METASTABLE MAGNETIC GROUND-STATE OF hcp-Fe

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Local spin-density functional calculations using the ASW-method were carried out for hcp-Fe at different volumes. They give a non-magnetic ground-state, but at an expanded lattice an antiferromagnetic state appears followed by a high-spin ferromagnetic state. The latter is metastable with vanishing pressure. The band-structure shows this high-spin-state to be a case of strong magnetism. Our findings seem to be experimentally realized by epitaxially grown hcp-Fe on Ru-substrates.

Recently a number of ground-state calculations appeared for transition metals at expanded lattices focussing (among other things) on the appearance or disappearance of the magnetic moment. These calculations were based on density functional theory [1], [2] some examples being those of refs. [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13]. They could be dismissed as rather academic were it not for the experimental advance in the ability to grow thin films and to control interfaces at an atomic scale which has opened new possibilities to synthesize metastable metallic structures, see e.g. refs. [14], [15], [16], [17]. Here we want to focus our attention on expanded hexagonal Fe (ϵ-Fe) which has been produced quite recently by Maurer et al. [18].

Hexagonal closed-packed bulk Fe is obtained above a pressure of 130 kbar and is most likely to be in a non-magnetic state [19]. With an expanded lattice hcp-Fe was prepared by alloying with Ru or Os and it was found to be in a low-spin antiferromagnetic state [19]. This is in contrast to the hcp-Fe system produced by epitaxial growth on Ru that is stated to be in a high-spin state [18]. A theoretical guideline is obtained from fcc-Fe that has been studied rather extensively [4], [5], [6], [8], [11], but except for older results [3], hcp-Fe has not received the same attention. We, therefore, calculated some ground-state properties of interest for this system which we want to report here.

Using the local spin-density functional approximation [1], [2] and self-consistent band-structure calculations with the augmented-spherical-waves method (ASW) [20], the total energy was obtained for bulk hcp-Fe as a function of the volume for an assumed non-magnetic, an antiferromagnetic, and a ferromagnetic state. In the upper part of Fig. 1 we show the total energy in eV per atom counted from the total energy of the free Fe-atom [21] as a function of the Wigner-Seitz radius, S, in atomic units (1 a.u. $= 0.5292$ Å) the relation with the lattice constant, a, being $a^2 c = 16\pi S^3/\sqrt{3}$. We used the ideal c/a-ratio of c/a $= 1.633$ except for the dashed curve
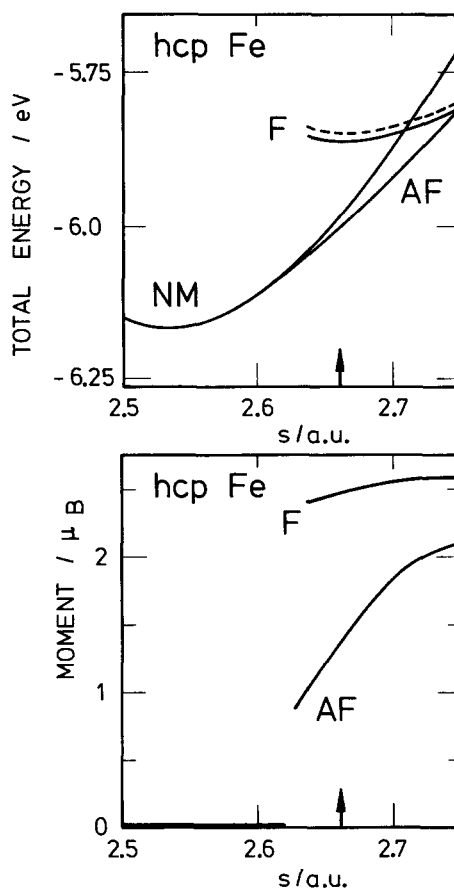

Fig. 1: Upper part: total energy per atom counted from the free-Fe-value [21] of hcp-Fe as a function of the Wigner-Seitz radius, S; NM non-magnetic, AF antiferromagnetic, F ferromagnetic, c/a $= 1.633$ except for dashed F-values where c/a $= 1.58$.

Lower part: Magnetic moments corresponding to upper part.

where $c/a = 1.58$ was used. In the lower part of Fig. 1 the magnetic moment is shown; here the smaller c/a-ratio has no visible effect. The results are qualitatively very similar to fcc-Fe: at smaller volumes the ground-state is non-magnetic, at $S \simeq 2.625$ a.u. (corresponding to an atomic volume of 11.2 Å^3) first a magnetic moment appears that is stable in an antiferromagnetic arrangement (AF), then at $S \simeq 2.63$ (corresponding to an atomic volume of 11.3 Å^3) a large magnetic moment appears that is stable in a ferromagnetic arrangement (F). There is one important difference to fcc-Fe [8], [11] (and also Mn [11]): the high-spin ferromagnetic state, F, has a local minimum in the total energy at $S = 2.66$ a.u. marked with an arrow in Fig. 1, i.e. if hcp-Fe can be stabilized at this volume (by MBE e.g.) it presumably will not be subject to any pressure, although it is unstable against an antiferromagnetic reordering resulting in a subsequent high-pressure situation. A further difference to fcc-Fe is the absence of two, non-zero spin-states in the ferromagnetic case. This can be seen with the help of Fig. 2 which shows the total energy as a function of a constrained ferromagnetic moment [22], [8] for four volumes. Curve (a) applies to a volume slightly smaller than that where the ferromagnetic solution sets in; clearly, only the non-magnetic case is stable. Curve (b) corresponds to the zero pressure case with both a

zero-magnetic moment and a high-spin magnetic moment. (Of course, there is also the antiferromagnetic solution not shown in Fig. 2.) Curve (c) corresponds to the volume estimated in the experiment of Maurer et al. [18]. Here only the high-spin ferromagnetic state is stable, the zero-moment state being unstable, but not the antiferromagnetic one, cf. Fig. 1. Curve (d) applies to a rather large volume where only the high-spin ferromagnetic tate (F) is stable. Fig. 2 should be compared with Fig. 3 of ref. [8], where two non-zero ferromagnetic states can be seen.

Commenting on the relative stability of the three kinds of iron, i.e. bcc-Fe, fcc-Fe, and hcp-Fe, we do find the fcc-Fe ground-state non-magnetic and of marginally higher total energy than ferromagnetic bcc-Fe - as it should be -, but the non-magnetic ground-state of hcp-Fe to have a lower total energy than bcc-Fe by 0.05 eV per atom. This error is small and probably a local-density-functional defect, the calculated trends shown in Figs. 1 and 2, however, we believe are reliable.

Fig. 3: Band-structure of majority-spin-electrons for the constrained ferromagnetic (unstable) case corresponding to curve (a) of Fig. 2.
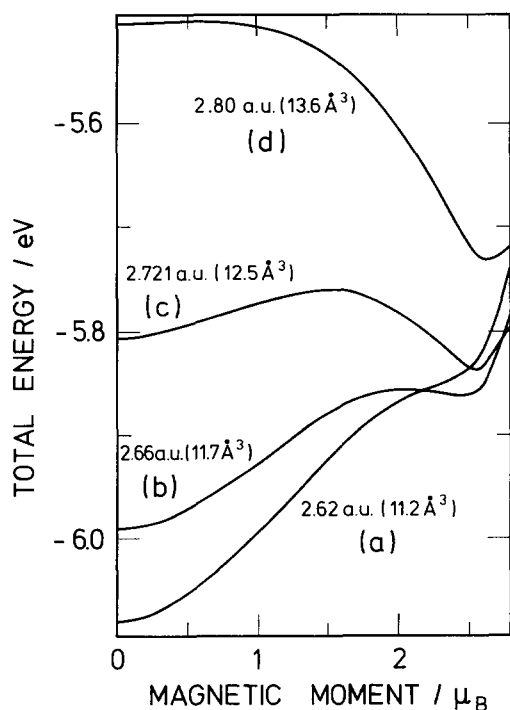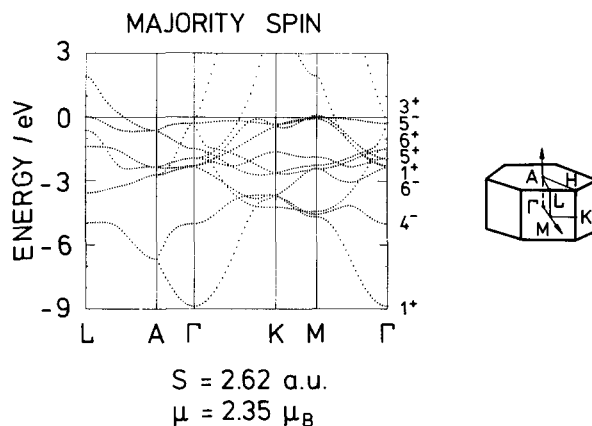

Fig. 2: Constrained ground-state calculation for hcp-ferromagnetic Fe giving total energy as a function of the magnetic moment for four different volumes as indicated.
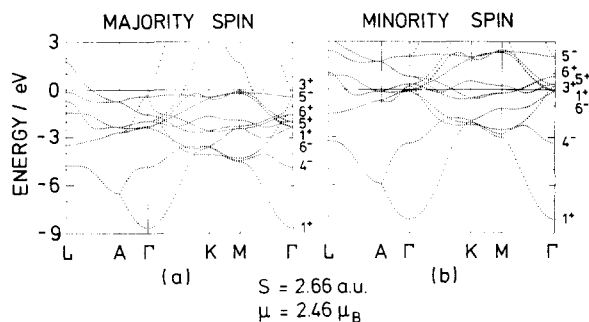

Fig. 4: Band-structure of (a) majority-spin-electrons (b) minority-spin-electrons for metastable ferromagnetic case corresponding to the local minimum in curve (b) of Fig. 2.

Finally an attempt is made to identify the reason for the abrupt appearance of the high-spin ferromagnetic state. Our findings support a previous observation of Bagayoko and Callaway [5] concerning fcc-Fe. For our case of hcp-Fe we show the band-structure of the majority-spin electrons in Fig. 3 at a volume corresponding to that of curve (a) in Fig. 2 and an unstable magnetic moment of $\mu = 2.35 \, \mu_B$. Comparing this with Fig. 4(a) which shows the majority-spin band-structure of the metastable state corresponding to curve (b) of Fig. 2 with a moment of $\mu = 2.46 \, \mu_B$ one notices the Fermi surface resulting from the rather flat d-states at $M\Gamma$ in Fig. 3 has disappeared in Fig. 4(a). Thus, just as in fcc-Fe, the high-spin-state becomes stable when the magnetism becomes strong. The minority-spin band-structure of both the unstable and the metastable cases are not visibly different; it is shown in Fig. 4(b). Unfortunately, no marked changes can be seen in the band-structure of antiferromagnetic hcp-Fe on going from a constrained but unstable case at S = 2.62 a.u. to a stable case at S $\gtrsim$ 2.63 a.u. (see Fig. 1, lower part). We therefore do not show its band-structure here.

On closing we summarize that local-spin-density-functional calculations for hcp-Fe give a non-magnetic ground-state. At an expanded lattice an antiferromagnetic state abruptly appears but having no (local) minimum in the total energy in contrast to a high-spin ferromagnetic state that is found to be metastable (with zero pressure). The band-structure shows this high-spin-state to be a case of strong magnetism. Our findings seem to be realized by epitaxially grown hcp-Fe on Ru [18].

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