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Epitaxial Bain path of tetragonal Fe

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The epitaxial Bain paths (EBP's) of tetragonal Fe are found by minimizing the total energy with respect to c at each a using first-principles total-energy calculations with the local-spin-density approximation plus a generalized gradient approximation and relativistic corrections. The energy minima along the EBP's give the equilibrium states of the ferromagnetic, nonmagnetic and two antiferromagnetic phases—the type-I phase, called here AF1, and a phase in which pairs of ferromagnetically coupled (001) layers alternate in moment, called here AF2. The AF2 phase is found to be lower in energy than AF1 when each is in equilibrium and also when the (001) plane lattice constant is strained to the Cu(001) lattice constant. Calculations of the six elastic constants of AF2 at equilibrium inserted in the four tetragonal stability conditions show that it is unstable for [100] and [010] shears in the (001) plane, but is stabilized by epitaxy on Cu(001). The AF2 phase is indicated to be the phase of the bulk of epitaxial Fe films on Cu(001). The bulk structure of Fe films on Cu(001) found by quantitative low-energy electron diffraction analysis is shown to be close to the EBP's of the AF1 phase, but farther from the AF2 phase. On substrates with slightly larger lattice constants than Cu(001), the ferromagnetic phase is found to be more stable than AF2.

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I. INTRODUCTION

Most theoretical studies of the electronic structure of bulk Fe considered just bcc and fcc structures and varied the volume per atom V.[1] A few studies found the electronic structure for tetragonal atomic structure,[2] usually at constant V as a function of aspect ratio c/a. One previous study[3] looked at the electronic structure at all a and c values, and found the states of minimum energy in both a and c for three phases of Fe, including an antiferromagnetic phase (AF2) in which pairs of ferromagnetically coupled (001) layers alternate in moment sign. The present work also considers tetragonal states at all a and c, finds the states of minimum energy for four phases of Fe, and in addition considers the stability of the dominant AF2 phase leading to a conclusion that it is macroscopically unstable, but that epitaxial films in that phase can be stabilized.

Tetragonal calculations at constant volume give approximate values of c/a and energy E at the minima of E with respect to a and c if V is chosen near the correct values, but do not give a, c, and V separately. The calculations here find the epitaxial Bain path (EBP) in each phase by finding the minimum of $E(c)$ at each a. The minima along $E^{\mathrm{EBP}}(a)$ are then minima with respect to both a and c and will be referred to as tetragonal equilibrium states. These states are stable with respect to tetragonal deformations, but may be unstable with respect to deformations that break the tetragonal symmetry. Hence it is necessary to distinguish these states when unstable in this way from true equilibrium states that are stable against all deformations, which are then either the overall ground state or metastable states. The EBP curves found here are also useful in checking low-energy electron diffraction (LEED) values of the bulk structure of epitaxial films, since the curves give all epitaxially strained states from the tetragonal equilibrium states. The measured LEED structure of Fe films on Cu(001) is compared later with the calculated EBP's to indicate the phase of the film.

Noncubic tetragonal equilibrium states are important for Fe, especially for antiferromagnetic (AF) states, which do not have cubic symmetry. But even the ferromagnetic (FM) states, which can have cubic symmetry, such as the energy minimum for FM bcc Fe, has a noncubic tetragonal equilibrium state at $c/a = 1.18$ (using face-centered-tetragonal lattice parameters). A reliable description of the magnetic behavior of bulk Fe cannot be obtained from calculations on cubic structures.

The phase AF2 with moment sequence $\uparrow\uparrow\downarrow\downarrow$ on successive (001) planes, called bilayer antiferromagnetic in Ref. 3, was found initially in several publications to be the lowest-energy state of fcc Fe (Ref. 4) and then was found to be the lowest in ultrathin Fe films, especially those with an even number of layers.[5] The general tetragonal analysis in Ref. 3 showed that AF2 was the lowest-energy tetragonal equilibrium state at c/a values around the fcc value of $c/a = 1$. Here we show that along the EBP, the AF2 phase dominates the high-c/a range from the equilibrium state at $a = 3.407$ Å to the Cu lattice constant 3.615 Å, but that at 3.657 Å and above the FM phase has the lowest energy. We also examine the stability of the AF2 phase at equilibrium determined by its six tetragonal elastic constants. One of the four stability conditions is violated, but we show that epitaxial constraint on cubic (001) surfaces stabilizes an epitaxial film in the AF2 phase.

II. CALCULATION PROCEDURES AND RESULTS

First-principles full-potential linearized-augmented-plane-wave (FLAPW) calculations with the WIEN97 code[6] were used to find the EBP's of four Fe phases: the nonmagnetic (NM), the ferromagnetic (FM), the type-I antiferromagnetic (AF1), and the antiferromagnetic with moment sequence on (001) planes $\uparrow\uparrow\downarrow\downarrow$ (AF2). The Kohn-Sham equations[7] were

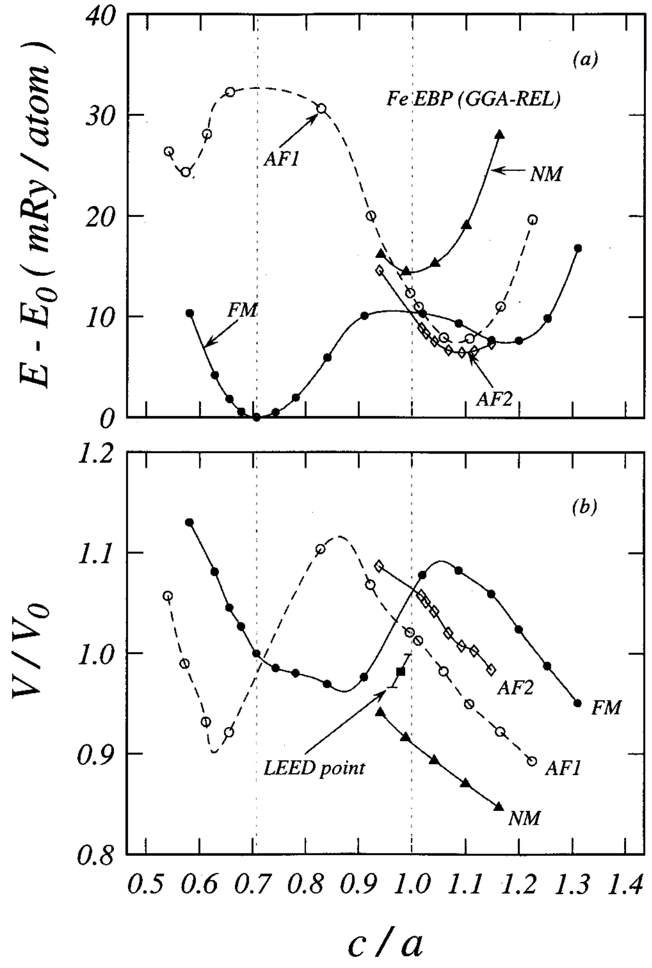

FIG. 1. (a) The $E^{\mathrm{EBP}}(c/a)$-E_0 curves of tetragonal Fe in the NM, FM, AF1 and AF2 phases from the GGA-REL calculations, where E_0 is the energy per atom in the bcc FM ground state. (b) The $\{V^{\mathrm{EBP}}/V_0\}(c/a)$ curves of tetragonal Fe in the NM, FM, AF1, and AF2 phases from the GGA-REL calculations, where V_0 is the theoretical volume per atom in the ground state, 11.57 Å^3. The data point with error bar is the experimental value of V/V_0 against c/a from the studies (Ref. 9) of Fe films on Cu(001), where $V_0 = 11.77$ Å^3 is the measured ground-state volume per atom. The solid and dased lines interpolate between the calculated points in (a) and (b).

solved using the local spin-density approximation (LSDA) with generalized gradient approximation (GGA) and relativistic corrections (called here GGA-REL). A two-atom tetragonal unit cell was used for the NM, FM, and AF1 calculations and a four-atom cell for the AF2 calculation. The detailed procedure for finding the EBP's is given in our paper on tetragonal Mn.[8]

The WIEN97 calculations used a plane-wave cutoff $R_{\mathrm{MT}}K_{\mathrm{max}}=9$, $R_{\mathrm{MT}}=1.7$ a.u., $G_{\mathrm{max}}=14$, and 360 k points in the irreducible wedge of the Brillouin zone. The k-space integration was done by the modified tetrahedron method.[6] All the calculations were highly converged. Tests with larger basis sets and different Brillouin-zone samplings yielded only very small changes in the results.

Figure 1(a) shows the energy along the EBP of each phase as a function of c/a from the GGA-REL calculations. Figure 1(b) shows the corresponding reduced volume per atom (V/V_0) along the EBP, where V_0 is the theoretical volume per atom of the bcc FM ground state, 11.57 Å^3. The experimental value of V/V_0 against c/a from the LEED studies[9] of Fe films on Cu(001) is also plotted in Fig. 1(b), where $V_0 = 11.77$ Å^3 is the measured ground-state volume per atom. Figure 2 shows the energy along the EBP as a function of the lattice parameter a from the GGA-REL calculations. There is a dashed vertical line at the Cu(001) value of a and vertical lines at the minima of E^{EBP} for the AF1, FM, and AF2 phases to indicate the tetragonal equilibrium states. Table I gives c/a, a, relative E values and local magnetic moments at the equilibrium states found in the GGA-REL calculation with WIEN97 to compare with the values found in Ref. 3, which used the same potential as GGA-REL, but a different band structure program called VASP.

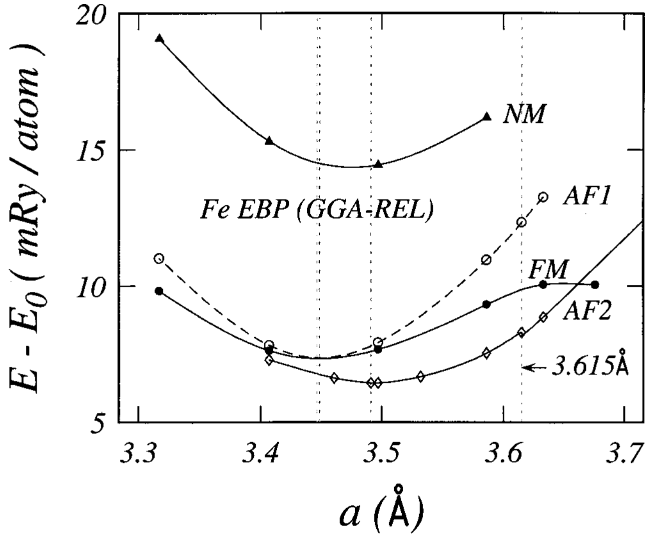

FIG. 2. The $E^{\mathrm{EBP}}(a)$-E_0 curves of tetragonal Fe in the FM, AF1, and AF2 phases in the range of $a = 3.3$–3.7 Å from the GGA-REL calculations, where E_0 is the energy per atom in the bcc FM ground state. The solid and dashed lines interpolate between the calculated points.

Since the AF2 phase is shown in Figs. 1(a) and 2 to be the lowest-energy phase over a range of a that includes the AF2 equilibrium value $a = 3.491$ Å and AF2 at the Cu(001) value $a = 3.615$ Å, which is imposed on epitaxial films of Fe on Cu(001), it is of interest to test the stability of the AF2 phase. Stability conditions can be given in terms of the six elastic constants of a tetragonal structure;[10] they express the positive definiteness of the strain energy with respect to all small deformations of the lattice. These four conditions are

$$c_{11} > |c_{12}|, \quad (c_{11}+c_{12})c_{33} > 2c_{13}^2, \quad c_{44} > 0, \quad c_{66} > 0. \tag{1}$$

Evaluation of the c_{ij} of AF2 at the equilibrium point requires six second derivatives of E with respect to particular deformations. These relations are given in terms of the magnitudes of the body-centered-tetragonal lattice vectors a', b', c, where $a' = b' = a/\sqrt{2}$, and the angles between the lattice vectors, θ_{ab}, θ_{bc}, θ_{ca}. The relations, evaluated at equilibrium, are

TABLE I. Lattice parameters, relative energies and magnetic moments at the minima of the $E^{\mathrm{EBP}}\ (c/a)$ curves of tetragonal Fe in the NM, FM, AF1 and AF2 phases in the region of high c/a values. Energies are in mRy/atom. E_0 is the energy per atom in the bcc FM ground state.

		FM	AF1	AF2	NM
GGA-REL	c/a	1.176	1.088	1.093	1.00
	a (Å)	3.449	3.447	3.491	3.480
	$\delta E = E - E(\mathrm{AF2})$	0.976	1.104	0	7.939
	$\delta E = E - E_0$	7.400	7.528	6.424	14.363
	$m(\mu_B/\mathrm{atom})$	2.332	1.569	2.075	0
Reference 3	c/a	1.18	1.06	1.10	
	a (Å)	3.40	3.40	3.42	
	$\Delta E = E - E(\mathrm{AF2})$	1.51	0.38	0	
	$m(\mu_B/\mathrm{atom})$	2.35	1.52	2.06	

$$c_{11} = \frac{2}{c}\left(\frac{\partial^2 E}{\partial a'^2}\right)_{\mathrm{eq}}, \tag{2}$$

$$c_{11} + c_{12} = \frac{1}{c}\left(\frac{\partial^2 E}{\partial a'^2}\right)_{\mathrm{eq},a'=b'}, \tag{3}$$

$$c_{33} = \frac{2c}{a'^2}\left(\frac{\partial^2 E}{\partial c^2}\right)_{\mathrm{eq}}, \tag{4}$$

$$c_{11} + c_{12} - \frac{2c_{13}^2}{c_{33}} = \frac{1}{c}\left(\frac{\partial^2 E^{\mathrm{EBP}}(a')}{\partial a'^2}\right)_{\mathrm{eq}}, \tag{5}$$

$$c_{44} = \frac{2}{ca'^2}\left(\frac{\partial^2 E}{\partial \theta_{bc}^2}\right)_{\mathrm{eq}}, \tag{6}$$

$$c_{66} = \frac{2}{ca'^2}\left(\frac{\partial^2 E}{\partial \theta_{ab}^2}\right)_{\mathrm{eq}}. \tag{7}$$

In Eq. (2) only a' varies and b' is fixed at the equilibrium value, whereas in Eq. (3), a' and b' are kept equal and varied together. In Eq. (5) the calculated $E^{\mathrm{EBP}}(a')$ curve is used. In the numerical evaluations generally five points are used at ±1% and ±2% deviation from the equilibrium value, and a best-fit cubic is found for the five points. The c_{ij} values for the AF2 phase in the equilibrium state at $a = 3.491$ Å $(a' = 2.469\ \text{Å})$ and $c = 3.816$ Å are

$$c_{11} = 3.082\ \text{Mbar}, \quad c_{12} = 0.400\ \text{Mbar}, \quad c_{13} = 1.142\ \text{Mbar},$$

$$c_{33} = 3.092\ \text{Mbar}, \quad c_{44} = 3.003\ \text{Mbar},$$

$$c_{66} = -65.41\ \text{Mbar}.$$

The first three stability conditions in Eqs. (1) are satisfied, but not the fourth condition $c_{66} > 0$.

The lattice constant of the bcc FM phase is found from the EBP minimum of the GGA-REL calculations to be $a = 4.031$ Å $(a' = 2.850\ \text{Å})$, which is 0.6% smaller than the experimental value[11] $a' = 2.866$ Å.

III. DISCUSSION

The EBP's of Fe in Figs. 1 and 2 tell us that antiferromagnetism dominates just the higher range of c/a for Fe, unlike Mn where antiferromagnetism dominates almost the entire range of c/a. In that higher range, we see from Fig. 2 that the AF2 phase has the lowest energy both at equilibrium $a = 3.491$ Å and for Fe epitaxial on Cu(001) at $a = 3.615$ Å, but the FM phase is lower for $a \geqslant 3.657$ Å.

Table I shows that the equilibrium values of c/a and the local magnetic moments for the FM, AF1, and AF2 phases from the GGA-REL calculations agree closely with the equilibrium values found in Ref. 3. Also, the energies found here for the FM and AF1 minima relative to the AF2 minimum differ from Ref. 3 by less than 1 mRy/atom. Herper *et al.*[2] find $E(c/a)$ for tetragonal Fe in the NM, FM, and AF phases, which show minima of these phases at $c/a = 1.0$, 1.16, and 1.06 to compare with the results in Table I of $c/a = 1.0$, 1.18, and 1.09, respectively. However, the calculations of Herper *et al.* differ from our calculations and that of Spišák and Hafner[3] in two ways: they find $E(c/a)$ at constant volumes taken from fcc calculations, and hence cannot find the correct volumes or energies of the tetragonal (high c/a) equilibrium FM and AF phases. They find the AF1 and AF2 phases to have identical $E(c/a)$ curves, whereas we and Spišák and Hafner[3] find the AF2 phase distinctly lower in energy and with slightly different lattice parameters.

Since the AF2 phase has the lowest energy at $a = 3.615$ Å, the GGA-REL calculations indicate that the bulk of Fe films on Cu(001) will be in the AF2 phase if the film is thick enough to have layers of bulk and, especially, if the number of layers is even.

The AF2 phase appears to be the closest approximation by a collinear spin description to the flat spin spirals of the noncollinear ground state,[12] as noted in Ref. 3, when the changes of successive layers in spin orientation in AF2 are 0°, 180°, 0°, 180°,... . These changes are replaced in a noncollinear description by 90°, 90°, 90°, 90°,... (or, when optimized, by values close to 90°), and it is plausible that the additional degree of freedom will lower the energy.

Measurements by quantitative LEED of the structure of Fe films on Cu(001) thick enough to have layers with bulk elastic behavior (e.g., eight or ten layers) (Ref. 9) give a

$=3.615$ Å, $c=3.54\pm0.06$ Å, $c/a=0.98\pm0.02$, $V=11.56$ Å^3, and $V/V_0=0.98\pm0.02$, where V_0 is the measured ground-state volume per atom, 11.77 Å^3. The LEED point and error line (due just to errors in c) are plotted on Fig. 1(b) using reduced quantities V/V_0 and c/a (which remove some of the absolute error in the calculations). The GGA-REL EBP curve for the AF1 phase is closest to the LEED point; the EBP for the AF2 phase is farther away. In general, the GGA corrections overestimate the magnetic moments and corresponding increase in volume per atom, which could account for the LEED point lying below the AF1 and AF2 EBP's in Fig. 1(b).

Figure 2 shows that a substrate with $a=3.49$ Å would be the most favorable substrate dimension to grow the AF2 phase epitaxially with least strain. This value of a is rather small; diamond (001) with $a=3.56$ Å may be the substrate that is closest, and Fe has been successfully grown on diamond (001).[13] Substrates with $a=3.65$ Å or larger, which may favor growth of the FM phase, are easier to find (fcc Rh $a=3.80$ Å, fcc Ir $a=3.87$ Å, fcc Pd $a=3.89$ Å). Then the GGA-REL calculations predict a FM bulk for such Fe epitaxial films if they can be grown with 5.8% epitaxial strain (stretched from $a=3.45$ to 3.65 Å). There is some experimental evidence for a FM phase at large c/a values. In two recent papers on Fe/Pd multilayers,[14,15] such FM phases are reported. At the lattice constant of Pd, epitaxial films of Fe would be in the range in which the FM phase has the lowest energy. Both papers measure magnetic moments greater than the bcc Fe ground state, as is found for the FM phase in Table I. Both papers state the structure is fcc, whereas our FM phase is tetragonal. But both papers deal with the Pd(111) surface, whereas our results would primarily apply to the Fe structure on Pd(001).

Two kinds of instability have been found: thus from Fig. 2 the FM phase at $a\geqslant3.657$ Å is lowest in energy, but appears to be in an unstable range of c/a for tetragonal structure since it is near the energy maximum vs c/a in Fig. 1(a). This instability means that changes of a and c are possible which preserve tetragonal structure and reduce E. However, an epitaxial film of Fe with a clamped at 3.615 Å will still be stabilized in the FM phase because E is a minimum with respect to c at that a; hence, a change of c alone cannot reduce E.

The other instability is shown by the AF2 phase at equilibrium, where the calculation of elastic constants above gives $c_{66}<0$. This condition means instability with respect to [100] and [010] shears in the (001) plane. Again, epitaxy will prevent such shears and film growth should be possible. This growth of AF2 should also be possible on Cu(001), where the phase is under 3.5% epitaxial tensile strain from equilibrium (strained from $a=3.491$ to 3.615 Å). Unlike the FM phase at $a=3.615$ Å, the AF2 phase is not in a state of tetragonal instability. However, the fact that AF2 at equilibrium is unstable with respect to [100] and [010] shears means that a free-standing crystal would not be stable. Thus the epitaxial film is not a true metastable phase even at equilibrium, but might be called a constrained metastable phase. Note that the calculation of any constrained phase is a constrained ground-state solution of the Kohn-Sham equations, i.e., it is not an excited-state calculation. If instead of $c_{66}<0$ the stability violation were $c_{44}<0$, then the AF2 phase would be unstable with respect to [101] and [011] shears corresponding to changes in θ_{ac} and θ_{bc}. In this case epitaxy which fixes the (001) plane would not inhibit the instability from developing, and we would expect that films thick enough to have bulk layers could not be grown.

There appears to be experimental evidence for the shear instability of Fe grown epitaxially on fcc surfaces. After a certain thickness of such Fe films is achieved, thick enough to have bulk layers, but depending strongly on growth conditions, a transition to a bcc structure takes place. In the work on $(\mathrm{Fe/Pd})_n$ multilayers with variable Fe thickness,[15] the transition is shown to occur essentially without volume change, which is consistent with a shear strain. A study[16] of nucleation centers of bcc Fe in Fe films on Cu(001) also shows that the transition to the bcc structure conserves volume.

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