

Application of a tight-binding total-energy method for Al, Ga, and In

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We apply our tight-binding (TB) methodology to the *sp* metals Al, Ga, and In, all of which have distinctive ground states. The results show that this approach works as well for such elements as it does for transition metals. Bulk properties such as lattice constants, bulk moduli, and elastic constants were found to be consistent with experiments. We emphasize that our method successfully predicts the correct ground states of both Ga and In, without inclusion of the corresponding first-principles data in the fit. In addition, we note the success of our method in Al, a metal not normally described by TB.

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Since Slater and Koster¹ introduced the tight-binding (TB) method, which calculated energy bands of a chosen structure based on the parametrization of Hamiltonian matrix elements, the development of TB methods has continued. TB methods in general have proven useful for calculating band structures and total energies of various systems including bulk, surface, and amorphous structures.

Among these methods, an approach developed at the Naval Research Laboratory (NRL) has been shown to work well for the transition metals.^{2,3} 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 agreement with experiment for all the nonmagnetic transition metals. Even structural properties of antiferromagnetic elements, such as manganese,⁴ were predicted correctly.

Now we wish to take the same approach to TB and determine whether this method works as well on elements other than transition metals. We chose Al, Ga, and In, which are located in column IIIb of the Periodic Table, each having three valence electrons. Interestingly, although these elements are in the same column of the Periodic Table, they have different ground-state structures. In the normal phase, Al is fcc, In is face-centered tetragonal, and Ga has a more complex structure (α Ga, space group *Cmca*, Pearson symbol *oC8*, *Strukturbericht* designation A11). In particular Ga is unique in that its volume contracts by 2.9% upon melting, in contrast to most metals.⁵

In this paper we demonstrate that our TB method correctly describes the bulk properties of the ground state and other phases of these elements. We use the TB scheme of Ref. 3, including the extra degrees of freedom which were applied to vanadium in that paper [see the discussion around Eq. (11) of Ref. 3]. The TB parameters in this paper are available from the authors or on the World-Wide Web at <http://cst-www.nrl.navy.mil/bind>.

In Al the fcc phase is the ground state at normal pressure. In the fitting we used the linearized augmented plane wave (LAPW) (Ref. 6) band structures and total energies for several different volumes in different phases. First-principles data from the fcc, bcc, sc, hcp, and diamond phases were included. In Al it is known that some of the *d* bands cross below the *p* bands in some regions of the Brillouin zone

including the region near the Γ point.⁷ This implies that the matrix elements associated with the *d* orbitals cannot be ignored in the fitting. We thus include matrix elements for *d* orbitals as well as *s* and *p*.

The band structure of Al was plotted in the fcc phase with a lattice constant of 7.65 a.u., which is the experimental equilibrium,⁸ and compared with the LAPW results for the same lattice constant at high symmetry points as shown in Fig. 1. As expected, there is good agreement between the calculations, indicating a good fit. We get equally good fits of the band structure in the other structures. Total energy versus volume curves was also plotted and compared with LAPW results used in the fitting (Fig. 2). Our TB method gives an excellent reproduction of all first-principles data of energies of the different phases, even for structures not included in the fit such as the A15 structure and the vacancy structures $L1_2$ and $D0_3$.³

Bulk properties of Al were calculated and compared with experiments. The lattice constant, bulk modulus, and elastic constants are consistent with experimental values and first-principles results (see Table I). The vacancy formation energy E_{vac} was calculated using a 27-site supercell with a

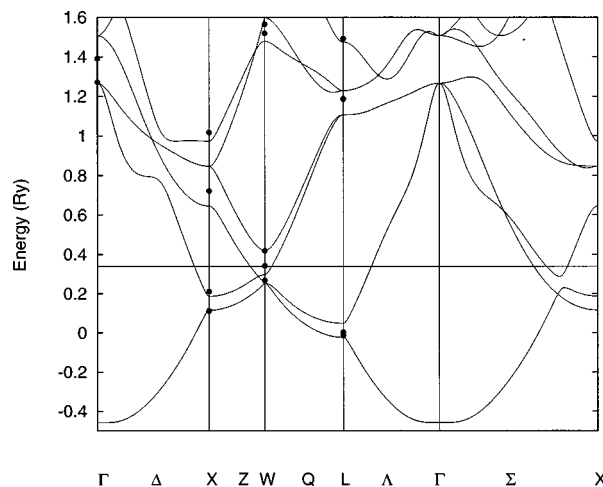


FIG. 1. The band structure of Al in the fcc phase with lattice constant of 7.65 a.u. The solid lines show our TB calculations, and the dots are the result of LAPW calculations at the high-symmetry points.

TABLE I. Bulk properties of Al and In, compared to first-principles LAPW and experiments. Lattice constants a and c are in a.u., bulk modulus B and elastic constants C_{ij} are in Mbar. Elastic constants are evaluated at the experimental room-temperature volume. The estimated uncertainty in the calculated elastic moduli is about 0.1 Mbar.

Property	Al			In	
	TB	LAPW	Exp.	TB	Exp.
a	7.56	7.54	7.60 (Ref. 9)	8.41	8.69 (Ref. 8)
c				9.63	9.35 (Ref. 8)
B	0.80	0.70	0.794 (Ref. 10)	0.52	0.411 (Ref. 12)
$C_{11}-C_{12}$	0.67	0.50	0.46 (Ref. 11)	0.083	0.050 (Ref. 12)
C_{44}	0.26	0.285	0.28 (Ref. 11)	0.134	0.0655 (Ref. 12)
C_{66}				0.226	0.1220 (Ref. 12)

vacancy at the center with $a=7.65$ a.u. Our TB yields 0.49 and 0.40 eV for unrelaxed and relaxed structures, somewhat smaller than the experimental value 0.66 eV (Ref. 13) and the value of 0.86 eV in an unrelaxed LAPW calculation.¹⁴

We also calculated surface energies using these TB parameters. First we constructed an eight-layer supercell representation of a $\langle 111 \rangle$ surface, removing 3 atoms from every unit cell, leaving a set of five-layer slabs. Our LAPW calculation for this surface yielded 0.974 ± 0.018 J/m² while our TB parameters produce a surface energy of 0.971 ± 0.016 J/m². Encouraged by this result, we calculated the surface energy of Al for several different surfaces using isolated 25-atom-thick unit cells.³ We compare our results to the first-principles work of Schöchlin *et al.*¹⁵ and experiment¹⁶ in Table II. The agreement is quite good, especially since we have not included surfaces in our fit. We conclude that we have developed a very accurate TB representation of Al, which is usually treated by plane-wave expansions. We are not aware of any particularly accurate linear combination of atomic orbitals treatment of Al.

We now consider gallium, whose ground-state structure is known to have an unusual crystalline phase, called α Ga, which may be described in terms of a face-centered orthorhombic lattice with four atoms in the primitive cell. The structure of this phase is described by the three lattice parameters a , b , and c of the orthorhombic cell, and two in-

ternal parameters μ and ν , which determine the orientation and lengths of the chemical bonds.¹⁷ The peculiarity of this Ga structure is that each atom has only the one nearest neighbor connected by a short bond at distance 2.44 Å, which is often referred to as a molecular bond. These dimers form buckled parallel planes with a thickness of 1.9 Å, perpendicular to the [001] direction in the orthorhombic cell.¹⁸ Also, there are six other neighbors, three sets of two each at distances between 2.71 and 2.79 Å.^{17,19}

The TB parameters for Ga were found based on LAPW calculations of only the fcc, bcc, and sc structures, fitting to both the total energies and band structures. Since a first-principles band-structure calculation⁷ shows that all occupied d bands are well below the s and p levels, only the s - and p -level matrix elements were used in the fitting of Ga. For the energy curves of the α Ga and hcp phase in Fig. 3, we found a full set of equilibrium structural parameters which minimize the total energy at each fixed volume based on a conjugate gradient scheme. The curve is then obtained by interpolating the energy values between several different volumes using cubic splines. Note that the α Ga and diamond structures were not used in the fitting. Even so, the energy predicted for the diamond structure was very close to the first-principles calculation, as seen in Fig. 3. We also predicted the correct ground structure, the α Ga phase, yielding an energy lower than fcc. Our predicted structural parameters and bulk modulus are in good agreement with first-principles results and experiments (see Table III).

The literature indicates that the ground-state structure of α Ga exhibits both molecular and metallic character because of the coexistence of strong Ga₂ covalent bonds formed by the short nearest-neighbor bond, and weak intermolecular bonding of a trivalent metal nature. Jones²⁰ pointed out that in his Al and Ga cluster calculations the average bond length

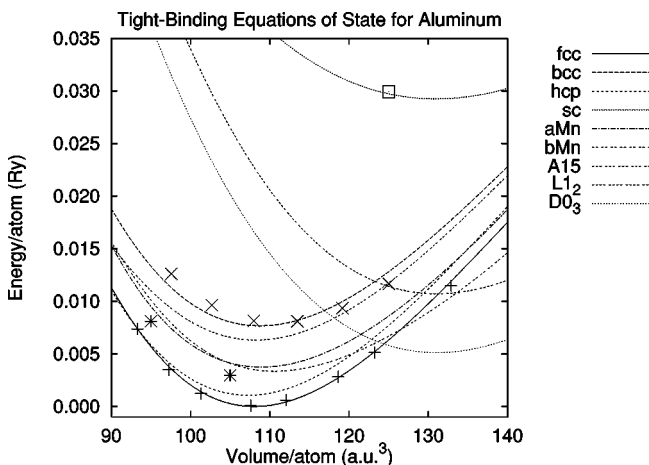


FIG. 2. Total energy of Al as a function of the atomic volume in different phases. The lines are the TB calculations, and the points are the LAPW results.

TABLE II. Surface formation energies E_{surf} of TB compared to the first-principles pseudopotential calculations (Ref. 15) and experiment in J/m².

Surface	TB (Not relaxed)	Schöchlin <i>et al.</i> (Relaxed)	Exp. (Isotropic) (Ref. 16)
$\langle 001 \rangle$	1.33 ± 0.09	1.081 ± 0.03	
$\langle 011 \rangle$	1.29 ± 0.09	1.090 ± 0.03	1.18
$\langle 111 \rangle$	0.87 ± 0.08	0.939 ± 0.03	

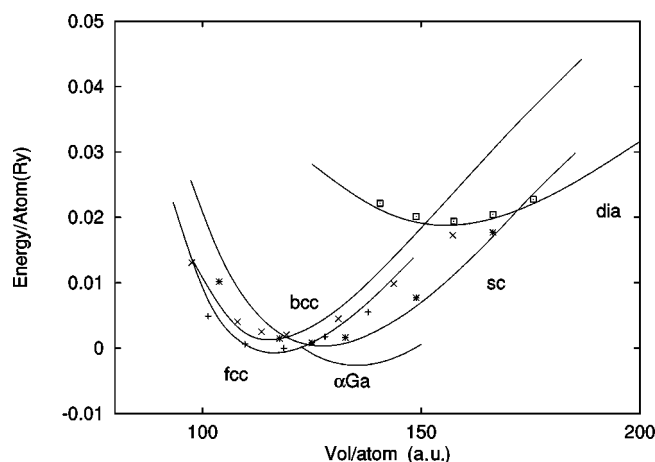


FIG. 3. Total energy of Ga as a function of the atomic volume in different phases. The lines are the TB calculations, and the points are the LAPW results. The correct ground structure of Ga, the α Ga phase is predicted.

of Ga was consistently smaller (about 5%) than that of Al even though Ga has a larger atomic number in the same column of the Periodic Table. He explained the partly covalent nature of Ga by using the argument that the presence of a weakly bound $3d$ core shell causes the incomplete screening of the nucleus so that Ga has a larger effective charge than Al, resulting in an anomalous spatial contraction of the valence charge.

On the other hand, Bernasconi, Chiarotti, and Tosatti,¹⁸ and Gong *et al.*²¹ sought to explain the covalency of Ga from the behavior of the electronic density of states (EDOS). Their first-principles calculations showed a pseudogap at the Fermi energy E_F . The connection between the pseudogap and covalency was as follows: the pseudogap contains a real gap and residual states in the gap. The gap is created by the dimers, and the residual states in the pseudogap are created by the overlap of wave functions in the buckled planes of those dimers, which results in metallic behavior.²² The experimental results²³ from ultraviolet photoemission spectra of occupied states of solid Ga also exhibit a sharp decrease in intensity at the Fermi level. We calculated the EDOS from our TB parameters and found a pseudogap near the Fermi

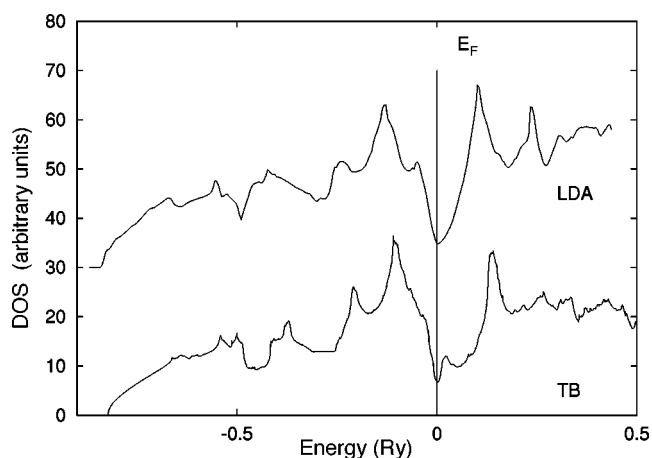


FIG. 4. Electronic density of states for α Ga. Notice a strong pseudogap in both LDA and TB. The LDA data are from Ref. 14.

level. The TB plot compares very well with the first principles calculations¹⁸ (see Fig. 4). Our calculations of the EDOS, the values of the internal parameters of the α Ga structure, and the correct ordering of the energy curves of different phases support the conclusion that our TB parametrization of Ga is a good choice for further study of this material.

Finally, we present our results for indium, which is known to have a face-centered tetragonal (fct) ground state (space group $I4/mmm$, Pearson symbol $tI2$, *Strukturbericht* designation A6). The axial ratio is 1.076,^{24,8} which corresponds to 1.57 for the equivalent body-centered (bct) structure. Hafner and Heine,²⁵ using first-principles pseudopotential calculations, showed that the fcc and hcp structures are unstable at a normal pressure, i.e., a small distortion from these ideal structures lowers the band-structure energy. As in Ga, the first-principles band-structure calculation⁷ shows that all occupied d bands are well below the s and p levels. Hence, only the s - and p -level matrix elements were used in our TB fitting of In. We found the TB parameters by fitting to LAPW calculations of the fcc, bcc, and sc lattices.

Figure 5 shows the impressive result that our TB method yields the correct ground state, namely the fct structure, even though the first-principles data for this phase and the hcp

TABLE III. Lattice and internal parameters of our TB results at the equilibrium volume of α Ga phase compared with experimental and local-density approximation (LDA) results. The experimental data taken from the handbook by Wyckoff (Ref. 17) were measured at 4.2 K and atmospheric pressure. LDA data are from Ref. 8. The bulk moduli were also computed and compared with the other results.

	a (a.u.) μ	b/a ν	c/a vol. (a.u. ³)	B_o (Kbar)
TB	8.752	1.648	0.977	651
	0.1555	0.0904	135	
LDA	8.271	1.688	0.994	669
	0.1567	0.0803	119	
Exp.	8.523	1.695	1.0013	613
	0.1525	0.0785	131	

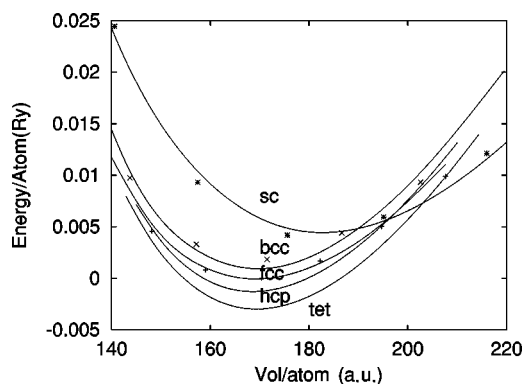


FIG. 5. Total energy of In as a function of atomic volume. The lines are the TB calculations, and the points are the LAPW results. Note that although no first-principles data were provided in the fitting for hcp and fct, the correct ground-state structure, fct is predicted.

phase were not included in the fit. We found the equilibrium axial ratio of 1.145, compared to the experimental value of 1.076. The remainder of the total energy versus volume curves show the correct ordering of metastable phases. The energies of the fct and hcp structures were fully relaxed at a fixed volume.

Bulk properties were calculated and compared with experiments. C_{11} - C_{12} , C_{44} , and C_{66} were calculated by applying small, volume conserving distortions to the equilibrium structure.²⁶ The lattice constant, bulk modulus, and elastic constants are consistent with experimental values (see Table I).

In summary, we have presented the results obtained from a TB parametrization of Al, Ga, and In. To the best of our

knowledge, this is probably the first accurate TB description of Al. It is also a rather impressive TB treatment of Ga and In, predicting the correct ground-state structures, without fitting to first-principles data for these structures. Thus, we have shown that the NRL method^{2,3} works well not only for the monatomic transition metals but also for *sp* elements such as Al, Ga, and In.

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