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The magnetic phases of face-centred-cubic iron

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Abstract. The energy bands and magnetic moments of the magnetic phases of face-centred-cubic iron are calculated from first principles with the augmented spherical wave method and the fixed-spin-moment procedure. An antiferromagnetic phase that requires a four-atom cell to exist is added. This phase is the current ground state of the bulk layers of Fe film epitaxial on Cu(001). A ferrimagnetic phase and a very-low-spin phase are also found and compared with previous work. In a narrow range of volume that includes the bulk layers of the Fe films on Cu(001) at least eight magnetic phases exist.

1. Introduction

The electronic structure of iron in the face-centred cubic (fcc) atomic structure has been the subject of many theoretical studies in recent years [1–6]. One reason is the rich variety of magnetic phases, which range over non-magnetic (NM), ferromagnetic (FM) and antiferromagnetic (AF). There are in fact several FM and AF phases. The phases are sensitive to volume and are close in energy, so that experiment can show many types of magnetic behaviour. A second reason is the large body of experimental work on epitaxially stabilized films of Fe on Cu(001), which are nearly fcc in the bulk layers ($c/a = 0.98$), but have the Cu lattice constant $a = 3.61$ Å, $r_{WS} = 2.67$ au, where r_{WS} is the Wigner–Seitz radius (see references in [7]).

Separate FM and AF total energies as functions of the volume per atom $E(r_{WS})$ were found in [8] and [9] along with the corresponding atomic or local magnetic moments $m(r_{WS})$. However the detailed behaviour of $E(r_{WS})$ and $m(r_{WS})$ was made precise within the local spin-density approximation (LSDA) by use of the fixed-spin-moment (FSM) procedure in [10] for the FM phase and in [11] for the AF phase. This precise behaviour has been verified many times, e.g. in [1–3]; in [3] a non-collinear AF phase with a spin-spiral magnetic (SM) structure is added.

The present work adds to the phases of fcc Fe an AF phase which exists only in a four-atom cell (or larger), which will be called AF2 (the usual AF phase will then be called AF1). It has a lower energy at the Cu lattice constant than the AF1 and SM phases. We also find a ferrimagnetic (FIM) phase, which has been found previously [4], and a third very-low-spin (VLS) FM phase, also in agreement with [4], which has a lower energy and moment than the low-spin (LS) phase in [11]. The existence of these additional magnetic phases is demonstrated easily with the FSM procedure, whose sensitivity to magnetic phases will be illustrated. We also show that the AF2 phase is analogous to the antiferromagnetic phase of FeCr in the CsCl (B2) structure.

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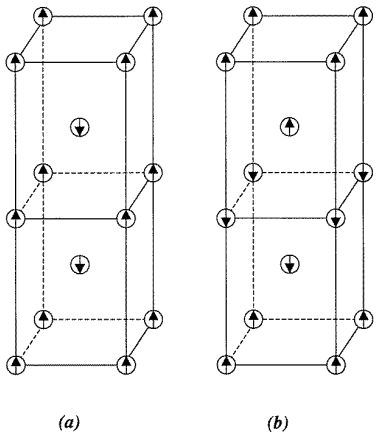

Figure 1. Two body-centred tetragonal cells ($c/a = \sqrt{2}$) making up the four-atom unit cells used to calculate the magnetic phases of fcc Fe; (a) spin configuration used for the AF1 phase; (b) spin configuration used for the AF2 phase.

2. Computational details

The total energies were calculated with the augmented spherical-wave (ASW) method [12], which is implemented in an efficient and accurate program equipped with the FSM procedure. The pure Kohn–Sham (KS) equations [13], which incorporate the LSDA [14], were solved without semi-relativistic or non-local corrections, since this formulation has been shown to give reliable results for magnetic structure in good agreement with experiment (e.g. see [15] for applications to FeRh and Cr).

The FSM procedure is a powerful and sensitive way to find and trace magnetic phases and to determine their stability and existence limits. It has been in use in band calculations since 1984 [16], but the idea of the FSM is still not fully appreciated, so we review its special features and answer a recent criticism. That criticism of the FSM procedure is that under the constraint of fixed total moment M per unit cell the solutions of the KS equations considered might be limited, hence might not include the correct solution ([4], p L277). In fact the FSM procedure includes more solutions than the usual procedure, which lets M float while iterating to self-consistency. The FSM procedure holds M fixed, as well as other constraints, such as the volume per atom V, the symmetry, e.g. bcc or fcc, the atomic composition etc, while the electron configuration is iterated to self-consistency. At electronic self-consistency the energy E is a minimum at the M and V that were used. Then the M is varied to generate the function $E(M)$ at the given V.

The solutions at the minima of $E(M)$ at the given V are the solutions which give the magnetic phases at that V. These solutions of the KS equations at the M of the minima would also be obtained without the constraint on M with the usual procedure of iterating to a minimum energy while M is allowed to float, which gives a minimum of E with respect to both M and the electron configuration. The FSM procedure actually finds all the solutions that would be found with floating-moment calculations, but embeds them in a continuous range of solutions corresponding to the effects of a magnetic field that acts only on the spin moments. At the minima of $E(M)$ this field vanishes. We call each self-consistent solution of the KS equations for each value of M a state of the system, but only the minima with respect to M are called

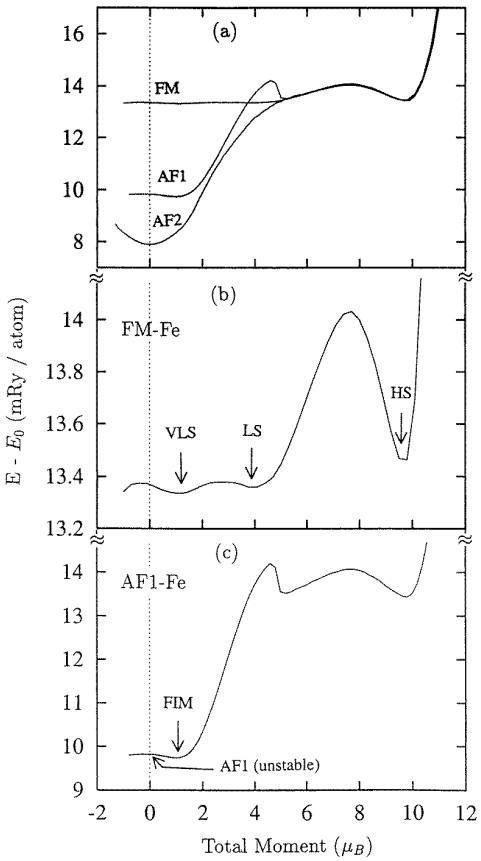

Figure 2. (a) Total energy per atom E in mRyd per atom (relative to E_0, the energy of the NM minimum at $r_{WS} = 2.54$ au) as a function of the total moment M of the four atoms in μ_B at $r_{WS} = 2.67$ au (the Cu lattice constant). Three branches of solutions of the KS equations are shown for the FM, AF1 and AF2 phases. (b) The FM $E(M)$ curve on an energy scale expanded by a factor of ten to show the three minima which track the VLS, LS and HS FM phases. (c) The AF1 $E(M)$ curve on an energy scale expanded by a factor of two to show the FIM phase minimum—the AF1 phase at $M = 0$ is at a maximum, hence is unstable when the FIM phase exists. The minimum at $M = 4.6\ \mu_B$ does not correspond to a phase, but is the result of a transition from the AF1 branch to the FM branch. The minimum at $M = 9.7\ \mu_B$ is the HS FM phase.

magnetic phases, since they do not require a magnetic field to maintain them and potentially could be stabilized by an applied stress such as an epitaxial stress.

The important extension of the FSM procedure to AF states made in [11] is based on the recognition that the solutions of the KS equations fall into separate branches. There is an FM branch in which the local atomic moments all have the same direction and there are various AF branches in which the local moments in a many-atom cell are half in one direction and half in the opposite direction. The AF calculations made here are with the two spin configurations in the four-atom cell shown in figure 1. The FM calculation uses the same cell, but all moments are in the same direction. A minimum in the energy of the FM branch $E^{FM}(M)$ at $M = 0$ indicates a stable NM phase; a maximum at $M = 0$ indicates an unstable NM phase; a minimum at a finite M indicates a FM phase. A minimum in the energy of the AF branch $E^{AF}(M)$ at $M = 0$

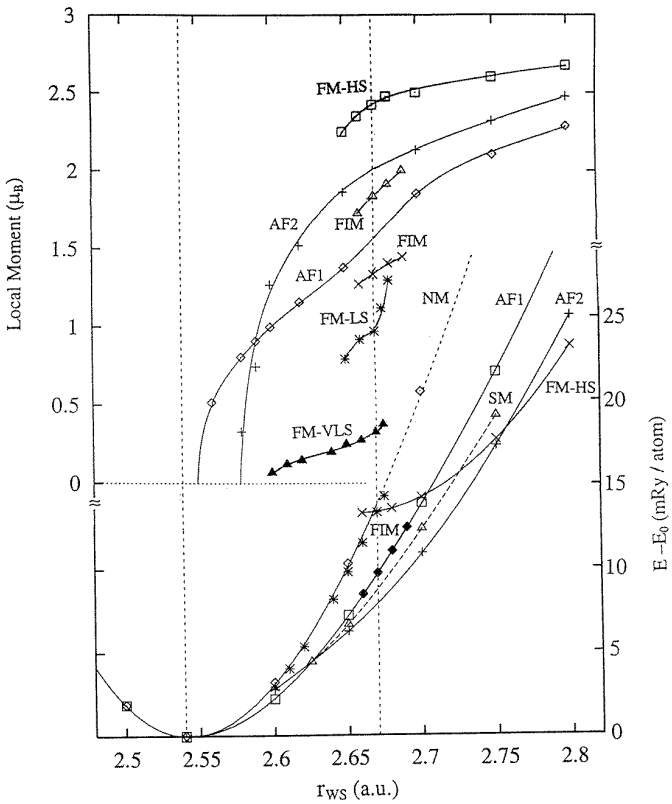

Figure 3. The energy bands $E(r_{WS})$ relative to E_0, the energy at the NM minimum, and local moments per atom $m(r_{WS})$ for eight magnetic phases of fcc Fe, the FM-HS, AF1, AF2, FIM (two moments), FM-LS, FM-VLS, SM and NM phases. The SM phase $m(r_{WS})$ is not shown since it is not available in [3]; $E(r_{WS})$ for the FM-LS phase is not shown because it has a very small range. The $E(r_{WS})$ of the SM phase has been taken from [3] (figure 1) (with an adjustment of the energy scale to allow for the smaller energy separations of the phases here). There is one vertical dotted line at $r_{WS} = 2.54$ au, the equilibrium value, and one at $r_{WS} = 2.67$ au, the Cu lattice value. The four filled diamonds on the AF1 $E(r_{WS})$ curve between $r_{WS} = 2.67$ and 2.69 au are the FIM phase energies. The asterisks next to the NM $E(r_{WS})$ curve are the VLS phase energies.

indicates a stable AF phase; a maximum at $M = 0$ indicates an unstable AF phase; a minimum at finite M (for an element) would mean unequal local moments, i.e. an FIM phase. In the FIM phase the AF phase is unstable, as shown by the maximum in E at $M = 0$ in figure 2(c), and the up and down spins become unequal in magnitude, as shown in figure 3. The values of the up and down spin moments are determined by the solution to the KS equations at the M of the minimum E^{AF} and are not variables that can be controlled.

Three branches of solutions $E(M)$ in the four-atom cell of figure 1 are shown in figure 2 at a particular r_{WS} at which the FM, AF1 and AF2 phases all exist. The different branches are generated by using different initial spin configurations, such as the configurations in figure 1, which give the AF1 and AF2 branches. Once convergence of the iterations at an initial M is achieved, solutions at closely adjacent M values are easily found by starting with the final self-consistent solution for the charge density and potential of the previous M value. At the

particular value of r_{WS} in figure 2 magnetic phase solutions exist with several minima in both the AF and FM $E(M)$ curves. Figure 2(a) shows the FM, AF1 and AF2 branches. Expansions of the energy scale in figures 2(b) and 2(c) show the minima more clearly. There is an apparent minimum in the AF1 curve at $M = 4.6\ \mu_B$ but that is a result of a non-adiabatic transition from the AF1 branch to the FM branch and does not indicate a phase.

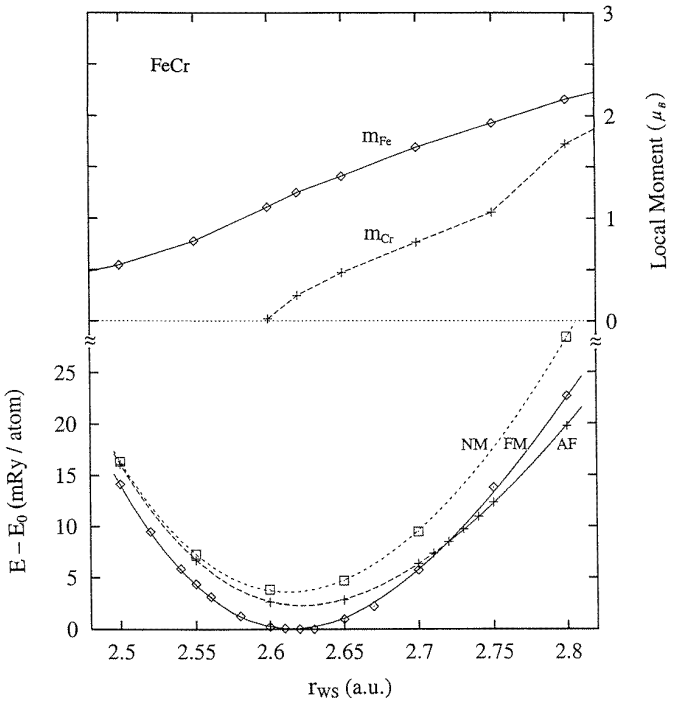

Figure 4. Energy per atom $E(r_{WS})$ in the NM, FM and AF phases and moment per atom $m(r_{WS})$ in the AF phase for the binary compound FeCr in the B2 structure from [12]. The m curves show that at the equilibrium point $r_{WS} = 2.62$ au both the Fe and Cr sublattices have finite AF moments.

3. Results

The values of E and M at the minima of the three branches of solutions shown in figure 2 are plotted against r_{WS} in figure 3. The NM, FM and AF1 curves for $E(r_{WS})$ and $m(r_{WS})$ are like these curves in [11], but have been recalculated with a four-atom cell, which provides greater stability against jumping to another branch, especially near phase degeneracies. The $E(r_{WS})$ of the NM phase was found with an unpolarized calculation and did not require $E(M)$ curves. Here m is the atomic or local moment, which equals $M/4$ in the FM phase, and equals the magnitude of one of the four atomic moments for the AF phase. Added in figure 3 to the previously found phases are the AF2 phase, the SM phase from [3] (figure 1), the FIM phase (with two values of m), the LS phase and the VLS phase.

Note that the AF2 energy curve branches away below the NM energy curve $E^{NM}(r_{WS})$ at $r_{WS} = 2.58$ au, which is above the equilibrium point $r_{WS} = 2.54$ au at which $E^{NM}(r_{WS})$ has a minimum, and above $r_{WS} = 2.55$ au where the NM and AF1 phases are degenerate. The AF2

energy curve crosses the AF1 energy curve at $r_{WS} = 2.60$ au and becomes the lowest energy state for larger r_{WS}—including at the Cu lattice constant $r_{WS} = 2.67$ au—but crosses the FM energy curve at $r_{WS} = 2.76$ au.

The SM energy curve branches off below the AF1 curve and lowers the energy by turning the spin directions more gradually than the 180° reversal in successive layers in AF1, i.e. through 108° in successive layers. The energy lowering achieved by the spin configuration ↑↑↓↓↑↑↓↓ is seen to be still more effective than the SM phase in lowering the energy. Possibly a non-collinear SM2 phase branching down from the AF2 phase would give a still more stable phase than the AF2.

4. Discussion

The AF2 phase is not unexpected. It is analogous to the AF phase of FeCr in the CsCl (B2) atomic structure [17]. The binary compound FeCr, studied with a four-atom cell, has an AF phase in which both the Fe and Cr sublattices are AF above $r_{WS} = 2.60$ au, hence both sublattices are AF at equilibrium at $r_{WS} = 2.62$ au (figure 4), although the ground state is FM. The moment sequence in successive (001) layers in the AF phase is then ↑↑↓↓↑↑↓↓, but in general with unequal moments on the Fe and Cr atoms in each direction. Although the ground state at equilibrium is FM, when r_{WS} increases from 2.62 to 2.71 au the AF phase of FeCr becomes the ground state. Similarly AF2 becomes the ground state of fcc Fe at $r_{WS} = 2.60$ au above equilibrium at $r_{WS} = 2.54$ au.

The occurrence of a more stable AF phase in the four-atom cell than any that exist in a two-atom cell points out that we really cannot be sure of the ground state without knowing what phases exist in larger cells. We can only say AF2 is the current ground state of fcc Fe for some range above $r_{WS} = 2.60$ au. The extreme case of Cr with the 40-atom AF moment configuration illustrates this uncertainty.

An AF phase with a moment sequence ↑↑↓↓ like AF2 has also been found in [5] by a dynamical method. The asymptotic solution of equations of motion for spins is found at various atom densities. In figure 2 of [5] a magnetic phase with the moment sequence ↑↑↓↓ is found to exist for r_{WS} from 2.35 to 2.73 au and to be the lowest energy state from 2.61 to 2.70 au with a minimum of 2.67 au. This behaviour shows only a slight relation to AF2, which does not exist below $r_{WS} = 2.60$ au and does not show a true minimum of E. Figure 2 of [5] does not show the AF1 phase or the NM phase, but shows a number of non-collinear phases and an FM phase.

The $E(M)$ curves in figure 2 also enable us to make some comparisons with the FIM phase, the LS phase and the VLS phase reported in [4]. The value of $r_{WS} = 2.67$ au ($a = 3.61$ Å) used in figure 2 is in the range of the FIM phase here and in [4]. The FIM phase here has a range width $\delta r_{WS} = 0.03$ au, which is about half the range width found in [4]. Plausibly the FIM phase is actually a collinear projection of a non-collinear phase in which all the atoms are equivalent as has been shown recently for the FIM phase of bcc Mn [18]. The LS and VLS phases in figure 3 are very similar to those phases in [4], and have about the same range in r_{WS}, 0.03 and 0.08 au respectively.

5. Conclusions

This first-principles study of fcc Fe with the ASW method and pure KS equations leads to two significant conclusions about the electronic structure of bulk iron grown epitaxially on Cu, which produces fcc Fe at the Cu lattice constant. One conclusion is that the AF2 phase, which

mixes FM and AF alignments on successive (001) layers, has a lower energy than the SM phase and is the current candidate for the ground state of the bulk of the experimental films. These results predict the energy sequencing and moment magnitudes of the known phases. However various spin configurations in larger cells and various non-collinear phases, such as the SM2 phase suggested at the end of section 3, might also exist, one of which might be still more stable than AF2.

A second conclusion is that fcc Fe is remarkably rich in magnetic phases in a narrow range of lattice constants that happens to include the Cu lattice constant. At least eight magnetic phases exist in an energy range of 5 mRyd/atom. Experiment might find transitions among these states. In the course of developing these phases we have verified the work in [4] which found the FIM and VLS phases, although there are some differences in the shapes and existence ranges in r_{WS} of the $m(r_{WS})$ curves. There is also a difference in the shape of the AF1 $m(r_{WS})$ curve.

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