Tetragonal magnetic states of Fe and Mn

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Tetragonal states of Fe and Mn have been studied by finding total energies at constant volume V as a function of c/a with the full-potential linearized-augmented-plane-wave method. Minima in $E_V(c/a)$ give the c/a values of equilibrium states. Both Fe and Mn are shown to have stable and metastable equilibrium states in each of several magnetic phases. The calculations on Fe show an antiferromagnetic (AF) face-centered-tetragonal (fct) equilibrium state at $c/a=1.08$, which has been stabilized as a strained epitaxial film. The calculations on Mn show an AF equilibrium state at $c/a=0.96$ (fct), in agreement with the measured value of $c/a=0.95$ on a crystal stabilized by alloying. Also AF bcc Mn is shown to be unstable, but an equilibrium AF state at $c/a=0.60$ exists. [S0163-1829(99)03446-3]

I. INTRODUCTION

Crystals of the metallic elements in tetragonal structure usually have two equilibrium states at different values of c/a, the aspect ratio of the tetragonal unit cell. First-principles total-energy calculations by full-potential band-structure methods have demonstrated the existence of these two equilibrium states, one of which is the tetragonal ground state and the other a metastable state.[1] The minima of the total energy E as a function of a and c give the equilibrium states. In this paper the double minimization with respect to a and c is not done, but the simpler procedure of minimizing $E(c/a)$ at constant $V(=ca^2/4)$ is used. If the volume is not too different from the volume of the equilibrium states, the c/a values at the minima of $E(c/a)$ locate the equilibrium states. The reasons why the c/a values and energies at the minima depend little on volume are discussed below.

In the case of magnetic elements the description of tetragonal states is more complicated because each magnetic phase can have two equilibrium states, as will be shown for Fe and Mn for their ferromagnetic (FM), nonmagnetic (NM), and antiferromagnetic (AF) phases.

The AF phases of Fe and Mn are of particular interest because both can be produced in experiment: AF Fe can be stabilized by coherent epitaxial growth on suitable substrates and the AF phase of Mn by small concentrations of impurities (which can be extrapolated to zero concentration).

The tetragonal states of Fe have been studied by Peng and Jansen[2] (PJ) in first-principles full-potential calculations of total energy at constant volume. Their results have been used previously to evaluate the c/a values of equilibrium AF and FM states at face-centered-tetragonal (fct) values of $c/a>1$, and to show that epitaxy on Cu strains the Fe lattice to a near fcc structure at the Cu lattice constant.[3] The points calculated by PJ at constant volume are sparse; the present work verifies their points, but fills out complete curves, including the NM phase, for which PJ found only two points. Reference 3 shows that the minima of $E(c/a)$ at constant V give the c/a values of the equilibrium states—highly accurately for cubic equilibrium states and to a good approximation for noncubic tetragonal equilibrium states. The minima also give an estimate of the energies of the equilibrium states, but do not fix the equilibrium volumes or individual a and c values.

The reason the c/a values at the minima of E depend little on V is that at equilibrium states of cubic symmetry c/a and V are orthogonal coordinates, so that E depends separately on the deviations from the equilibrium point $\delta(c/a)$ and δV. At tetragonal noncubic equilibrium points the cross term in $\delta V\delta(c/a)$ is small, as discussed in Ref. 4. The reason that E depends only weakly on V around the equilibrium value is that at a minimum changes in E are second order in δV.

The tetragonal AF states of Mn were studied around the fct minimum by Oguchi and Freeman,[5] but not with a full-potential method. In the present work the same full-potential method that was used for Fe is applied to Mn, giving again three phases with separate energy curves at constant volume $E_V(c/a)$ with results that differ from Ref. 5 and agree better with experiment.

The first-principles total-energy calculations on Fe and Mn in tetragonal structure were performed using the full-potential linearized-augmented-plane-wave (FLAPW) method[6] with the local-spin-density-approximation[7] without relativistic corrections (LSDA-NREL). Magnetic properties of metals have been calculated with considerable success using the LSDA-NREL corrections for electron-electron interaction, e.g., in establishing the observed type-II AF ground state of FeRh in CsCl (B2) structure.[8] The LSDA-NREL calculation failed to give the correct ground state of elemental Fe by a few mRy/atom,[9] but this paper is not concerned with deciding which equilibrium state is the ground state, but only their c/a values. Calculations with the generalized-gradient approximation and relativistic corrections have in fact shown that the c/a values of the equilibrium states are the same as with the LSDA-NREL corrections.[10]

A two-atom tetragonal unit cell with a constant volume per atom V was used in the calculations; $V=ca'^2/2=ca^2/4$ where a' is the lattice constant of the square cross section of

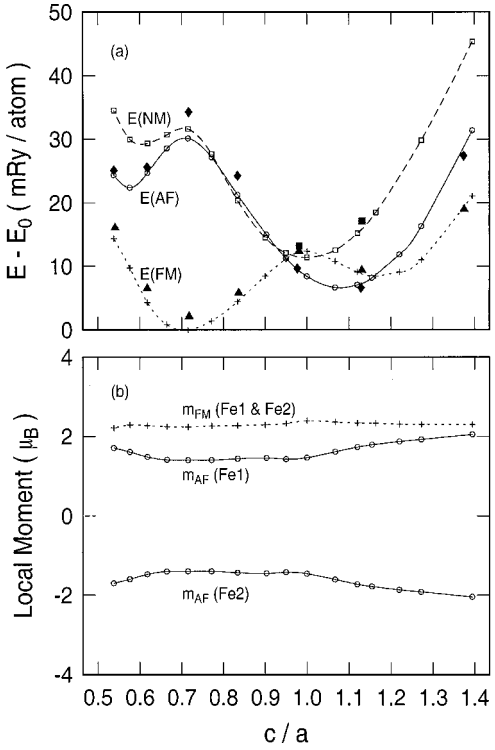

FIG. 1. (a) The energies of tetragonal Fe in the FM, AF, and NM phases as functions of c/a at the experimental value of the volume per atom $V=11.53\,\text{Å}^3$. The data points connected by a solid or a dashed line are from present work. The filled triangles, diamonds, and squares are the data of PJ (Ref. 2) at the same V in the FM, AF, and NM phases, respectively. The reference energy E_0 is given in Table I. (b) The local moments of the Fe atoms as functions of c/a in both the FM and AF phases.

a body-centered-tetragonal (bct) description, and $a=\sqrt{2}a'$ is the lattice constant for a fct description. Three different initial magnetic configurations, i.e., parallel, antiparallel, and zero moment spin arrangements in the unit cell, were used for the FM, AF, and NM calculations, respectively. The FLAPW calculations reported here used the WIEN97 (Ref. 6) code with a plane-wave cutoff $R_{\text{MT}}\,K_{\max}=9$, $R_{\text{MT}}=2.1$ a.u, $G_{\max}=14$ and 360 k points in the irreducible wedge of the Brillouin zone. The Fermi energy is calculated and k-space integration is done by the modified tetrahedron method.[6] All the calculations were highly converged. Tests with large basis sets and different Brillouin-zone samplings yield only very small changes in the results.

II. RESULTS

Figure 1(a) shows the energies of tetragonal Fe in the FM, AF, and NM phases relative to the ground state as functions of c/a at the experimental value of the volume per atom $V=11.53\,\text{Å}^3$ of the bulk of the Fe film epitaxial[11] on Cu (001). The data points connected by a solid or a dashed line are from the present work. The filled triangles, diamonds, and squares are the data of PJ[2] at the same V in the FM, AF, and NM phases, respectively. It is apparent that the data points of PJ are close to our more complete energy curves. All three energy curves in Fig. 1(a) show the characteristic two minima of tetragonal structures. Tetragonal Fe has a FM ground state at the bcc point $c/a=0.707$, a metastable FM state at $c/a=1.172$, and metastable AF states at $c/a=0.576$ and 1.082. The $E_V^{\text{NM}}(c/a)$ curve has two minima, one is at the fcc point $c/a=1.000$ and the other at $c/a=0.605$. The local moments as functions of c/a in both the FM and AF phases are shown in Fig. 1(b). The moment in the FM phase has essentially a constant value $m_{\text{FM}}\approx 2.30\mu_B$, while the moment in the AF phase increases by $\sim 0.50\mu_B$ when c/a changes from 1.0 to 1.4. The minimum energies (including the reference energy E_0) and the corresponding c/a values are tabulated in Table I.

TABLE I. c/a and relative energy values at the minima of the $E_V^{\text{FM}}(c/a)$, $E_V^{\text{AE}}(c/a)$, and $E_V^{\text{NM}}(c/a)$ curves for Fe at $V=11.53\,\text{Å}^3$ and Mn at $V=12.94\,\text{Å}^3$.

State	c/a	$E-E_0$ (mRy/atom)	E_0 (Ry/atom)
FM Fe	0.707	0.000	−2522.819 698
FM Fe	1.172	8.464	
AF Fe	0.576	22.354	
AF Fe	1.082	6.637	
NM Fe	0.605	29.181	
NM Fe	1.000	11.389	
AF Mn	0.958	0.000	−2292.629 711
AF Mn	0.600	7.295	
FM Mn	0.839	11.845	
NM Mn	1.000	11.015	

Figure 2(a) shows the energies of tetragonal Mn in the FM, AF, and NM phases as functions of c/a at the experimental value[12] of the volume per atom $V=12.94\,\text{Å}^3$. Reference 12 found the lattice constants of pure γ-Mn at low temperatures by extrapolating the lattice constants of alloys, which stabilized the tetragonal structure of Mn by addition of nickel impurities, to zero concentration of impurity. This extrapolation gives $a=3.796\,\text{Å}$, $c=3.592\,\text{Å}$, $V=12.94\,\text{Å}^3$/atom, $c/a=0.946$. Figure 2(a) shows that Mn has an AF tetragonal equilibrium state at $c/a=0.958$, and an AF metastable equilibrium bct state at $c/a=0.600$. However the AF bcc state at $c/a=0.707$ is inherently unstable, since the energy has a maximum there. The $E_V^{\text{FM}}(c/a)$ curve of Mn is discontinuous between $c/a=0.925$ and 1.075, and has a horizontal inflection point at $c/a=0.707$, consistent with cubic symmetry. The $E_V^{\text{NM}}(c/a)$ curve has a minimum at the fcc point $c/a=1.000$ and a horizontal inflection point at $c/a=0.707$. Figure 2(b) shows the local moments as functions of c/a in both FM and AF phases. The FM moments drop to zero between $c/a=0.925$ and 1.075 where the $E_V^{\text{FM}}(c/a)$ curve is interrupted. The minimum energies (including the reference energy E_0) and the corresponding c/a values for Mn are also tabulated in Table I.

III. DISCUSSION

The total-energy curves $E_V(c/a)$ sweeping across the tetragonal plane reveal the rich complexities of behavior shown by Fe and Mn when tetragonal and magnetic structure are combined. In these strongly magnetic elements the curves show that AF and FM phases compete for the lowest

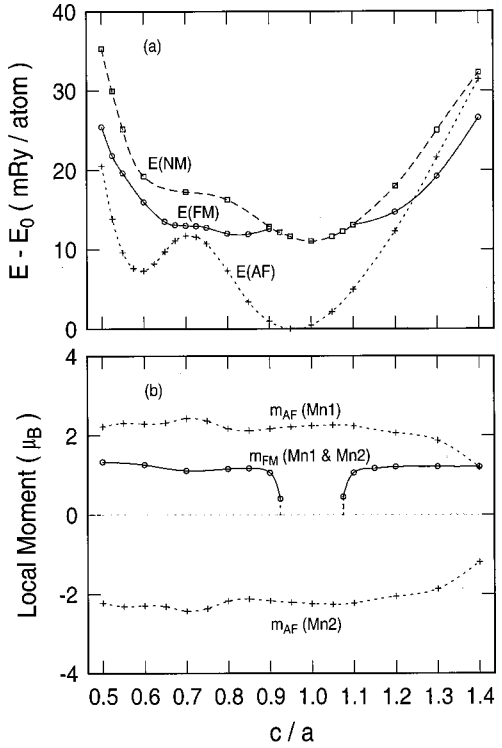

FIG. 2. (a) The energies of tetragonal Mn in the FM, AF, and NM phases as functions of c/a at the experimental value of the volume per atom $V=12.94\,\text{Å}^3$. The reference energy E_0 is given in Table I. (b) The local moments of the Mn atoms as functions of c/a in both the FM and AF phases.

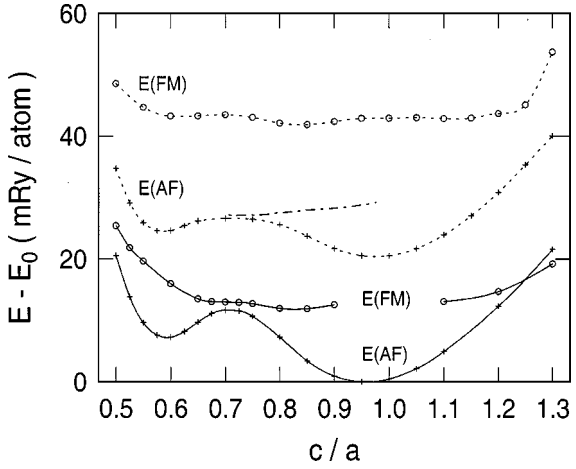

FIG. 3. The energies of tetragonal Mn in the FM and AF phases as functions of c/a at the experimental value of the volume per atom $V=12.94\,\text{Å}^3$ (data points connected by solid lines), and at $V=14.50\,\text{Å}^3$ (data points connected by dotted lines). The common reference energy E_0 is given in Table I. For comparison, the $E_V^{\text{AF}}(c/a)$ curve of Mn at $V=14.50\,\text{Å}^3$ from the tight-binding calculations by Krűger *et al.* (Ref. 14) is shown as a dot-dashed line which has been shifted to match the value of $E_V^{\text{AF}}(c/a)$ at $c/a=0.707$ of the present work.

energy state and that the fcc side of the plane is more favorable for the AF states than the bcc side. In Fe the AF minimum at $c/a=1.082$ is only a few mRy above the FM minimum at $c/a=0.707$ and the difference would be reduced at a volume closer to that of the actual equilibrium AF phase. That the difference will be reduced is known from previous LSDA-NREL calculations,[9] which show that the fcc AF Fe minimum energy at $c/a=1$ is actually lower than the bcc FM Fe minimum energy at $c/a=0.707$. The fct AF Fe minimum energy at $c/a=1.08$ will be even lower. In Mn the AF phase is lower at all c/a and the FM phase even disappears over a range of c/a that includes the fcc structure ($c/a=1$) at the volume 12.94 Å^3/atom.

The Fe results for the AF and FM energy curves, which verify the results of Ref. 2, have already been used in Ref. 3 to draw conclusions about Fe films epitaxial on Cu and strained from the minima at $c/a=1.082$ and 1.172. Such films are shown to be nearly fcc with the Cu lattice spacing and the bulk of the film is then stabilized by the epitaxy in the AF phase, but the bulk is inherently unstable in the FM phase.[4]

The Mn results for the AF phase show good agreement of the deep minimum at $c/a=0.958$ with experiment[12] at $c/a=0.946$. This agreement is evidence for the reliability of the FLAPW calculations, since the previous calculation in Ref. 5 found the minimum to be at $c/a=0.90$ with an linear muffin-fin orbital method in the atomic-sphere approximation. Reference 5 also gives a qualitative argument and prediction that a cubic structure will contract in the direction perpendicular to the FM planes of a type-I AF crystal, such as occurs in γ-Mn. However the prediction does not hold for our result on γ-Fe where the equilibrium AF phase at $c/a=1.08$ indicates expansion of c from the fcc value.

Figure 2 also shows that AF Mn is unstable at the bcc structure, since E has a maximum at $c/a=0.707$, but that a bct equilibrium state exists at $c/a=0.600$, which might be stabilized by epitaxy. However, further calculation is needed to find the correct V of the equilibrium state and hence the correct value of the in-plane lattice constant for a suitable substrate.

The vanishing of the FM phase for fcc Mn at $V=12.94\,\text{Å}^3$ is consistent with previous fcc Mn energy calculations.[13] In Ref. 13 it is shown that the FM phase does not exist in the fcc structure for V less than 14.1 Å^3.

In a more recent theoretical paper[14] on the magnetic structure of Mn using a tight-binding method, an $E_V(c/a)$ curve for the AF phase is given which is quite different from our Fig. 2. In Fig. 3 of Ref. 14 $E_V(c/a)$ at $V=14.5\,\text{Å}^3$ is shown to have a shallow minimum at the bcc point, where we have a maximum, and no minimum is shown near the fcc point where we find the major minimum, which is the minimum that agrees with experiment. The AF $E_V(c/a)$ at $V=14.5\,\text{Å}^3$ from Ref. 14 is shown in Fig. 3 as the dot-dash line placed together with our AF $E_V(c/a)$ curve at the same volume (data points connected by a dotted line). Figure 3 also shows the AF and FM energy curve at $V=12.94\,\text{Å}^3$ (data points connected by solid lines) and the FM curve at $V=14.5\,\text{Å}^3$ (data points connected by a dotted line). Comparison shows that the c/a values at the energy minima change only slightly, hence the same values should apply at the minima of the equilibrium phases when the values of the equilibrium V's have been found. Figure 3 also shows that the AF phase lies further below the FM phase at 14.5 Å^3 than it does at 12.94 Å^3, and that the FM phase at 14.5 Å^3 now exists continuously across the tetragonal plane.

In a recent paper[15] calculations for Fe with WIEN97 have found $E_V(c/a)$ for the FM and NM phases, but not the AF phase (Fig. 2 of Ref. 15), at $V=11.72$ Å^3. The c/a values of the minimum and maximum agree with Fig. 1, but are not carried up to the FM minimum at $c/a=1.17$.

The next stage in discussing the tetragonal states of Fe and Mn is to find the epitaxial Bain path of each phase,[3,16] which will give the a, c, and V values of the equilibrium states. Finding the equilibrium states requires a second minimization with respect to V at the c/a values of the minima found here assuming the c/a values do not change with V. More precisely, a double minimization with respect to both a and c is required.

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