Magnetic analytic bond-order potential for modeling the different phases of Mn at zero Kelvin

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It is known that while group VII 4d Tc and 5d Re have hexagonally close-packed (hcp) ground states, 3d Mn adopts a complex χ -phase ground state, exhibiting complex noncollinear magnetic ordering. Density functional theory (DFT) calculations have shown that without magnetism, the χ phase is still the ground state of Mn implying that magnetism and the resultant atomic-size difference between large- and small-moment atoms are not the critical factors, as is commonly believed, in driving the anomalous stability of the χ phase over hcp. Using a canonical tight-binding (TB) model, it is found that for a more than half-filled d band, while harder potentials stabilize close-packed hcp, a softer potential stabilizes the more open χ phase. By analogy with the structural trend from open to close-packed phases down the group IV elements, the anomalous stability of the χ phase in Mn is shown to be due to 3d valent Mn lacking d states in the core which leads to an effectively softer atomic repulsion between the atoms than in 4d Tc and 5d Re. Subsequently, an analytic bond-order potential (BOP) is developed to investigate the structural and magnetic properties of elemental Mn at 0 K. It is derived within BOP theory directly from a new short-ranged orthogonal d-valent TB model of Mn, the parameters of which are fitted to reproduce the DFT binding energy curves of the four experimentally observed phases of Mn, namely, α , β , γ , δ , and ϵ -Mn. Not only does the BOP reproduce qualitatively the DFT binding energy curves of the five different structure types, it also predicts the complex collinear antiferromagnetic (AFM) ordering in α -Mn, the ferrimagnetic ordering in β -Mn, and the AFM ordering in γ -, δ -, and ϵ -Mn that are found by DFT. A BOP expansion including 14 moments is sufficiently converged to reproduce most of the properties of the TB model with the exception of the elastic shear constants, which require further moments. The current TB model, however, predicts values of the shear moduli and the vacancy formation energies that are approximately a factor of 2 too small, so that a future more realistic model for MD simulations will require these properties to be included from the outset in the fitting database.

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I. INTRODUCTION

In contrast to the other group VII elements, 4d Tc and 5d Re, which adopt nonmagnetic hexagonally close-packed (hcp) ground-state structures, at room temperature 3d Mn has a paramagnetic ground state which has a complex 58-atom cubic unit cell with 4 inequivalent atomic sites [1]. This structure, termed α -Mn, is isomorphic with the χ phase of alloys such as Fe₃₆Cr₁₂Mo₁₀ and the binary Sc₅Re₂₄, and below a Néel temperature of $T_N = 95$ K has been found to exhibit complex noncollinear antiferromagnetic ordering [2,3]. The reason for the anomalous stability of the χ phase for Mn has commonly been attributed to the presence of magnetism [4]. With increasing temperature, up to a melting temperature of 1517 K, a further three phases are stabilized: complex 20-atom β -Mn, fcc γ -Mn, and bcc δ -Mn [5]. Relatively little is known of the interplay between these competing structure types particularly at higher temperatures, and in comparison to other 3d metals there is a scarcity of data and theoretical models for Mn. Additionally, a better understanding of elemental Mn would be useful to model Fe-Mn alloys, the phase diagram of which is complicated by the effects of magnetism in both Fe and Mn [6,7]. High-Mn steels have been found to exhibit extraordinary strength and ductility [8,9] on account of twinning-induced plasticity (TWIP) [10] and transformationinduced plasticity (TRIP) [11], the presence of which have been shown to depend sensitively on the intrinsic stacking fault energy of the material [12]. Zero-temperature DFT calculations for Fe-Mn predict values of the stacking fault energy of the wrong sign [13] indicating that local magnetic fluctuations play a critical role in phase stabilization in Fe-Mn alloys by stabilizing fcc over hcp at high temperatures, just as Hasegawa and Pettifor found in the Fe phase diagram [14]. One approach to investigate temperature-dependent phase transformations is to use interatomic potentials to drive large-scale atomistic simulations. This paper provides an explanation for the anomalous stability of the χ phase in 3d Mn due to core orthogonality effects and details a magnetic bond-order potential (BOP) which models the relative structural stabilities of the five primary phases of elemental Mn, namely, α , β , γ , δ , and ϵ , at T = 0 K. However, the current TB model predicts shear elastic moduli and vacancy formation energies that are a factor of 2 too small, so that future work will include these properties in the original fitting data base in order to improve the BOP model so that it may be used to simulate the magnetic and lattice fluctuations at $T \neq 0$ K using MD.

Interatomic potentials should describe cohesion and, where present, magnetism sufficiently well to reproduce reliable energies, atomic forces, structural properties, elastic constants, thermal properties, defect behavior, and surface characteristics. Two interatomic potentials that have been used widely in the past to model nonmagnetic metallic systems are the embedded-atom method (EAM) [15] and the Finnis-Sinclair potential [16]. These are comprised of two functions: a simple repulsive pair potential and an attractive embedding function both of which depend on the atomic positions and the local atomic charge densities. In a Finnis-Sinclair potential, the embedding term is proportional to the square root of the local charge densities. However, the local atomic charge densities are spherically averaged and for this reason both EAM and Finnis-Sinclair potentials neglect the directional character of the covalent d bonds found in transition metals. Additionally, they lack explicit valence dependence which can further restrict their transferability. Lee and Baskes refined the EAM model to produce the more transferable modified embedded-atom method (MEAM) [17–19] which includes some directional bonding character by considering the atomic charge density as a sum of angularly dependent partial charge densities but which still does not explicitly include magnetism or consider the electronic structure.

Only two semiempirical potentials for Mn could be found in the literature. For use in simulations of surface alloying and mixing at an Mn/Fe(001) interface, Torelli *et al.* [20] parametrized a MEAM model to reproduce a number of properties of α -Mn. However, they gave no indication of the transferability of the model to other structure types. Kim *et al.* [21] parametrized a MEAM model for pure Mn, the 14 independent parameters of which were fitted to reproduce DFT relative stabilities of α -, β -, γ -, δ -, and ϵ -Mn at T = 0 K (taken from Refs. [22,23]), elastic constants of α -Mn and the vacancy formation energy of α -Mn.

One general issue with classical interatomic potentials, that also applies to the parametrizations discussed above, is that they fail to describe explicitly the effects of magnetism, a quantum mechanical effect, on the formation of chemical bonds. Given the crucial importance of magnetic fluctuations to the properties of transition metals and their alloys, such as temperature-dependent phase stabilities, elastic constants, and defect energies, if the temperature-dependent phase stabilities of magnetic Mn and Fe-Mn are to be investigated, then a potential that explicitly considers magnetism is required. Some EAM-type interatomic potentials for transition metals which do include an explicit treatment of magnetism have been developed. For example, Ackland et al. [24] described the total energy per atom as a sum of the up- and down-spin band energies and an additional exchange term, where the band energies were calculated within the second-moment approximation to the tight-binding model by a Finnis-Sinclair-type expression. Dudarev and Derlet [25] extended this approach further using an energy derived from the Stoner theory of magnetism [26] and mean field Ginzburg-Landau theory. In both cases, the potentials were fitted for use with ferritic Fe and capture volume-dependent changes in the magnetic moments in this particular structure type. The lack of information about the shape of the density of states (DOS) near the Fermi level means that they are unable to describe the subtle structural dependence of the magnetic energy and therefore lack the physical basis for modeling phase transformations. Indeed it has been shown that fourth-, fifth-, sixth-, and higher-moment contributions to the local DOS are important for modeling defect energies as well as the phase diagram of iron [27].

The tight-binding (TB) approximation provides a step between *ab initio* density functional theory and interatomic potentials [28]. It is less computationally expensive than DFT, allowing the simulation of thousands of atoms, and yet provides a transparent, intuitive physical description of bonding in solids. The tight-binding approximation can be derived directly as a second-order expansion of DFT with respect to charge and magnetic fluctuations [27,29,30]. The DFT approach for solving for the eigenfunctions and eigenvalues of a Hamiltonian is followed within TB except that the Hamiltonian is simplified, being composed of distance-dependent Slater-Koster-type bond and overlap integrals [31]. These can be obtained by projecting DFT wave functions onto basis sets of atomiclike orbitals [32–34] which can then be optimized and, if required, orthogonalized such that the overlap integrals are zero. The calculation of total energies within TB also requires repulsive, and often embedding, functions which can be parametrized from DFT total energies and forces. The Stoner model of itinerant magnetism extends the TB approximation to magnetic materials and it has been shown to work well for 3*d* transition metals [35,36].

Mehl et al. [37] developed a nonorthogonal TB model for Mn, but its scope was restricted to nonmagnetic structures. Alternatively, Süss and Krey [38] used an orthogonal TB model with a Hubbard-type exchange Hamiltonian to model antiferromagnetic α -Mn and fcc γ -Mn. They were unable to obtain magnetic moments consistent with experiment unless they used a different value of the Hubbard-U parameter for each of these two structure types nor did they provide a comparison of the predicted relative stabilities. Additionally, they attempted to calculate an antiferromagnetic α -Mn structure with noncollinearly ordered magnetic moments but this failed to converge self-consistently with respect to the energy and the spin polarization. More recently, McEniry et al. developed an orthogonal d-valent magnetic TB model which was used to study a number of nonmagnetic phases [34]. The model predicts an α -Mn ground state but it fails to reproduce the correct relative stabilities of a number of the other phases and it severely underestimates the nonmagnetic fcc-hcp energy difference. The results presented in Fig. 5 of Ref. [34] are for unrelaxed structures, but having tested the model further we find that, first, the nonmagnetic and antiferromagnetic α -Mn structures do not undergo correct relaxation of their internal coordinates for atomic volumes greater than $\sim 11 \text{ Å}^3/\text{atom}$, and, second, that the β - and δ -Mn phases exhibit mechanical instability, with a negative C' for ferrimagnetic β -Mn and a negative C_{44} for antiferromagnetic δ -Mn.

Bond-order potentials (BOPs) are a class of real space, order (N), interatomic potentials based on the TB description for the binding energy including magnetism. BOPs retain the quantum mechanical character of the TB model and explicitly include the valence dependence of bond formation and, as a result, account for charge transfer and magnetism in a physically transparent way [27,39,40]. Furthermore, the angular characteristic of bonding is retained within the BOP formalism and a Hellmann-Feynman-type term is used to evaluate atomic forces. This numerical BOP formalism [41] was applied by Mrovec et al. [42] to provide an accurate description of the electronic and magnetic structure of Fe at 0 K that reproduces the behavior of lattice defects such as dislocations, which induce changes in bond lengths, bond angles, and local magnetic moments. However, in the numerical BOP formalism, for low-moment expansions, the Hellmann-Feynman forces [43] can only be calculated approximately. In contrast, the recently developed analytic BOP [27] formalism gives the binding energy and forces for a collection of atoms as analytic functions of the moments of the local DOS. Because the force expressions are analytic, they can be evaluated accurately and rapidly, and thus analytic BOP is well suited to performing large-scale dynamic simulations as has been demonstrated for nonmagnetic W [44]. Drautz and Pettifor [40] showed that analytic BOP theory with six moments was able to predict the different ferromagnetic moments of the bcc, fcc, and hcp phases of 3d Fe and, more recently, Ford *et al.* [45] developed a nine-moment magnetic analytic BOP for Fe capable of reproducing the behavior of the local magnetic moments in defect structures. Seiser *et al.* [46] further extended analytic BOP theory to ensure that the BOP DOS does not include any unphysical negative regions.

This paper is organized as follows. In Sec. II, details of the various stable allotropes of elemental Mn and their magnetic configurations are given. In Sec. III, TB and BOP theory are discussed and the parameters for the TB and BOP model are presented. In Sec. IV, the computational details of the TB, BOP, and reference DFT calculations are given. In Sec. V A, we investigate the anomalous stability of the χ phase in Mn and in Secs. V B–V E, we examine the results of the new TB and BOP models at T = 0 K. In Sec. VI, we conclude.

II. MANGANESE

Manganese has complex structural and magnetic properties. Under ambient conditions, the most stable Mn allotrope, α -Mn, has a complex cubic structure with a 58-atom unit cell (with 29 atoms in the primitive unit cell). From the perspective of developing models for Mn, further complexity is added by the most stable allotropes being very closely spaced in energy at their equilibrium volumes. In contrast to Fe where, at 0 K, the magnetic energy stabilizing the ferromagnetic (FM) bcc structure over nonmagnetic (NM) bcc is ~500 meV/atom, in Mn the magnetic energy stabilizing the antiferromagnetic (AFM) α -Mn structure over NM α -Mn was found in recent DFT calculations [22] to be around 40 meV/atom with a number of magnetic and nonmagnetic structures all lying within just 70 meV of the ground state.

A. α-Mn

The room-temperature ground-state structure for Mn, paramagnetic α -Mn [1], has a 58-atom cubic unit cell (Structure Report symbol A12, Pearson symbol cI58, space group $T_d^3 - I\bar{4}3m$) which is comprised of four crystallographically inequivalent sites I, II, III, and IV, with relative population 2:8:24:24. (We will see later in Sec. II A that below a Néel temperature of 95 K, a slight tetragonal distortion splits both sites III and IV into two further subgroups.) These sites are surrounded by coordination polyhedra with 16, 16, 13, and 12 atoms, respectively. These local coordination polyhedra are illustrated in Fig. 1. Each site I atom [Fig. 1(a)] is surrounded by a Z16 Frank-Kasper coordination polyhedron [47,48] comprised of 12 Mn IV atoms arranged as four triangles on the faces of a tetrahedron formed by 4 Mn II atoms. A shorthand description [I:II:III:IV], giving the relative population of sites I, II, III, and IV atoms in each local coordination polyhedron, can be adopted and the coordination polyhedra around site I atoms can therefore be denoted as [0:4:0:12]. The second nearest-neighbor shell of the Mn I atoms consists of 24 Mn III atoms. The 8 site II Mn atoms [Fig. 1(b)] are also surrounded by Z16 coordination polyhedra comprised of atoms [1:0:6:9]. The site III atoms [Fig. 1(c)] are surrounded by Z13 coordination polyhedra (which are not Frank-Kasper polyhedra because they contain a nontriangular face) comprised of atoms [0:2:7:4]. The site IV atoms [Fig. 1(d)] are surrounded by Z12 coordination polyhedra [1:3:5:3]. Although the α -Mn structure is not strictly a topologically close-packed (TCP) phase because it contains Z13 polyhedra, χ -phase structures such as α -Mn are often considered analogous to TCP phases because they share some of the same features, namely, that they can be represented by stacking local coordination polyhedra of different radii, typically with larger atoms occupying the highest coordination sites and smaller atoms occupying lower coordination sites. A number of χ -phase binary alloys are formed between group VII 4d Tc and 5d Re with transition elements to their left in the periodic table, such as $Nb_{0.25}Tc_{0.75}$, $Zr_{0.14}Tc_{0.86}$, $Ta_{0.25}Re_{0.75}$, and $Hf_{0.14}Re_{0.86}$ [4]. In these binary structures, the 16-fold coordinated sites are typically found to contain the larger atoms of the minority alloying elements while the 12- and 13-fold coordinated sites typically contain the smaller Tc or Re atoms. One common interpretation of the α -Mn structure is that atoms at the different sites behave as if of different sizes [49] with the sites I and II atoms, which occupy the higher coordination sites, able, as we will see, to support large magnetic moments and the sites III and IV atoms, which occupy lower coordination sites, able to support only small magnetic moments. In this way, α -Mn has been termed a self-intermetallic compound [50] by analogy with common intermetallic χ -phase structures. Thus, it has been generally thought that the presence of magnetism allows elemental Mn to behave like a binary χ -phase compound which is stabilized by the atomic-size difference between the constituent atoms for favorable electron-per-atom ratios of band filling, and it is this behavior that drives the stability of the χ phase over hcp in contrast to elemental Tc and Re. Importantly, however, we will find in Sec. V A that DFT predicts that α -Mn is still the most stable phase even when it is nonmagnetic, so that magnetism is not the critical factor in stabilizing this complex crystal structure.

 α -Mn also takes a complex magnetic ground state. Analysis of neutron diffraction data [3,50] has found that it is not only antiferromagnetic, as is expected for a 3*d* element in the middle of the transition-metal series (see Fig. 8.1 of Ref. [4]), but also that it has magnetic moments that are aligned noncollinearly. In particular, below a Néel temperature of $T_N = 95$ K [2,3], noncollinear AFM α -Mn has large magnetic moments at sites I and II, with moments on each Mn I atom approximately antiparallel to both those of its Mn II nearest neighbors and its closest Mn I neighbors, and much smaller, but canted, moments at sites III and IV. The phase transition below the Néel temperature has also been found to be coupled to a slight tetragonal distortion which splits the site III and IV atoms into two further subgroups, leading to a total of six inequivalent sites [50,51].

In DFT calculations, Hobbs *et al.* [22] managed to converge noncollinear AFM solutions but these only became more stable than the collinear AFM ground-state structure at atomic volumes expanded above 13 Å³/atom, ~18% above the calculated equilibrium volume of collinear AFM α -Mn of (a) Site I, 2 atoms in cubic unit cell, Z16 coordination polyhedron



(c) Site III, 24 atoms in cubic unit cell, Z13 coordination polyhedron



(b) Site II, 8 atoms in cubic unit cell, Z16 coordination polyhedron



(d) Site IV, 24 atoms in cubic unit cell, Z12 coordination polyhedron



FIG. 1. (Color online) Illustration of the relaxed local coordination polyhedra that surround each of the four inequivalent atoms in α -Mn. Atoms at each site are indicated by spheres of the following size and color; site I: large, dark red; site II: large, pale yellow; site III: small, dark blue; site IV: small, white. The atomic coordinates plotted are taken from the DFT-calculated equilibrium volume of AFM α -Mn and the DFT magnetic moments are illustrated with green arrows. For comparison, the magnetic moments from TB (red arrows) and 14-moment BOP (blue arrows) calculations, using the DFT-relaxed internal coordinates, are also included.

11.08 $Å^3$ /atom. This was attributed to the overbinding of the GGA which results in an equilibrium volume 7% smaller than that observed experimentally. They concluded that the onset of noncollinear antiferromagnetism was driven by the frustration of the AFM exchange interaction of the 12-fold coordinated Mn IV atoms that are arranged in triangular motifs on the faces of the Z16 coordination polyhedra which surround the Mn I atoms. Above 13 $Å^3$ /atom, the Mn IV magnetic moments grew larger and, within each triangular motif, ordered roughly 120° to each other, similar to the arrangement of nearest-neighbor spins in the Néel phase of a frustrated triangular antiferromagnet. The resultant coupling drove the Mn III moments to rotate out of collinearity with the Mn I and Mn II atoms, and a very minor canting of the Mn II spins. Below 13 Å³/atom, the local moments on the Mn IV atoms collapsed completely, which was sufficient to reduce the frustration and hence stabilize the collinear AFM magnetic structure. At atomic volumes $\ge 14 \text{ Å}^3/\text{atom}$, it was also shown that the increased frustration in the collinear AFM α -Mn structure could be stabilized, not by the canting of spins, but by a structural distortion.

DFT investigations into collinear AFM a-Mn structures [52–54] have not all agreed on the size and alignment of the magnetic moments at each of the Mn sites. However, recent consensus [22], in agreement with experimental findings, indicates the presence, first, of large moments on each Mn I atom that are oriented antiparallel to slightly smaller moments on its Mn II nearest neighbors, and, second, significantly smaller moments on sites III and IV. In the case of site IV atoms, the magnetic moments are virtually zero. A crystal can reduce the kinetic energy cost of magnetic ordering by undergoing a lattice expansion [55] which leads to a reduction of the bandwidth. Hence, crystals with a decreased packing density, such as the site I and II atoms which are surrounded by Z16 polyhedra, are able to support larger local magnetic moments, while those with an increased packing density, such as the site III and IV atoms which are surrounded by the more closely packed Z13 and Z12 polyhedra, will have a broader *d* band and, as a result, smaller local magnetic moments. For the 12 coordinated site IV atoms, this increased local packing density completely quenches magnetism.

As DFT calculations [22] find only collinear AFM α -Mn to be stable around the equilibrium volume, noncollinear AFM α -Mn has not been studied in this paper.

B. β -Mn

At elevated temperatures, other allotropes of Mn are stable. β -Mn is stable between 1000–1368 K and has a 20-atom cubic unit cell with A13 (*cP20*, *P4*₁32 – *O*⁶) symmetry [56] consisting of two inequivalent sites I (8 atoms) and II (12 atoms). The structure is more closely packed around the site I atoms which are surrounded by distorted icosahedra comprised of three Mn I and nine Mn II atoms. The site II atoms are surrounded by Frank-Kasper Z14 polyhedra comprised of six Mn I and eight Mn II atoms. Most examples of the A13 structural symmetry occur as binary alloys, e.g., Fe₂Re₃ and Mg₃Ru₂ [57].

Between 1000–1368 K, β -Mn is paramagnetic and although it remains paramagnetic down to very low temperatures, it has been shown to exhibit strong spin fluctuations [58,59] and NMR data [60] have been interpreted as showing that the site I atoms are approximately NM but that the site II atoms carry small paramagnetic moments. β -Mn has been considered as a spin liquid, on account of structural frustration leading to a quenching of magnetism [61], but addition of a range of dopants has been found to drive a transition from the spinliquid state to a spin-glass structure [60,62]. Consistent with the experimentally observed spin-liquid behavior, DFT calculations [23] have predicted that at equilibrium volume, a NM structure and an almost ferrimagnetic (FiM) structure (with site I moments almost zero) are energetically degenerate. However, at expanded volumes FiM structures [23,52] and even a noncollinear magnetic structure [54] have been predicted.

C. y-Mn

Face-centered-cubic γ -Mn is stable between 1368– 1406 K. γ -Mn can be quenched to room temperature transforming via a magnetically induced transition [63] to a tetragonally distorted face-centered-tetragonal (A5) structure below a Néel temperature of $T_N = 500$ K [64,65]. With the addition of 5% Cu, this reverts back to the fcc structure. Type-1 AFM ordering, which consists of successive *z* planes ferromagnetically polarized with alternating signs from one plane to the next, has been found to be the lowest-energy magnetic configuration of the fcc structure. From experimental data extrapolated to 0 K, magnetic moments of $2.1\mu_B$ have been reported for such a structure [66].

D. δ-Mn

Body-centered-cubic δ -Mn is stable between 1406–1517 K. DFT calculations have predicted magnetic ordering to be type-2 AFM (AFM2) with a transition to a type-1 AFM structure at atomic volumes greater than 14 Å³/atom [23]. In type-2 AFM ordering, spins within a given [111] plane are parallel and spins on neighboring [111] planes are antiparallel. The melting temperature of Mn is 1517 K.

E. e-Mn

Under pressures of 158–165 GPa, α -Mn transforms to a phase interpreted as being either bcc, fcc, or hcp [67]. From DFT data, Hafner *et al.* [23] predict that this phase is hcp in line with the stable crystal structures of the nonmagnetic group VII metals Tc and Re. Their results also predict hcp to be nonmagnetic at equilibrium volume in contrast to fcc which is antiferromagnetic.

III. THEORY

A. Tight-binding model

The TB model used in this work is based on that used by McEniry *et al.* [34]. In summary, within the *d*-valent, two-center, orthogonal TB bond model [29], and with the onsite levels adjusted to fulfill the condition of local charge neutrality (LCN) [41], the binding energy functional can be written as

$$U_B = U_{\text{bond}} + U_X + U_{\text{emb}} + U_{\text{rep}},\tag{1}$$

where U_{bond} is the bond energy and U_X is the exchange energy. U_{emb} is an attractive embedding energy, accounting for the contribution of the *s* electrons and *sd* hybridization which are not included in the TB Hamiltonian. The Finnis-Sinclair [16] square-root embedding function is chosen with the embedding potential given by [33]

$$U_{\rm emb} = -\sum_{i} \sqrt{\sum_{j \neq i} \left(a_{\rm emb}^{ij}\right)^2 \exp\left[-b_{\rm emb}^{ij}(R_{ij})^{c_{\rm emb}^{ij}}\right]}.$$
 (2)

 $U_{\rm rep}$ is a pairwise, repulsive energy which accounts for the overlap repulsion, double-counting energy, and ion-ion repulsion. In this work, it is represented by two stretched exponential terms

$$U_{\rm rep} = \sum_{i} \sum_{j \neq i} \left[a_{\rm rep}^{ij} \exp\left[-b_{\rm rep}^{ij} (R_{ij})^{c_{\rm rep}^{ij}} \right] + a_{\rm hcr}^{ij} \exp\left(-b_{\rm hcr}^{ij} R_{ij} \right) R_{ij}^{-c_{\rm rep}^{ij}} \right].$$
(3)

The first term follows the form of the repulsive energy used in Ref. [34], while the second, a hard-core repulsion which has a form similar to a Yukawa potential, has been introduced to ensure that the internal coordinates of α -Mn and vacancycontaining structures relax correctly. Readers are directed to Ref. [34] for details of the functional form of the bond energy, the bond integrals, the exchange energy, and that of the cosine cutoff function which controls the range over which the bond integrals, repulsive energy, and embedding energy all extend.

B. Choice of TB parameters

The TB parameters, given in Table I, were fitted as follows. First, the bond integrals $\beta_{dd\lambda}(R)$ were fitted to the matrix elements of the Mn dimer which McEniry *et al.* obtained by projecting an extended multiple- ζ basis set, taken from DFT calculations based on the linear combination of atomic orbitals (LCAO) approach, onto an optimized single- ζ basis set which was then orthogonalized via the Löwdin transformation [34]. Within the *d*-band model, *s* and *p* electrons are not explicitly treated and so the number of *d* electrons N_d is an input parameter. The value in the model was chosen to minimize

TABLE I. TB model parameters: repulsive energy, embedding potential, bond integrals, Stoner parameter, and electron count. The functional form of the bond integrals is given in Eq. (1) of Ref. [34].

	Repulsive energy		
$a_{\rm rep}~({\rm eV})$	$b_{\rm rep}$ (Å ⁻¹)	$c_{\rm rep}$	
896.80	3.362	0.907	
$a_{\rm hcr}~({\rm eV})$	$b_{ m hcr}$ (Å ⁻¹)	Chcr	
10000	0.01	15	
	Embedding potential		
$a_{\rm emb}~({\rm eV}^2)$	$b_{\rm emb}$ (Å ⁻¹)	$c_{\rm emb}$	
2.513	0.0631	2.542	
	Bond integrals		
	<i>a</i> (eV)	b (Å ⁻¹)	
$dd\sigma$	-24.723	1.404	
$dd\pi$	81.218	2.101	
$dd\delta$	-83.284	2.892	
Sto	Electron coun		
	I_d (eV)	N_d	
	0.65	5.7	

the error between the TB and DFT bonding energies of NM hcp ϵ -Mn and NM fcc γ -Mn structures at equilibrium volume.

The parameters for the hard-core part of the repulsive function were set to ensure a strong repulsion at atomic distances of less than 2 Å and the remaining repulsive and embedding parameters were then fitted to minimize errors between the TB binding energies and DFT energy-volume curves for NM α -, β -, γ -, δ -, and ϵ -Mn and AFM α -, γ -, and δ -Mn for atomic volumes of 8–14 Å³/atom. With the efficient implementation of large-scale BOP simulations in mind, this model was parametrized with shorter-ranged cutoffs than those of previous models [34] such that the Hamiltonian matrix elements are cut off by the fourth-, and the $U_{\rm rep}$ and $U_{\rm emb}$ functions by the fifth-, nearest neighbors in fcc γ -Mn. Specifically, the cutoffs are $R_{\rm cut} = 4.5$ Å and $d_{\rm cut} = 1.0$ Å for the bond integrals, and $R_{\rm cut} = 5.5$ Å and $d_{\rm cut} = 0.5$ Å for the repulsive and embedding functions.

The value of the Stoner parameter I_d , which is used to determine the exchange energy U_X , was chosen to best reproduce the behavior of the magnetic states of the most stable structures. While in principle its value should depend on the atomic environment [68], in keeping with the simplicity of the TB model it is kept constant across all structure types ignoring volume-dependent effects, which are small [69].

C. BOP

A brief overview of analytic BOP theory is given here, but readers are referred to Refs. [27,40,45,46] for comprehensive details. Analytic BOP theory [27,40] approximates the local DOS as a sum over Chebyshev polynomials which allows the analytic integration of the bond energy. The moments of the local TB DOS

$$\mu_{i\alpha\nu}^{(n)} = \int E^n n_{i\alpha\nu}(E) dE \tag{4}$$

may be evaluated without explicit knowledge of the DOS by relating the moment of order n to the self-returning hopping

paths of length *n* that start and end on spin orbital $|i\alpha\nu\rangle$:

$$\mu_{i\alpha\nu}^{(n)} = \sum_{i_{1}\alpha_{1}\nu_{1}, i_{2}\alpha_{2}\nu_{2}, \dots, i_{n-1}\alpha_{n-1}\nu_{n-1}} \langle i\alpha\nu|\hat{H}|i_{1}\alpha_{1}\nu_{1}\rangle$$
$$\times \langle i_{1}\alpha_{1}\nu_{1}|\hat{H}|i_{2}\alpha_{2}\nu_{2}\rangle \dots \langle i_{n-1}\alpha_{n-1}\nu_{n-1}|\hat{H}|i\alpha\nu\rangle.$$
(5)

The TB Hamiltonian can be represented in the form of a semiinfinite one-dimensional chain with onsite matrix elements a_n and nearest-neighbor hopping matrix elements b_n using the Lanczos recursion algorithm. This also generates associated polynomials that form an orthogonal and complete set if the DOS is used as a weight function in the definition of the scalar product [70]. As such, if the DOS of a reference Hamiltonian is known, the associated polynomials may be used to expand the DOS of a different Hamiltonian. The reference Hamiltonian used [40] is that of a semi-infinite chain with constant matrix elements $a_n = a_{i\alpha\nu}^{(\infty)}$ and $b_n = b_{i\alpha\nu}^{(\infty)}$, which has a semielliptic DOS

$$n_{i\alpha\nu0}(\epsilon) = \frac{2}{\pi}\sqrt{1-\epsilon^2},\tag{6}$$

with

$$\epsilon = \frac{E - a_{\infty}}{2b_{\infty}}.\tag{7}$$

Using Chebyshev polynomials of the second kind [71] $U_n(\epsilon)$, the DOS can be guaranteed to be positive everywhere by adapting the kernel polynomial method [46,72,73] and writing

$$n_{i\alpha\nu}(\epsilon) = \frac{2}{\pi} \sqrt{1 - \epsilon^2} \left[\sum_{n=0}^{n_{\max}} g_U^{(n)} \sigma_{i\alpha\nu}^{(n)} U_n(\epsilon) + \sum_{n_{\max}+1}^{n_{\exp}} g_U^{(n)} \sigma_{i\alpha\nu}^{(n)} U_n(\epsilon) \right],$$
(8)

where $g_U^{(n)}$ are damping factors appropriate to Chebyshev polynomials of the second kind [46].

The expansion coefficients up to n_{max} moments are calculated explicitly, while the remainder, running up to n_{exp} , are obtained from the square-root terminator [46]. The asymptotic recursion coefficients $a_{i\alpha\nu}^{(\infty)}$ and $b_{i\alpha\nu}^{(\infty)}$ must be approximated and we have used the following identities [74]:

$$a_{i\alpha\nu}^{(\infty)} = (\epsilon_{\max} + \epsilon_{\min})/2, \tag{9}$$

$$b_{i\alpha\nu}^{(\infty)} = (\epsilon_{\max} - \epsilon_{\min})/4, \qquad (10)$$

where ϵ_{\max} and ϵ_{\min} are calculated from the maximum and minimum values of $a_{ni\alpha\nu}$ and $b_{ni\alpha\nu}$:

$$\epsilon_{\max} = a_{ni\alpha\nu}^{\max} + 2b_{ni\alpha\nu}^{\max},\tag{11}$$

$$\epsilon_{\min} = a_{ni\alpha\nu}^{\min} - 2b_{ni\alpha\nu}^{\max}.$$
 (12)

Within BOP, unlike in a TB calculation, a direct minimization of the binding energy with respect to the charges and magnetic moments must be performed in order to ensure that the energies and forces are consistent [27]. This is done by ensuring that the gradients of the binding energy with respect to the Hamiltonian onsite levels are zero, namely,

$$\sum_{i\alpha\nu} \frac{\partial U_B}{\partial E_{i\alpha\nu}} = 0.$$
(13)

The derivatives of the binding energy can be rewritten in terms of the local moments, and the gradients of the local moments with respect to the onsite levels can then be found [27,45]. The calculation of these also allows a Hellmann-Feynman–type expression for the exact analytic forces to be evaluated at no extra computational cost.

IV. COMPUTATIONAL DETAILS

A. Density functional theory

DFT calculations were performed with the Vienna *ab initio* simulation package (VASP) [75,76] using the allelectron projector-augmented wave (PAW) method. For spinpolarized exchange and correlation potentials, the Perdew-Burke-Ernzerhof (PBE) [77] parametrization of the generalized gradient approximation (GGA) was used. The Brillouin zone was sampled using the Monkhorst-Pack scheme [78] and the tetrahedron integration method [79]. *k*-point grids were used such that a convergence in the total energy of at least 1 meV/atom was achieved. The cutoff energy for the plane-wave expansion was fixed at 350 eV for all calculations. For relaxation of the internal coordinates, the forces were converged to at least 1 meV/Å.

B. Tight binding

TB calculations were performed using the BOPFOX code [80]. The Brillouin zone was sampled using the Monkhorst-Pack scheme and integrated using the tetrahedron method [79] such that a convergence in the binding energy of at least 1 meV/atom was achieved. Local charge neutrality (LCN) was enforced such that the magnetic moments were found self-consistently under the constraint that the final atomic charges were numerically zero.

C. Bond-order potential

BOP calculations were also performed using the BOPFOX code [80] using the bond integral and repulsive and embedding parameters from the TB model. In the original analytic BOP paper [40] it was discussed that some BOP DOS showed small negative regions at the band edges. More recently, it was shown that, even for elements for which the Fermi level lies towards the middle of the band, regions of negative DOS can significantly affect the outcome of defect structure calculations and that in calculations with noncollinear magnetism regions of negative DOS can occur in the middle of the band [81]. This motivated the development of an adaptation to analytic BOP theory [46] in which two of the present authors showed how to ensure an analytic BOP DOS which is positive across the whole band, as briefly discussed in Sec. III C. This strictly positive DOS can be seen in Fig. 2 which is a comparison of the DOS for NM γ -Mn, ϵ -Mn, and α -Mn as calculated using DFT, and the newly developed TB and analytic BOP models.



FIG. 2. (Color online) Comparison of the electronic density of states in nonmagnetic γ -Mn (left panel), ϵ -Mn (central panel), and α -Mn (right panel), as calculated using DFT (top), TB (upper center), 20-moment BOP (lower center), and 14-moment analytic BOP (bottom). The plots have been shifted such that the Fermi level lies at the zero of energy and is marked with a dashed vertical line. Methfessel-Paxton *k*-space integration with a smearing of 0.1 eV has been used in the TB and DFT calculations.

The analytic BOP calculations have been performed with 14 and 20 exact moments and a terminator with $n_{exp} = 100$, as have all other BOP calculations in the paper. It can also be seen that while the BOP expansion with 14 exact moments $n_{max} =$ 14 reproduces the general shape of the TB DOS, much more detail is reproduced in the $n_{max} = 20$ DOS. The convergence of BOP results to those of TB, as a function of the number of moments, will be discussed in Sec. V. With the version of the BOPFOX code used in this work, the speed of a TB calculation, for a four-atom unit cell, was comparable to that of a 17-moment BOP calculation.

V. RESULTS

A. Origin of the ground-state structural trend from χ to hcp down group VII

It has been noted that Mn is anomalous in that its ground state is the complex χ -phase structure rather than hcp as is the case for the other group VII elements 4d Tc and 5d Re. It has been commonly reported that the reason for the stability of the χ phase in Mn is its self-intermetallic character driven by the atomic-size difference of the two sets of inequivalent sites with the site I and II atoms, and their larger local coordination polyhedra, behaving as larger atoms which are therefore able to support larger magnetic moments, and the site III and IV atoms, and their smaller local coordination polyhedra, behaving as smaller atoms. However, as may be deduced from the results of a previous DFT investigation into the stable phases of Mn [22,23], and as will be shown in Sec. V B Fig. 7, even without the magnetic energy which stabilizes AFM α -Mn in the manner described above, NM α -Mn remains more stable than the nonmagnetic and magnetic forms of all the other structure types. Thus, magnetism and the atomic-size difference present in the χ phase are not the critical factors in stabilizing α -Mn.

1. Electronic structure and internal coordinates

A number of features of Mn, Tc, and Re have been examined and it is found that differences in the electronic structure and relaxed internal coordinates of the χ phase are not significant enough to explain the anomalous χ -phase stability in Mn.

DFT structural energy differences for the NM bcc, hcp, fcc, and χ -phase structures of the 3*d* transition elements, from V to Co, and the corresponding 5*d* elements are plotted in the left-hand panel of Fig. 3. It can be seen that DFT reproduces the experimentally observed anomaly of 3*d* Mn having a χ phase ground state while 5*d* Re is hcp. The 4*d* series behaves qualitatively the same as the 5*d* series with 4*d* Tc also predicted by DFT to have an hcp ground state.

A comparison of the DFT total DOS for Mn, Tc, and Re, plotted in the upper panels of Fig. 4, indicates that there are no significant differences in the relative contributions of *s*, *p*, and *d* orbitals in the NM χ phases of the three elements with, as expected, very few *s* and *p* states in the *d* band. The *d*-orbital DOS at E_F does exhibit a small difference, lying at the shoulder of a peak in Mn but lying in a small trough in Tc and Re. The sources of this difference are shallow troughs in the local DOS at E_F of the site II, III, and IV atoms in Tc and Re which are absent in Mn. In the lower panels of Fig. 4, the total normalized DOS has been plotted as a function of band filling. In order to negate differences in the bandwidths of the three elements, each has been normalized with respect to the DOS at E_F of the χ phase at a band filling of N = 7(corresponding to the seven valence electrons of the group VII



FIG. 3. (Color online) Left-hand panels: Structural energy differences calculated with DFT total energies for (upper left) 3*d* transition metals, V to Co, and (lower left) 5*d* transition metals, Ta to Ir. Right-hand panels: Structural energy differences calculated with TB bond energies using structural energy difference theorem [see Eq. (19)] versus the number of *d* electrons N_d for (upper right) the Mn TB model detailed in this paper and (lower right) the canonical TB model detailed in Ref. [82]. The energies are normalized with respect to U_{fcc}^* which for the DFT calculations is the group VII fcc total energy and for the TB calculations is the fcc bond energy at $N_d = 5.7$ (the valence electron count for the Mn TB model).



FIG. 4. (Color online) Upper panels: Comparison of DFT total DOS for NM χ phase for Mn, Tc, and Re including the partial contributions from *s*, *p*, and *d* orbitals. The Fermi level is marked with a dashed vertical line. Lower panels: DFT total DOS as a function of band filling *N* for the χ phase, fcc, bcc, and hcp structures for Mn, Tc, and Re. For each element, the DOS has been normalized with respect to the value of the DOS at the Fermi level for the χ phase at N = 7 (the valence electron count for the group VII elements). The value of the absolute DOS per atom of the χ phase at N = 7 is 0.989 states/eV for Mn, 0.722 states/eV for Tc, and 0.718 states/eV for Re.

elements). From these plots, however, it can be seen that the small differences in the χ -phase DOS of Mn, Tc, and Re are not significant enough to drive the change in hcp- χ stability observed from the 3*d* to the 4*d* and 5*d* elements.

The DFT valence band structures have been plotted for Mn, Tc, and Re in Fig. 5 within the primitive fcc unit cell. In order to compare them directly, they have been normalized by the bandwidth of the respective element. It can be seen that the differences between the band positions and curvatures are minor and that the separation between the top of the *s* band and the bottom of the *d* band at the Γ point, although varying slightly, does not indicate that significantly different degrees of *s*-*d* hybridization are present within the three elements. Similarly, analysis of the total charges per orbital in the χ phase showed trends consistent only with a decrease in effective nuclear charge moving down the group from 3*d* to 4*d* to 5*d*. This seems to discount the possibility of variations in *sp*-*d* hybridization or the relative numbers of valence *d* electrons being the critical factor in stabilizing the χ phase in Mn.

Additionally, we find that there are only minor differences between the relaxed internal coordinates of χ -phase Tc and Re and those of NM α -Mn (given later in Table III) and that, furthermore, when the DFT structural energy differences seen in Fig. 3 for Mn were recalculated using the relaxed Tc and Re internal coordinates, and vice versa, the relative stabilities of the χ phase and hcp were left unchanged, i.e., Mn still stabilized the χ phase while Tc and Re still stabilized hcp. This suggests that the differing behavior of Mn and Tc/Re is not driven by a structural effect.



FIG. 5. (Color online) Band structure, normalized by the bandwidth, of the fcc primitive cell for Mn, Tc, and Re, plotted at their respective equilibrium volumes.

2. Effective atomic repulsion

The canonical TB *d*-band model of Seiser *et al.* [82], previously used to investigate trends within topologically close-packed structures in the 4*d* and 5*d* series, was then used to further investigate the source of the relative stabilities of hcp and the χ phase in the group VII elements. Within the canonical TB model, the binding energy is given as the sum of a bond energy and a repulsive energy. The bond integrals take the simple canonical form [83,84]

where

$$\beta(R) = CR^{-n},\tag{15}$$

and *C* is a constant. The repulsive energy is assumed to be pairwise and given by the Wolfsberg-Helmholz approximation [4] decaying with distance as a power of the bond integral, namely,

$$U_{\rm rep} = \sum_{i,j,i\neq j} \Phi(R_{ij}),\tag{16}$$

where

$$\Phi(R_{ij}) = k[\beta(R_{ij})]^m.$$
(17)

The repulsive function is therefore dependent on both exponents n and m with

$$U_{\rm rep} \propto R^{-nm}$$
. (18)

By varying the exponents n and m, which control the decay of the bond integrals and the repulsive energy, the role of the relative hardness of the potential on phase stability for a nearly half-filled d band was investigated. Previous work has shown that changes in the relative hardness significantly affect structural stability. For *sp*-valent carbon the graphite ground state was shown to be stabilized over diamond by decreasing the relative hardness of the potential compared to silicon [85]. The origin of the decreased hardness for carbon as compared to silicon is due to the absence of *p*-core electrons in carbon, which leads to a weaker repulsion of the *p*-valence electrons from the core region [4]. The variation of the s-plevel splitting then drives the stability from Si diamond to the close-packed fcc ground state of Pb down group IV, but can not explain the graphite ground state of C [86]. Thus, C (graphite), N (dimer), and O (dimer) all take more open ground-state structures than their counterparts in the remaining rows of the groups because they have a decreased hardness, due to the absence of p electrons in their cores [4]. Related structural trends were also observed for four-atom molecules modeled by a simple pair potential. A harder potential was shown to stabilize the close-packed tetrahedron and rhombus over the more open square, but when the hardness is decreased, the relative stabilities of the rhombus and the square switch [4]. Specifically, the change in relative stability of the rhombus and square occur as the degree of normalized hardness α_h , given by (m-1)/m, decreases from $\frac{1}{2}$ to $\frac{1}{3}$.

Figure 6 shows a plot of the structural energy difference of hcp relative to χ as a function of both *n* and *m* as calculated using the canonical TB model with a valence electron count of



FIG. 6. (Color online) Plot of U_{bond}^{χ} - U_{bond}^{hcp} energies, calculated using the structural energy difference theorem [Eq. (19)], as a function of the exponents *n* and *m*. The domain of χ -phase stability, plotted in green and corresponding to negative values of U_{bond}^{χ} - U_{bond}^{hcp} , lies in the lower right of the plot where *m* is small and *n* large. The domain of hcp stability is plotted in blue and corresponds to positive values of U_{bond}^{λ} - U_{bond}^{hcp} .

 $N_d = 5.7$. The calculations used a constant of proportionality of 1 in Eq. (18) and, for comparison with Fig. 3, the bonding energies have been normalized with respect to $U_{\text{bond}}^{\text{fcc}}$ using m = 2 and n = 4. Increasing n relates to the bond integrals decaying more rapidly, while decreasing m relates to the repulsive function decaying less rapidly. The χ phase is stabilized over hcp as n is increased above ~ 4.25 and as *m* is decreased from 2.00 to 1.50, which corresponds to α_h decreasing from $\frac{1}{2}$ to $\frac{1}{3}$. That is, the χ -phase structure becomes more stable than the more close-packed hcp structure as the potential is softened. The source of the structural trend of the group VII elements therefore appears to be analogous to that of the group IV elements [85,86]. Mn is expected to have a softer core because it lacks core d states and its valence electrons are therefore able to readily penetrate the core region. This favors the more open-packed χ -phase structure over the closer-packed hcp. In contrast, 4d Tc and 5d Re have harder cores which stabilize the closer-packed hcp. Consistent with this argument, it is found that the hcp- χ -phase energy difference for 5d Re, which we would expect to have a harder core than 4d Tc, is larger, 48 meV/atom, than that of 4d Tc, 32 meV/atom.

It is apparent that the repulsion in the canonical TB with m = 2 and n = 4 is hard enough to stabilize close-packed hcp over the χ phase, thus reproducing the relative structural stabilities characteristic of 4*d* Tc and 5*d* Re [82]. In contrast, we will see in the following section that in the newly parametrized Mn TB model, the repulsion is soft enough to reproduce the χ -phase stability characteristic of 3*d* Mn.



FIG. 7. (Color online) Plots of the binding energy relative to NM α -Mn for the α , β , γ , δ , and ϵ phases of Mn. The curves for magnetic states, namely, AFM α -Mn, FiM β -Mn, AFM γ -Mn, and AFM2 δ -Mn, are marked with triangles. Results are shown for DFT (left), TB (center left), 20-moment BOP (center right), and 14-moment BOP (right).

B. Relative structural stabilities of the nonmagnetic phases of Mn

Results for the DFT, TB, and BOP calculations are presented in the following sections. Figure 7 shows a plot of the binding energy curves for the five primary phases of Mn calculated with DFT (left-hand panel), TB (center left), 20-moment BOP (center right), and 14-moment BOP (right). For α - and β -Mn, the internal coordinates have been fully relaxed using DFT, TB, and BOP, respectively. Looking at the left-hand panel of Fig. 7 and considering only the nonmagnetic structures, DFT predicts the relative ordering from $\alpha \rightarrow \beta \rightarrow$ $\epsilon \rightarrow \gamma \rightarrow \delta$. The TB and BOP models reproduce this ordering with even the very small energy difference between the β and ϵ structures correctly characterized. Additionally, the NM γ - ϵ energy differences in TB, 20-moment, and 14-moment BOP of 29, 34, and 38 meV, are close to the DFT value of 35 meV. The absolute TB and BOP binding energies are all within 0.5% of the DFT total energies, while the equilibrium atomic volumes, given in Table II, are all within 3% of DFT. Our DFT atomic volumes are all within 2% of those of the DFT calculations given in Ref. [23].

Table III lists the internal coordinates, as relaxed using DFT, TB, and BOP, for nonmagnetic α - and β -Mn. The labeling conventions used here can be matched to those used in Refs. [22,23] for the α and β phases, respectively. It can be seen that in both cases, the TB relaxed internal coordinates are similar to the DFT coordinates with slightly larger errors in the α -Mn site II coordinates and the β -Mn site I coordinate. The differences between BOP and TB are smaller than the differences between TB and DFT.

The convergence of the analytic BOP NM binding energies to the TB binding energies are plotted in Fig. 8 for fcc γ -, hcp ϵ -, and α -Mn. It can be seen that the BOP energies converge systematically as the number of moments is increased. It is noted that the binding energy of NM ϵ oscillates out of phase with the energies of the other structures.

The structural energy difference theorem [87] allows differences in the structural energy to be approximated as the

difference in the *d*-band energy alone, once the atomic volumes have been prepared such that all structures display the same average repulsive energy per atom. That is, to first order,

$$\Delta U = [\Delta U_{\text{bond}}]_{\Delta U_{\text{ren}}=0}.$$
(19)

The TB NM structural energy differences as a function of band filling for the bcc δ -Mn, hcp ϵ -Mn, and α -Mn are plotted with respect to the bond energy of NM fcc γ -Mn in Fig. 3 with the results for the current Mn TB model in the upper right panel and those of the canonical TB model (with m = 2 and n = 4) in the lower right panel. In both cases, the plots have been centered around $N_d = 5.7$ which is the *d*-electron count in the Mn model. It can be seen that the Mn TB model qualitatively reproduces the behavior observed for the 3*d* transition series (upper left panel), with χ most stable at $N_d = 5.7$, and the canonical model reproduces the behavior of the 5*d* series (lower left panel), with hcp most stable at $N_d = 5.7$.

TABLE II. Equilibrium atomic volumes for the nonmagnetic and magnetic forms of the five primary allotropes of Mn, calculated using DFT, TB, and 20- and 14-moment BOP.

		Atomic volume (Å ³)							
				В	OP				
Allotrope	Magnetic state	DFT	TB	μ_{20}	μ_{14}				
	AFM	11.16	11.04	11.00	11.05				
α	NM	10.74	10.82	10.84	10.84				
0	FiM	10.93	10.81	10.80	10.80				
р	NM	10.82	10.81	10.80	10.80				
	AFM	11.54	11.47	11.40	11.39				
γ	NM	10.68	10.70	10.70	10.72				
\$	AFM2	11.26	11.52	11.28	11.49				
0	NM	10.69	10.76	10.74	10.74				
	AFM	10.74	10.71	10.67	10.68				
e	NM	10.72	10.71	10.67	10.68				

TABLE III. Relaxed internal coordinates for nonmagnetic and magnetic forms of α - and β -Mn. The labeling conventions used here can be matched to those used in Refs. [22,23] for the α and β phases, respectively. For NM hcp ϵ the optimized c/a ratio of NM hcp ϵ -Mn was calculated to be 1.619 using TB, 20-moment, and 14-moment BOP. This is very close to the value of 1.628 calculated within DFT and the ideal c/a ratio of 1.633. However, in this work the ideal c/a ratio was used for fcc γ - and hcp ϵ -Mn and the ideal rhombohedral angle was used for bcc δ -Mn.

			Internal coordinates											
				DFT			TB			BOP μ_{20}			BOP μ_{14}	
Allotrope	Magnetic state	Site	x	у	z	x	у	z	<i>x</i>	у	z	<i>x</i>	у	z
		Ι	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500
	NIM	Π	0.318	0.318	0.318	0.345	0.345	0.345	0.349	0.349	0.349	0.350	0.350	0.350
	INIM	III	0.357	0.357	0.038	0.349	0.349	0.030	0.349	0.349	0.033	0.347	0.347	0.035
		IV	0.088	0.088	0.281	0.089	0.089	0.296	0.089	0.089	0.298	0.089	0.089	0.299
α	AFM	Ι	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500
		Π	0.319	0.319	0.319	0.322	0.322	0.322	0.327	0.327	0.327	0.327	0.327	0.327
		III	0.356	0.356	0.035	0.351	0.351	0.032	0.352	0.352	0.030	0.350	0.350	0.030
		IV	0.088	0.088	0.283	0.086	0.086	0.288	0.088	0.088	0.291	0.087	0.087	0.288
				x			x			x			x	
	NIM	Ι		0.052			0.041			0.038			0.038	
ρ	INIM	Π		0.197			0.196			0.194			0.193	
ρ	E') (Ι		0.054			0.041			0.038			0.038	
	F1M	Π		0.198			0.196			0.194			0.193	

C. Relative structural stabilities of the magnetic phases of Mn

Referring to the DFT results in the left-hand panel of Fig. 7, it can be seen that with the inclusion of magnetism (curves marked with triangles) the relative stabilities of the phases are left unchanged with the exception of AFM (fcc) γ , which is stabilized significantly with respect to its NM counterpart and which we predict becomes more binding than β and ϵ as a result. Within our DFT results, the FiM β and AFM ϵ structures are virtually degenerate in energy with FiM β found to be just 1 meV more stable. Hafner and Hobbs [23] also predict these two structures to be very closely spaced in energy, but instead predict AFM ϵ -Mn to be 2 meV more stable than FiM β -Mn. This highlights just how difficult it is to calculate the small energy differences between the different Mn structures, even with accurate ab initio methods. The ordering of the magnetic phases as per our DFT calculations, namely, $\alpha \rightarrow \gamma \rightarrow \beta \rightarrow$ $\epsilon \rightarrow \delta$, is correctly reproduced by the TB and BOP models and the correct forms of magnetism are stabilized, i.e., complex collinear AFM in α -Mn, FiM in β -Mn, and AFM in the other three structures. While the atomic volume at which the onset of magnetism occurs for α -, γ -, and δ -Mn in the TB and BOP calculations is in good agreement with DFT, the FiM β -Mn and AFM ϵ -Mn structures are only stabilized within TB and BOP at expanded atomic volumes.

Table IV gives the energies of the magnetic phases relative to the AFM α -Mn ground state as well as the magnetic energy for each phase, i.e., the difference in energy between the nonmagnetic and magnetic forms of the structure at their respective equilibrium volumes. It can be seen that the magnetic energies for α -Mn calculated using TB, 20-moment BOP, and 14-moment BOP (25, 23, and 30 meV, respectively) are in good agreement with the DFT calculated value of 36 meV. Additionally, the relative stabilities of the γ and ϵ phases are also well reproduced. The observation that it is only with the inclusion of magnetism that γ -Mn becomes more stable than ϵ -Mn demonstrates the importance of local magnetism in stabilizing the fcc structure relative to hcp,

TABLE IV. Binding energies relative to the AFM α -Mn ground state for the nonmagnetic and magnetic forms of the five primary allotropes of Mn, calculated using DFT, TB, and 20- and 14-moment BOP. The magnetic energy, defined as $U_{\rm NM}(V_{\rm eq}^{\rm NM})$ - $U_{\rm Mag}(V_{\rm eq}^{\rm Mag})$, is given for each allotrope. The relative energies of the nonmagnetic and magnetic γ and ϵ phases are also given. The BOP calculations reproduce the results of the TB model reasonably well, while slightly larger differences are found between the DFT and TB results.

		Relative energy (meV/atom)							
				B	BOP				
Allotrope	Magnetic state	DFT	TB	μ_{20}	μ_{14}				
	AFM	0	0	0	0				
α	NM	36	25	23	30				
	Mag. Energy	36	25	23	30				
	FiM	86	61	57	60				
β	NM	88	61	57	60				
	Mag. Energy	2	0	0	0				
	AFM	80	58	57	49				
γ	NM	124	92	97	104				
	Mag. Energy	44	34	39	55				
	AFM2	155	120	111	107				
δ	NM	199	170	157	169				
	Mag. Energy	44	49	46	62				
	AFM	87	63	63	66				
ϵ	NM	89	63	63	66				
	Mag. Energy	2	0	0	0				
	AFM	7	5	6	17				
U_{ϵ} - U_{γ}	NM	- 35	- 29	- 34	- 38				



FIG. 8. (Color online) Convergence of BOP binding energies to TB binding energies as a function of increasing number of moments for NM and AFM (fcc) γ -Mn, NM (hcp) ϵ -Mn, and NM and AFM α -Mn.

just as Hasegawa and Pettifor first predicted for Fe at high temperatures [14]. Figure 8 shows the convergence to the TB values of the AFM analytic BOP binding energies for fcc γ -and α -Mn. The convergence is systematic as the number of moments is increased.

The equilibrium atomic volumes of AFM α -Mn as predicted by TB, 20-, and 14-moment BOP, and given in Table II, are 1.65%, 1.90%, and 1.85%, respectively, smaller than that predicted by DFT, differences which are slightly larger than for NM α -Mn. The DFT equilibrium atomic volume is 7% smaller than the experimental atomic volume, reported as 12.05 Å by Lawson [50], in agreement with Ref. [22]. While this may seem unusual for a GGA calculation it has been noted previously that GGA is less successful in correcting overbinding in the LSDA in antiferromagnetic 3d metals than in ferromagnetic metals [22]. For example, GGA calculations have predicted equilibrium atomic volumes for AFM bcc Cr [88] and AFM γ -Fe [89] that are ~4% and ~7%, respectively, smaller than comparable experimental values. Table III lists internal coordinates, relaxed using DFT, TB, and BOP, for the magnetic forms of α - and β -Mn. The TB relaxed internal coordinates for AFM α -Mn are closer to the DFT coordinates than their NM counterparts. The 14-moment and 20-moment BOP relaxed internal coordinates for AFM α -Mn are all very close to the TB values. At equilibrium volume, the FiM β -Mn is only fractionally more stable than NM β -Mn and it can be seen from the two sets of DFT coordinates that their structures are very similar. In our TB model, the FiM β -Mn state only becomes more stable than NM β -Mn at volumes a little above the equilibrium volume, and so the two sets of coordinates are identical. This is also observed in the results of the 14- and 20-moment BOP calculations.

Table V lists the magnitudes of the magnetic moments for each structure calculated with DFT, TB, and 20- and 14-moment BOP at their respective, fully relaxed, equilibrium atomic volumes. The TB and BOP models are found to correctly reproduce the complex collinear antiferromagnetic magnetic structure of α -Mn. Not only are the correct parallel and antiparallel alignments at each site correctly reproduced [as may be seen in Fig. 1 where the DFT (green arrows), TB (red arrows), and 14-moment BOP (blue arrows) magnetic TABLE V. Magnitudes of the local magnetic moments of Mn allotropes calculated with DFT, TB, and 20- and 14-moment BOP at their respective, fully relaxed, equilibrium atomic volumes.

			Local magnetic momen (μ_B/atom)					
					BOP			
Allotrope	Magnetic state	Site	DFT	TB	μ_{20}	μ_{14}		
		Ι	2.97	3.27	3.34	3.32		
	A EM	II	2.40	2.88	2.87	2.87		
α	Агм	III	1.39	1.38	1.16	1.70		
		IV	0.02	0.06	0.08	0.08		
ρ	EM	Ι	0.11	0.00	0.01	0.04		
ρ	ГШИ	II	0.30	0.00	0.01	0.01		
γ	AFM	Ι	1.98	2.37	2.26	2.26		
δ	AFM2	Ι	1.58	2.47	2.32	2.36		
ϵ	AFM	Ι	0.54	0.00	0.00	0.00		

moment vectors have been calculated using the DFT-relaxed atomic coordinates], but also the relative sizes of the magnetic moments at each site, which decrease from sites I \rightarrow II \rightarrow III \rightarrow IV, are correctly reproduced. This is in contrast to a number of published DFT results [52,54] which predict different alignments of the Mn I and/or Mn II moments. Additionally, the TB and BOP models correctly predict that the site IV magnetic moment is virtually zero. The TB and BOP predictions of the size of the moments in AFM γ -Mn are in reasonable agreement with those of DFT while those for AFM2 δ -Mn are less good. This is because the TB and BOP models predict a too large equilibrium atomic volume for AFM2 δ-Mn which results in an overestimation of the equilibrium magnetic moment. As has been mentioned, while DFT predicts FiM β -Mn and AFM ϵ -Mn to be fractionally more stable than their NM counterparts, the TB and BOP models significantly stabilize magnetism within these two structure types only at volumes above ~12 Å³/atom for β -Mn and 11.5 Å³/atom for ϵ -Mn. As a result, the magnetic moments predicted at equilibrium volumes are zero in TB and virtually zero in BOP, whereas DFT predicts small but nonzero moments. The small disparities between TB and BOP result from differences in the shape of the DOS.

D. Elastic constants

Calculation of the elastic constants, which are given by the second derivative of the energy with respect to strain, is a sensitive test of the capabilities of an interatomic potential. Table VI lists values of the bulk modulus (B_0), the tetragonal shear constant (C'), and the trigonal shear constant (C_{44}) for the nonmagnetic and magnetic cubic Mn structures as calculated by applying appropriate strains to each unit cell [28]. Unlike the MEAM models [20,21], our TB and BOP model parameters were not explicitly fitted to any elastic constant data, although because the TB parameters were fitted to binding energies over a range of atomic volumes (see Sec. III), values of the bulk moduli will be approximately reproduced. Additionally, the tetragonal shear constant C', a measure of the curvature of the Bain path between bcc and fcc structures and defined as ($c_{11} - c_{12}$)/2, was implicitly inferred because

TABLE VI. Table of the elastic constants B_0 , C', and C_{44} , calculated using DFT, TB, and 20- and 14-moment BOP for the nonmagnetic and magnetic cubic Mn allotropes. For each method, the elastic constants were calculated at the equilibrium volumes and the atomic positions were fully relaxed for each deformation applied.

		B_0 (GPa)					C' (0	GPa)	<i>C</i> ₄₄ (GPa)				
				В	BOP			BOP				BOP	
Allotrope	Magnetic state	DFT	ТВ	$\overline{\mu_{20}}$	μ_{14}	DFT	TB	μ_{20}	μ_{14}	DFT	TB	μ_{20}	μ_{14}
	NM	280	237	257	235	133	57	55	47	88	41	37	30
α	AFM	175	163	193	152	130	54	73	72	84	68	85	77
0	NM	269	256	256	259	51	40	37	21	94	78	86	70
p	FiM	205	218	220	210	53	49	51	39	87	78	86	74
	NM	280	237	240	241	74	43	10	17	167	82	70	107
γ	AFM	155	166	179	189	50	64	77	75	93	80	101	110
6	NM	284	248	250	248	30	-65	-45	-42	116	18	-32	4
0	AFM2	148	72	111	97	25	-1	1	6	146	42	18	41

differences in the equilibrium binding energies of the bcc δ and fcc γ structures were included in the fitting [90,91].

There is a scarcity of experimental data available for comparison and, to our knowledge, no DFT predictions of C' and C_{44} for any Mn phase have been published. Our DFT predicted bulk moduli are in good agreement with those of Hafner and Hobbs [23] although some minor differences result because they calculated B_0 by fitting energies to the Birch-Murnaghan [92] equation and the Vinet equation of state [93], while ours were calculated directly from the two elastic constants c_{11} and c_{12} [28] using $B = \frac{1}{3}(c_{11} + 2c_{12})$. For example, we calculate B_0 for AFM2 δ -Mn to be 148 GPa, whereas if we fit to the Birch-Murnaghan equation we obtain 166 GPa, which matches the value given by Hafner and Hobbs. Our DFT calculations predict B_0 for collinear AFM α -Mn to be 175 GPa while Hafner and Hobbs predict a value of 188 GPa for their noncollinear AFM α -Mn. Both of these values are higher than experimentally determined ones, which show a significant spread. More recently published experimental values include 131 [94], 137 [95], and 158 [67] GPa, while older values tend to be lower, e.g., 60 [96] and 93 [97] GPa. Just like the other magnetic 3d transition metals where the bulk modulus is smaller than is expected from the skewed parabolic behavior across the NM 4d and 5d series due to magnetic pressure [11,55], we see in Table VI that it is indeed the presence of magnetism and not the complex structure that leads to the softness of α -Mn. It is also seen that the inclusion of magnetism drives a softening of the bulk moduli in the other structure types and that this behavior is correctly reproduced in the TB and BOP models.

In general, the reproduction of the DFT shear moduli C'and C_{44} by the TB model is less satisfactory than for B_0 . The TB model predicts all of the allotropes examined here to be mechanically stable with positive shear constants except for a small negative C' for AFM2 δ -Mn and a negative C' for NM δ -Mn. While in the DFT calculations of the tetragonal deformation pathway, i.e., the Bain pathway, the energy relating to the NM bcc δ -Mn structure lies in a small local minimum at the peak of a global maximum, thus its tetragonal shear constant C' has a small but positive value. In contrast, in the TB model, this small local minimum is smeared out and the energy corresponding to the bcc structure lies at the top of the maximum, resulting in a tetragonal shear constant which is therefore negative. The same observations are made for AFM2 bcc δ -Mn. That a previous TB model [34] also, according to our calculations, predicted a negative C_{44} for AFM2 δ -Mn and a negative C' for FiM β -Mn indicates just how challenging it is to capture all of the characteristics and complexities of elemental Mn within a simple model.

Figure 9 illustrates the convergence of the three cubic elastic constants for NM and AFM γ -Mn as a function of the number of moments used in BOP. It can be seen, by comparing with Fig. 8, that more moments are required to converge the elastic constants than are required to converge the binding energies [98]. Additionally, from Fig. 9 it is evident that B_0 converges more quickly than the shear constants C' and C_{44} . This is because C' and C_{44} rely on the convergence of the cancellation of oscillating force constants which extend out many levels into a structure [99,100]. Distortions caused by shearing also cause distortions of the Fermi surface, shown to be responsible for observed anomalies in the temperature dependence of shear constants in V, Nb, Ta, Pd, and Pt [101,102], but because the BOP DOS are always smooth, the effects of these distortions on the fine structure of the DOS close to



FIG. 9. (Color online) A plot of the convergence of BOP elastic constants to TB values for up to 30 exact moments, for AFM γ -Mn.

the Fermi level can not be reproduced, even using a large number of moments. As a result, accurate prediction of the shear constants is challenging. The strongly oscillating C' for NM γ -Mn as a function of the number of BOP moments is thought to be an example of this. Given that little emphasis was placed on reproducing the elastic constants, it is perhaps not surprising that their reproduction with both TB and BOP is poor in some instances. Ultimately, in order to reproduce experimental or DFT elastic constants and to perform realistic mechanical simulations, it will be required to specifically refit the BOP model just as Mrovec *et al.* [42] did for a 9-moment numerical BOP for Fe.

For hcp structures, there are five independent elastic constants; C_{11} , C_{12} , C_{13} , C_{33} , and C_{44} . For AFM hcp ϵ -Mn the values of these elastic constants, in GPa, as calculated by DFT, TB, 20- and 14-moment BOP, respectively, are C_{11} : 707, 502, 418, 465; C_{12} : 107, 196, 245, 207; C_{13} : 155, 218, 232, 230; C_{33} : 182, 132, 130, 130; and C_{44} : 156, 96, 92, 98. The resultant values of the bulk modulus are 270, 267, 265, and 266 GPa.

E. Vacancy formation energies

The formation energies of a single vacancy were calculated using the supercell method [103] and the formula

$$U_f^V = U_B^V - \frac{N^V}{N} U_B, \qquad (20)$$

where *N* is the number of atoms in the perfect supercell, U_B is the binding energy of the perfect supercell, and N^V and U_B^V are those respective quantities for the vacancy-containing supercell, such that $N^V = N - 1$. Tests of the convergence of the energy with respect to the supercell size showed that, in agreement with other calculations [104], 32-atom supercells were sufficient for γ -Mn and 54-atom supercells were sufficient for δ -Mn and ϵ -Mn. The 58- and 20-atom unit cells were shown to be sufficient for α - and β -Mn, respectively.

Table VII lists the unrelaxed and relaxed vacancy formation energies for the magnetic forms of α -, β -, γ -, δ -, and ϵ -Mn as calculated with DFT, TB, and 20- and 14-moment BOP. DFT calculations predict that AFM2 bcc δ -Mn has the smallest PHYSICAL REVIEW B 89, 134102 (2014)

relaxed single-vacancy formation energy, with the β sites I and II and the α site IV having slightly larger energies, and then fcc γ , hcp ϵ , and the α sites II, III, and IV having somewhat larger energies. This trend is also reflected in the unrelaxed vacancy formation energies.

For α -Mn there are four possible atoms which can be removed in order to create a vacancy. To our knowledge, in all of the examples found in the literature, the site-specific details of the vacancy formation energy of α -Mn are either not given or not relevant to the level of theory used. For AFM α -Mn, our DFT calculations predict that an unrelaxed vacancy created by the removal of a site IV Mn atom has the lowest formation energy followed by site III, site II, and then site I. This trend is preserved upon structural relaxation around the vacancies and accompanied by a modest reduction of the formation energy. These trends are also observed for NM α -Mn, indicating that they are a result of structural, rather than magnetic, effects. Indeed, this ordering of the α -Mn vacancy formation energies reflects the local coordination, with the higher-coordinated Z16 Mn I site having the largest vacancy formation energy, followed by the Z16 Mn II site, the Z13 Mn III site, and finally the lowest-coordinated Z12 Mn IV site. This behavior is consistent with the vacancy formation energy being proportional to a reduction in the cohesive energy caused by the loss of local coordination, which is proportional to the local coordination number of the bulk structure z, scaling as $\sim \sqrt{(z-1)/z}$ [104]. The TB and BOP models correctly predict the relative ordering of the relaxed U_f^V at each α -Mn site, although for the unrelaxed vacancies TB and BOP predict the U_f^V of site III to be smaller than that of site IV. The absolute TB and BOP values of U_f^V for AFM α are all somewhat lower than their DFT counterparts, however, they are comparable to the values found in the literature for α -Mn, namely, 0.93 [105], 1.16 [21], and 1.20 [20] eV/atom.

Our DFT calculations show that for FiM β -Mn, of the two possible vacancy sites the lower-coordinated Z12 site I vacancy has a smaller relaxed formation energy than that of the Z14 coordinated site II. This is consistent with the observations of the effects of local coordination on the vacancy formation energies of the inequivalent sites in α -Mn. The TB

TABLE VII. Unrelaxed and relaxed single-vacancy formation energies calculated using DFT, TB, and 20- and 14-moment BOP, for the magnetic forms of α -, β -, γ -, δ -, and ϵ -Mn.

			Vacancy formation energy (eV/atom)										
				Unre	laxed	Relaxed							
					BOP				BOP				
Allotrope	Magnetic state	Site	DFT	TB	μ_{20}	μ_{14}	DFT	TB	μ_{20}	μ_{14}			
α		Ι	2.94	1.99	1.93	1.92	2.85	1.75	1.70	1.71			
		Π	2.81	1.83	1.85	1.81	2.60	1.45	1.44	1.39			
	AFM	III	2.78	1.80	1.84	1.78	2.57	1.20	1.27	1.16			
		IV	2.41	1.85	1.88	1.81	1.98	0.98	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$				
0	E'M	Ι	2.30	1.86	1.81	1.76	1.93	0.41	0.39	0.36			
β	F1M	II	2.23	2.02	2.03	1.97	2.05	0.73	0.59	0.76			
γ	AFM	Ι	2.34	1.82	1.80	1.77	2.29	1.53	1.50	1.43			
δ	AFM2	Ι	2.00	1.67	1.70	1.70	1.19	0.95	0.88	0.91			
ϵ	AFM	Ι	2.55	2.06	2.04	2.04	2.42	1.04	1.03	1.03			

and BOP models correctly predict this relative stability of the vacancy energies of two sites within FiM β -Mn, however, a shortcoming of the models is that while the unrelaxed energies are reasonably close to the DFT values, the relaxed values are significantly underestimated. We find that this is a result of the vacancy-containing β -Mn structure relaxing to a structure far from that predicted by DFT. For example, in the DFT calculations the nearest-neighbor distance in bulk FiM β -Mn is 2.29 Å and in the vacancy supercell it is 2.27 Å. However, in the TB calculations, while the nearest-neighbor distance in the bulk supercell is 2.28 Å, in good agreement with DFT, in the vacancy supercell it is 2.04 Å. This, and the more modest underestimation in the α -Mn structure, may be due to the simple pair repulsion used in our model not being sufficient to model the nature of the bonding and forces in the vacancycontaining structures. This, however, could be mitigated by making the repulsive energy environment dependent. For example, in the numerical BOP for W developed by Mrovec et al. [106], the repulsive term was described by a screened Yukawa-type potential, the screening exponent of which was fitted to experimental data for bcc W to ensure the reproduction of the correct sign of the Cauchy pressure, thus allowing the BOP to be applied to the investigation of extended defects. Similarly, Aoki et al. [107] applied the same principles in the parametrization of numerical BOPs in order to model mechanical properties in hcp Ti and bcc Mo.

DFT predicts that for the three common crystal structures fcc, bcc, and hcp, that AFM2 bcc δ -Mn has the smallest unrelaxed vacancy formation energy, with the close-packed AFM fcc γ -Mn and AFM hcp ϵ -Mn having larger energies. For AFM2 δ -Mn, just as for α - and β -Mn, we find that there is a modest change in the vacancy formation energy upon relaxation of the supercell but in contrast, for the more compact fcc γ and hcp ϵ vacancy supercells, the changes are much smaller, in agreement with the work of Willaime et al. [108]. While TB and BOP reproduce the relative ordering of the unrelaxed vacancy formation energies for these three structures, the relaxed vacancy formation energy for ϵ -Mn is anomalously small. Just as for β -Mn, this is found to be due to the TB and BOP relaxed vacancy-containing structures having collapsed somewhat as compared to their DFT counterparts. Using a self-consistent Green's function method, Korzhavyi [104] calculated vacancy formation energies in magnetic γ - and δ -Mn, although they do not state the type of magnetic ordering considered for either structure. Additionally, they neglected the effects of local lattice relaxations which, as shown for δ -Mn, can be significant. Their values of 1.51 eV/atom for δ -Mn and 2.51 eV/atom for γ -Mn are consistent with our unrelaxed vacancy formation energy results.

Overall, while the TB and BOP models underestimate the absolute values of the DFT vacancy formation energies, they reproduce the relative trends between the inequivalent sites in both α - and β -Mn and predict larger values of U_f^V for the more close-packed γ and ϵ structures and smaller values for the more open α , β , and δ .

VI. CONCLUSION

In this paper, we have investigated why 3*d* Mn has a complex χ -phase ground state in contrast to the other group VII elements 4*d* Tc and 5*d* Re which are hexagonally close

packed. DFT calculations have confirmed that magnetism and the resulting effective atomic-size difference are not the critical factor in driving the anomalous stability of the χ phase in Mn. Additionally, it has been shown that structural differences in the χ -phase geometry of the three elements and variations in the electronic structure are not significant enough to be responsible. Using a simple canonical TB model, which allows the effective potential to be varied in a transparent way, we found that for a more than half-filled *d* band, harder potentials stabilize close-packed hcp whereas a softer potential stabilizes the more open χ phase. We propose therefore that by analogy with the structural trend from open to close-packed phases down the group IV elements, the anomalous stability of the χ phase in Mn is due to 3*d* valent Mn lacking core *d* states and therefore having a softer repulsion than either 4*d* Tc and 5*d* Re.

Furthermore, an analytic BOP has been derived from a new short-ranged, d band, TB model and used to investigate the structural and magnetic properties of Mn. In spite of their simplicity, the TB and BOP models not only qualitatively reproduce the small structural energy differences in the DFT binding energy curves of the five primary phases of Mn, but they also predict the complex collinear AFM ordering in α -Mn, the FiM ordering in β -Mn, and the AFM ordering in γ -, δ -, and ϵ -Mn that are predicted by DFT. The TB model reproduces trends in the bulk moduli observed in the DFT results, but values of the elastic shear constants C' and C_{44} , which were not included in the fitting of the model, are approximately a factor of 2 too small. A BOP expansion including 14 moments is sufficiently converged to reproduce most of the properties of the TB model with the exception of these elastic shear constants, which require further moments. Therefore, future realistic MD simulations will require that the shear constants be included in the fitting database from the outset. The TB and BOP models correctly reproduce trends in the relative sizes of the vacancy formation energies in antiferromagnetic α -Mn which reflect the local coordination of the four inequivalent sites, with the lowest coordinated site IV atom having the smallest vacancy formation energy, followed by sites III, II, and I. One limitation of the current model is that the absolute vacancy formation energies are somewhat smaller than those predicted by DFT. This is particularly true in the case of vacancies in the β -Mn structure and was found to be due to poor structural relaxation of the vacancy-containing structure. An improved TB model might therefore include an environment-dependent repulsive potential.

In summary, the current model captures the most important structural and magnetic features of the complex low-energy Mn phases. This makes the BOP model suitable for performing large-scale dynamic simulations in the future, so that, for example, it could model the local magnetic fluctuations with temperature that may be responsible for stabilizing the different Mn phases at high temperatures.

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