}(R). \tag{6}$$

The parameters A, B, C, and D are to be fitted. For like-atom ($\tilde{j} = \tilde{i}$) interactions, there are ten independent Slater–Koster parameters:

$$ss\sigma, \ sp\sigma, \ pp\sigma, \ pp\pi, \ sd\sigma, \ pd\sigma, \ pd\pi, \ dd\sigma, \ dd\pi, \ dd\delta.$$

When the atoms are of different types, we must include an additional four parameters:

$$ps\sigma, \ ds\sigma, \ dp\sigma, \ dp\pi.$$

Note that we do not distinguish between t_{2g} and e_g orbitals when computing the hopping integrals.

Since we are using a non-orthogonal basis set, we must also parametrize the overlap integrals. These have a form similar to that of the hopping integrals:

$$S_{\ell\ell'\mu}(i, j; R) = [O_{\ell\ell'\mu}(\tilde{i}, \tilde{j}) + P_{\ell\ell'\mu}(\tilde{i}, \tilde{j})R + Q_{\ell\ell'\mu}(\tilde{i}, \tilde{j})R^2] \exp[-T_{\ell\ell'\mu}^2(\tilde{i}, \tilde{j})R]\mathcal{F}(R), \tag{7}$$

where O, P, Q, and T also represent parameters to be fitted. Again we do not distinguish between t_{2g} and e_g orbitals.

For a two-component system with s, p, d orbitals, including t_{2g} and e_g on-site terms, there are 330 parameters (λs, a, b, c, d, A, B, etc) which are used in the fit, in contrast to 97 for a single-element parametrization [5]. These parameters are chosen so as to reproduce the eigenvalues ε' and energies E in equation (1). While the number of parameters may seem rather large, one must remember that we are using this method to map the electronic structures and total energies of a large number of first-principles calculations onto a TB database. With this in mind, the number of parameters seems quite reasonable.

The basic aim of our procedure is to represent the Slater–Koster Hamiltonian using simple functional forms with the parameters chosen to reproduce the first-principles calculations over a wide range of pressure and structures [5, 7]. The parameters are obtained by fitting to band structures and the total energies of first-principles augmented-plane-wave (APW) and linearized augmented-plane-wave (LAPW) calculations [16, 17]. We constructed a database of electronic band structures and total energies for various structures at several different volumes around the equilibrium density. In all cases we used a uniform regular k-point mesh which corresponds to 85 points in the irreducible part of the face-centred cubic (fcc) lattice (for the NaCl phase) or 55 points in the body-centred cubic (bcc) lattice (for the bcc-like phases). The core levels were treated fully relativistically and the outer electrons of each element were treated semi-relativistically [18]. The Hedin–Lundqvist parametrization [19] was used to approximate the exchange–correlation functional within the local density approximation to DFT [20]. The total database of eigenvalues and total energies contains about 5000 entries. We used the Levenberg–Marquardt algorithm to adjust our TB parameters to give the best possible reproduction of the database. The total energies are usually weighted at about 200 times larger than a single band [5]. We fit to the total energies of all structures as well as the band structure for the CsCl phase. The RMS error of the total energy is less than 1 mRyd for all the structures. In the CsCl structure, the RMS error of the lowest 12 bands is approximately 20 mRyd.

In the fitting procedure we find that it is very important to know the symmetry properties of the electronic band states at the high-symmetry k-points of the Brillouin zone [7]. Without this information it would be extremely difficult for the non-linear least-squares fit to correctly identify the character of each eigenstate. This identification is more difficult for binary compounds than it is for monatomic materials. We use an APW code which yields the symmetry information of the electronic band states at the high-symmetry k-points for various structures. We modified the fitting program to include the symmetry information provided by the APW calculations in the database so that it yields eigenvalues with the correct symmetry. This is done by imposing an additional constraint in which the routine fits the eigenvalues found by block-diagonalization of the TB Hamiltonian obtained from the symmetry group operations as well as the eigenvalues from the full Hamiltonian. Inclusion of the symmetry information is especially important at the initial stage of the fitting process. Without this additional constraint the energy functionals could easily fall into the wrong local minima of the multi-phase energy space. With the symmetry information of the eigenvalues provided by the APW calculations, the fitting routine usually yields the parameters that qualitatively reproduce degeneracy and symmetry information at any given high-symmetry k-point.

After obtaining the TB parameters from this symmetrized APW database, we proceed one step further, refitting the parameters to the more accurate LAPW full-potential results. Although the LAPW program does not yield the symmetry properties of the eigenvectors, it does produce angular-momentum and atom occupation information for each eigenstate, allowing some eigenvalues to be identified by symmetry. Thus further fitting does not change the symmetries of the eigenstates obtained with the muffin-tin APW fit. However, it is important to use the full-potential results because the energy differences obtained thus are better for describing the relative differences in energy between different phases. The correct energy difference between structures results in better transferability between different structural phases.
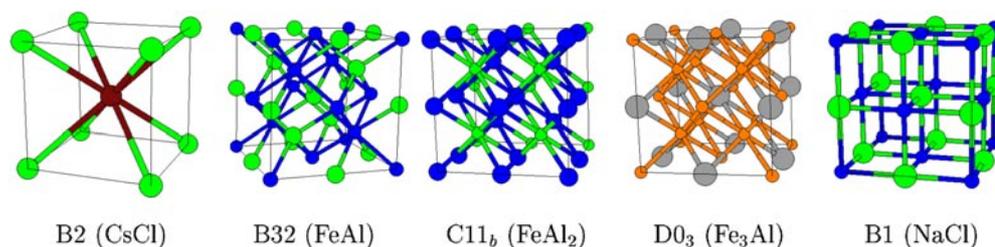
Figure 1. Structures used to develop the first-principles database for fitting the FeAl TB parameters. For a full description of these structures, see http://cst-www.nrl.navy.mil/lattice.
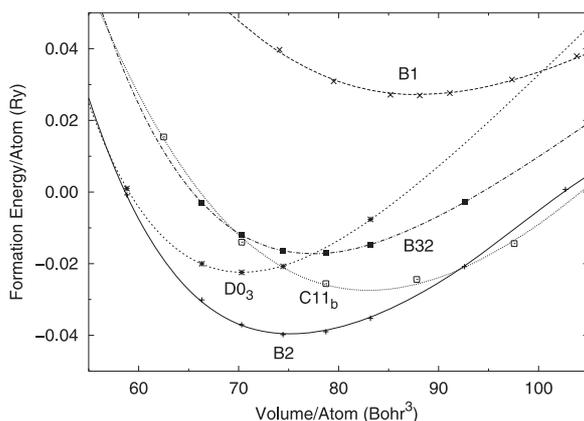

Figure 2. The formation energies versus atomic volume for ordered Fe_xAl_{1-x} structures, calculated using our TB parameters of and compared to first-principles LAPW calculations. The solid lines represent the TB results while the points represent the LAPW results. The formation energy is defined to be the energy of a compound of $Fe_xAl_{(1-x)}$ relative to equivalent amounts of bcc Fe and fcc Al. The figures are labelled by *Strukturbericht* designations, and keyed to the compositions listed in figure 1.

3. Results

We first fit the TB parameters to the ground state of FeAl, the CsCl (B2) structure, over a wide range of pressure. Once we find a good set of TB parameters, which properly describe the ground-state structure of FeAl over our volume range, we then extend the fit to other bcc-like structures as well. We tried to fit as many bcc-like structures as possible, including the structures as $D0_3$ ($AlFe_3$), $C11_b$ (Al_2Fe) and B32 (FeAl) shown in figure 1[3]. These structures differ from the CsCl by stoichiometry and geometric position in the compound. All these structures are expected to yield similar formation energies. Finally, we included the NaCl (B1) structure of FeAl in the fitting, which is expected to have a much higher energy. Figure 2 shows that the NaCl phase is about 0.07 Ryd higher in energy than the CsCl phase. This energy is substantially higher than in other bcc-like structures[4].

Figure 2 shows that there is excellent agreement between the LAPW results and the TB results over a wide range of pressures for all the fitted phases. The agreement is especially

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[3] A full description of these structures is available at http://cst-www.nrl.navy.mil/lattice.

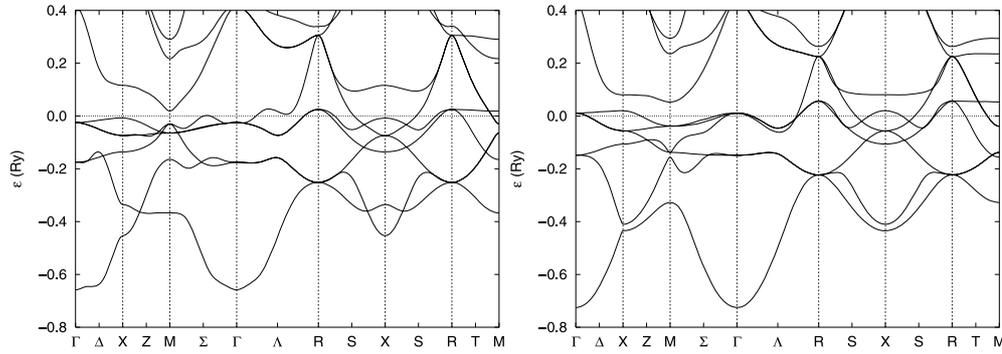[4] The codes needed to determine the TB parameters and use them to evaluate total energies, forces, and electronic structure are available at http://cst-www.nrl.navy.mil/bind/dodtb.

Figure 3. The band structure of FeAl in the CsCl structure, at the lattice constant $a = 2.94$ Å. The left-hand figure shows the TB band structure, while the LAPW results are on the right. In both cases the Fermi level has been set to zero.
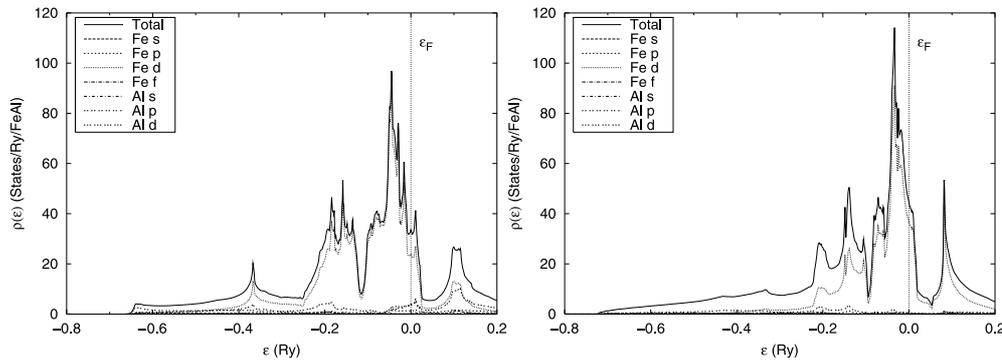

Figure 4. The electronic density of states of B2 (CsCl) FeAl, using the TB (left) and LAPW (right) methods, at the lattice constant $a = 2.94$ Å. In each case the Fermi level has been set to zero. The partial densities of states are given according to the key in each part of the figure. While the LAPW results have a longer tail at low energy, the densities of states are essentially similar near the Fermi level.

good in the ground-state CsCl (B2) structure. We plot the formation energy, which is defined as the energy gained by forming the alloy from its constituents:

$$E_f(x) = E(\text{Fe}_x\text{Al}_{1-x}) - xE(\text{Fe}) - (1-x)E(\text{Al}), \tag{8}$$

where $E(\text{Fe})$ is the equilibrium energy of bcc iron, and $E(\text{Al})$ is the equilibrium energy of fcc aluminium.

The TB and LAPW band structures of the B2 FeAl structure are shown in figure 3. The TB calculation reproduces the main features of the first-principles results, but in detail there are significant differences. We obtained the TB and LAPW electronic densities of states (DOS) by the tetrahedron method [21], using 165 k-points in the irreducible part of the Brillouin zone. In contrast to the band structures, the LAPW and TB DOS shown in figure 4 are in good agreement. The only serious discrepancy is a small peak above ε_F in the TB DOS, a feature not present in the LAPW result. Experimentally, the DOS at the Fermi energy is known only from specific-heat measurements, where it was measured to be $\rho(\varepsilon_F) = 31.1$ states Ryd^{-1}/FeAl molecule [22]. Our TB calculation yields $\rho(\varepsilon_F) = 39.4$ states Ryd^{-1}, consistent with the LAPW value $\rho(\varepsilon_F) = 38.6$. Other reports in the literature also find the theoretical value of $\rho(\varepsilon_F)$ to be greater than that from experiment [23–25]. It is known in general that a large

Table 1. Bulk structural and elastic properties of FeAl in the caesium chloride phase, determined from the TB parameters described in this paper and from first-principles electronic structure calculations.

Property	TB	LAPW
a (Bohr)	5.32	5.33 (5.49 from experiment [1])
B (GPa)	116	113
$C_{11} - C_{12}$ (GPa)	138	104
C_{11} (GPa)	199	182
C_{12} (GPa)	74	78
C_{44} (GPa)	91	45

peak near the Fermi level in many cases indicates that the structure is unstable [26]. Since the TB and LAPW theoretical results yield somewhat larger values than the experiment at the Fermi level, additional considerations, such as of magnetic contributions due to spin, might be required to obtain improvement of the result in these electronic structure calculations. In earlier work, Papaconstantopoulos and Hathaway [27] calculated the Stoner factor of FeAl in the CsCl structure, predicting FeAl to be non-magnetic at the LDA equilibrium volume, but finding that the Stoner criterion is satisfied at the experimental volume, e.g., the system should be magnetic. This situation is not consistent with the experimental results.

Our predicted equilibrium lattice parameters and bulk modulus are also in good agreement with the first-principles results shown in table 1. This is a result of the fitting procedure, as we fit the TB parameters (3–7) to total energies at several volumes. However, the shear elastic moduli that we computed [2, 28] for the CsCl phase were not included in the fit, and except for C_{44} are in good agreement with the experimental results.

In summary, we have presented a brief report of our TB study of the FeAl system. We showed that the parameters describe excellently several bcc and bcc-like phases as well as the NaCl phases.

Acknowledgments

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