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Application of a New Tight-Binding Method for Transition Metals: Manganese.

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Abstract. – A new tight-binding total-energy method, which has been shown to accurately predict ground-state properties of transition and noble metals, is applied to manganese, the element with the most complex ground-state structure among the *d* metals. We show that the tight-binding method correctly predicts the ground-state structure of Mn, and offers some insight into the magnetic properties of this state.

Most elements in the periodic table crystallize in the f.c.c., b.c.c., h.c.p. and diamond structures. Among the few exceptions is manganese, which has an equilibrium structure, denoted as αMn, which contains 29 atoms in the unit cell [1]. First-principles total-energy methods, such as the full-potential Linearized Augmented Plane Wave (LAPW) method [2, 3] are not very efficient in such systems, especially since the αMn phase has five internal parameters which must be adjusted to minimize the total energy in order to calculate the correct structure at each volume. The calculation of elastic constants, phonon frequencies, surface energies, vacancy formation energies, and other properties requires even more computational effort. A reliable approximate method, based on first-principles results, is necessary for efficient computational study of complicated crystals such as manganese.

In a recent paper, Sigalas and Papaconstantopoulos [4] introduced the idea that the energy bands of Augmented Plane Wave (APW) calculations for cubic structures at different volumes can be fitted to a non-orthogonal tight-binding (TB) Hamiltonian whose matrix elements are functions of the distance between pairs of atoms. The sum of eigenvalues resulting from the above TB Hamiltonian, together with a pair potential, were used to fit the total energies of the APW calculation, thus obtaining an interpolation formula that was employed to calculate the total energy for non-cubic structures. This procedure was applied to calculate the elastic constants of Pd, Ir, Au, Rh and Ta, which showed fairly good agreement with the experimental values. The phonon spectra and density of states for Au were also calculated [5], again in reasonable agreement with experiment.

In a subsequent paper, Cohen, Mehl and Papaconstantopoulos [6] made dramatic improvements to the above approach. They eliminated the pair potential in the fitting of the total energy, employed environment-dependent on-site TB parameters, and introduced exponentially damped polynomial expansions of the hopping and overlap integrals, thus extending the parametrization to an arbitrary number of neighbors. This new total-energy methodology [6] was applied to calculate elastic constants, phonon spectra and vacancy formation energies for the noble metals and other transition metals. The results were impressive. Starting from only f.c.c. and b.c.c. structures, the method correctly predicted the ground-state structure in all of the elements tested, including those which exhibit a hexagonal close-packed (h.c.p.) ground state.

This paper shows how the new TB method can be applied to manganese. We first performed paramagnetic LAPW calculations at five volumes in each of the monatomic f.c.c. and b.c.c. structures, and then determined a set of TB parameters [6] which reproduced the electronic structure and total energy of these structures. We then used the resulting Hamiltonian to compute the total energy of manganese in the αMn, βMn [1, 7], f.c.c., b.c.c., h.c.p., and simple cubic (s.c.) structures. The αMn structure [1] (space group $I\bar{4}3m - T_d^3$, *Strukturbericht* designation $A12$, Pearson symbol $cI58$) has a b.c.c. unit cell containing twenty-nine atoms, with five internal parameters. The twenty-nine atoms are divided up into four types, with all atoms of a given type equivalent by symmetry. There is one atom of type I, located at the origin; four atoms of type II, located at $a(x_1, x_1, x_1)$ and equivalent points, where a is the cubic lattice constant; twelve atoms of type III, located at $a(x_2, x_2, z_2)$ and equivalent points, and twelve atoms of type IV, located at $a(x_3, x_3, z_3)$ and equivalent points. The βMn structure [1] (space group $P4_3 32\text{-}O^6$, *Strukturbericht* designation $A13$, Pearson symbol $cP20$) has a simple cubic structure containing twenty atoms, with two internal parameters. There are eight atoms of type I, located at $a(x_1, x_1, x_1)$ and equivalent sites; and twelve atoms of type II, located at $a(1/8, x_2, 1/4 + x_2)$ and equivalent sites. Neither structure has an inversion site, so we must solve the generalized eigenvalue problem for Hermitian matrices. The large number of atoms, coupled with the necessity of minimizing the total energy with respect to the internal parameters, makes the determination of structural properties difficult to handle by first-principles total-energy electronic-structure calculations. Within the tight-binding method, however, the calculation is relatively easy. In table I we show the equilibrium volume, relative energy, and bulk modulus as calculated by our TB procedure for manganese, as well as technetium and copper for comparison. Figure 1 shows the energy/volume relationship for several of the lower-energy phases, and table II compares the equilibrium structural parameters with the experimental ones. Our TB Hamiltonian correctly predicts the ground-state structure of manganese. The calculation

TABLE I. – *The equilibrium volume* (V_0) *in cubed Bohr units and energy* (E_0) *in* mRy per atom, *and bulk modulus* (B_0) *in* GPa *for manganese, technetium, and copper, as calculated by the tight-binding method.* E_0 *is set to zero for the ground-state energy of each element.*

Atom		f.c.c.	b.c.c.	h.c.p.	s.c.	diamond	αMn	βMn
Mn	V_0	68.7	68.7	68.4	74.0	96.8	69.3	69.6
	E_0	8.2	15.5	3.1	91.0	172.0	0.0	1.6
	B_0	315	324	314	199	119	320	318
Tc	V_0	94.2	95.4	93.6	102.5	127.2	95.1	95.1
	E_0	6.5	23.9	0.0	57.2	73.2	0.2	2.6
	B_0	309	306	303	244	175	299	298
Cu	V_0	73.6	73.9	73.8	82.6	106.5	75.2	75.5
	E_0	0.0	3.5	1.5	25.1	70.9	6.0	5.4
	B_0	190	186	186	141	64	176	177

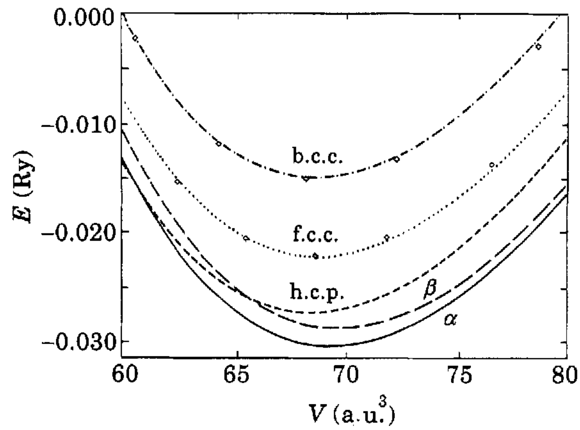

Fig. 1. – The total energy of manganese in several structures as a function of volume, obtained from the tight-binding Hamiltonian outlined in the text. We show energy per atom *vs.* volume per atom for ease in comparison. The ◇ symbols indicate the f.c.c. and b.c.c. phase LAPW energies used in the fit. The αMn phase is correctly predicted to be the ground state.

shows that the βMn phase is close in energy to the αMn phase, indicating that it is a likely candidate for the high-temperature phase of manganese, in agreement with experiment [1]. Our calculations also predict that αMn will transform into an h.c.p. structure at a pressure of 50 GPa.

Of course this agreement with experiment could be an artifact of the way we constructed the Hamiltonian. To test this, we constructed TB Hamiltonians for technetium, which is also a column VIIB element, and copper by determining tight-binding parameters which reproduced the results of APW (for technetium) and LAPW (for copper) calculations as outlined above. The resulting equation-of-state data is presented in table I. Our parametrization correctly predicts that the h.c.p. phase is the ground state for technetium although the αMn and βMn phases are close in energy. Copper is correctly predicted to be in the f.c.c. phase, while the αMn and βMn phases are, respectively, 6.0 mRy and 5.4 mRy higher than the f.c.c. phase.

Our calculations for manganese were performed assuming a paramagnetic phase, while experiment [8] and theory [9-12] suggest that several phases of manganese exhibit some form of magnetism. The αMn phase is antiferromagnetic [8, 9], but the βMn phase is paramagnetic [9]. Magnetism will thus lower the energy of the αMn phase with respect to the βMn phase. Other phases are several mRy above the αMn phase, so it is unlikely [13] that magnetization will cause these to become the ground state. Thus our calculation suggests that the αMn state is the ground state, even in the presence of magnetism.

TABLE II. – *The experimental and* TB *equilibrium lattice and internal parameters for the* αMn *structure. The* b.c.c. *unit cell has twenty-nine atoms, divided into four classes, as explained in the text. The* x_i *are dimensionless parameters describing the location of the atoms in the cubic unit cell (see text and Donohue* [1]).

	a(Å)	x_1	x_2	z_2	x_3	z_3
Experiment	8.9129	0.31765	0.35711	0.03470	0.08968	0.28211
Tight-binding	8.41	0.31719	0.35787	0.03964	0.08971	0.27983

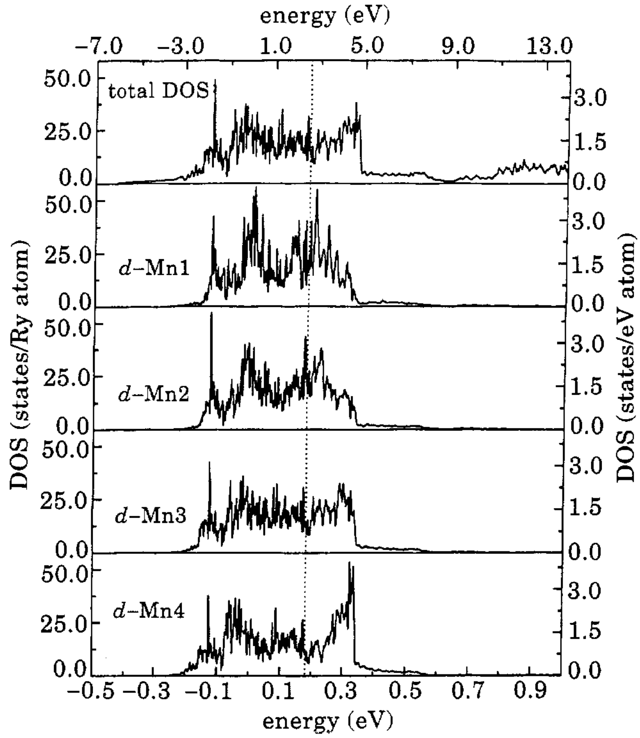

Fig. 2. – The electronic density of states (DOS) for the αMn phase. The top panel shows the total DOS, expressed in terms of states per atom. Each of the next four panels shows the d contribution to the DOS from a representative atom at the labeled site. The dotted vertical line denotes the Fermi energy.

Magnetism will affect the volume of the ground-state phase. Our equilibrium lattice constant is about 6% smaller than the experimental lattice constant. This error can be partially attributed to the neglect of magnetism and partially to the error inherent in the LDA [13]. Our calculated internal parameters (table II) are almost identical to the

TABLE III. – *The electronic density of states at the Fermi level for* αMn *at the minimum energy volume predicted by the tight-binding calculations. The partial* DOS *for the s, p, and d states are also shown for each atom type (see text). The Stoner criterion parameter is calculated assuming* $I_F = 0.03$ Ry [12]. *The coordination numbers are those assigned by Donohue* [1].

Atom			DOS at E_F				Stoner criterion
Type	Number	Coordination	Total (States/Ry/Atom)	Partial (States/Ry/Atom)			
				s	p	d	
I	1	12	23.60096	0.07778	0.70738	22.81580	0.68
II	4	10	25.78673	0.27634	0.43595	25.07444	0.75
III	12	13	15.28596	0.21981	0.64905	14.41710	0.43
IV	12	11	12.35029	0.13672	0.60299	11.61058	0.35

experimentally measured parameters, so we conclude that the internal parameters are not changed by magnetism.

Since the current formalism is not set up for spin-polarized calculations, we use our paramagnetic TB Hamiltonian to calculate the electronic density of states (DOS) for the αMn phase. Figure 2 shows the total DOS of αMn as well as the d partial DOS for the four different atom types. The width of the d states appears the same for all sites. However, there are differences in the details of the DOS structure. In particular, the Fermi level values of the DOS differ substantially. This is shown in table III where we note that the first two sites have DOS values which are a factor of two larger than the other two sites. Also from table III we note that the s- and p-like DOS at E_F are very small. We then applied the Stoner criterion [14, 15] using the DOS at the Fermi level in conjunction with a matrix element derived from f.c.c. and b.c.c. calculations [12]. Using an approximate value of $I_F = 0.03$ Ry [12], we obtained values of the Stoner nI of about 0.7 for atoms on sites I and II, and about 0.4 for atoms on sites III and IV. This is consistent with first-principles band structure calculations for the moments on the atoms [9], where it is found that atoms I and II have large moments, but atoms III and IV have smaller moments.

We conclude that our TB total-energy method is capable of predicting the correct total-energy ordering of various structures, including the complicated αMn structure, with computational costs orders of magnitude lower than standard first-principles calculations. In addition this scheme provides reliable energy bands and DOS for all phases of manganese.

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