CHEMICAL, MAGNETIC AND CHARGE ORDERING IN THE SYSTEM HEMATITE-ILMENITE, $Fe_2O_3 - FeTiO_3$

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Abstract

Spin polarized electronic structure calculations of total energies and magnetic moments for ordered supercells in the system $Fe_2O_3 - FeTiO_3$ suggest that some **layered** superstructures are more stable than an isocompositional mechanical mixture of hematite, Fe_2O_3, and ilmenite, $FeTiO_3$. This result contradicts established ideas about hematite-ilmenite phase relations, because it suggests that there may be stable phases which contribute to the "lamellar magnetism" named by (Robinson, Harrison, McEnroe and Hargraves, 2002). It is not clear if these results are artifacts of the approximations made in generalized gradient spin density functional calculations. The electronic structure of a 30 atom layered supercell was studied by a variety of techniques. The supercell structure is FTFFFT, where F is an Fe-layer and T is a Ti-layer perpendicular to the hexagonal c-axis. The idea was to investigate possible charge ordering on Fe-sites, but significant $Fe^{2+} - Fe^{3+}$ ordering is not predicted.

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1. INTRODUCTION

The hematite-ilmenite system, $Fe_2O_3 - FeTiO_3$, exhibits interesting and useful properties that vary with changes in chemical and magnetic ordering(Ishikawa and Akimoto, 1957; Ishikawa, 1958). In Fe_2O_3, iron has a nominal valence of plus three, Fe^{3+}, but in $FeTiO_3$ it is Fe^{2+}, so at intermediate compositions charge ordering of Fe^{2+} and Fe^{3+} is a possibility at low temperature (T). After the spinel solid solution, magnetite-ulvospinel ($Fe_3O_4 - Fe_2TiO_4$), hematite-ilmenite is the second most important system in rock magnetism(McEnroe, Robinson and Panish, 2001).

The crystal structures of hematite and ilmenite are closely related. Hematite and hematite-rich solid solutions (Hem_{ss}) adopt the corundum structure, space group $R\overline{3}c$, which can be visualized as a hexagonal closest packed array of O^{2-}-ions with Fe^{3+}-ions occupying two thirds of the octahedral interstices. Occupied and unoccupied octahedra are ordered such that each FeO_6-octahedron shares: three edges within $(0001)_{hex}$; one face in $(0001)_{hex}$ between two FeO_6-octahedra, e.g. in the $[0001]_{hex}$ direction; and the other face shared with an unoccupied $[\,]O_6$-octahedron, e.g. in the $[000\overline{1}]_{hex}$ direction. Ilmenite, and ilmenite-rich solid solutions (Ilm_{ss}) differ from hematite in that Fe^{2+}- and Ti^{4+}-ions preferentially occupy alternate $(0001)_{hex}$-layers, reducing space group symmetry to $R\overline{3}$.

As reviewed by Lindsley, (Lindsley, 1976), hematite is antiferromagnetic (AF) below the Morin transition, $T_{Morin} = 80K$: all Fe-moments align parallel to $[0001]_{hex}$; there is ferromagnetic (FM) ordering within $(0001)_{hex}$; and AF-coupling between nearest neighbor (nn) $(0001)_{hex}$-layers. At $80 < T < 898K$, Fe-spins are perpendicular to $[0001]_{hex}$, but spins in nn $(0001)_{hex}$-layers are slightly misaligned, or "canted," with respect to one another (Dzaloshinsky, 1958). Thus, the hematite, and Hem_{ss}, are described as canted antiferromagnets (CAFs). Ilmenite is AF, $T_N = 55K$: all Fe-moments align parallel to $[0001]_{hex}$; spins are FM-aligned within $(0001)_{hex}$-layers; and there is AF-coupling between nn $(0001)_{hex}$-layers that are occupied by Fe (i.e. there is AF coupling from Fe-layer to Fe-layer through intervening Ti-layers).

The hematite-ilmenite phase diagram (Burton and Davidson, 1988; Ghiorso, 1997), Fig. 1, exhibits: a chemical order-disorder transition in Ilm_{ss}, $R\overline{3}_{PM} \rightleftharpoons R\overline{3}c_{PM}$; a PM $\rightleftharpoons$ CAF transition in Hem_{ss}, $R\overline{3}c_{CAF} \rightleftharpoons R\overline{3}c_{PM}$; and three two-phase fields at $T \leq 930 - 1000K$. Subscripts on space group symbols (PM, AF, and CAF) indicate paramagnetic, antiferromagnetic and canted antiferromagnetic phases, respectively.

Magnetic studies of natural Ilm_{ss} samples with bulk compositions in the

neighborhood of 70-95 mol% ilmenite ($Ilm_{70} - Ilm_{95}$) (McEnroe, Robinson and Panish, 2001; McEnroe, Harrison and Langenhorst, 2002; Robinson, Harrison, McEnroe and Hargraves, 2002) indicate that they exhibit anomalously high demagnetization temperatures, 800-925K; homogeneous ferrimagnetic Ilm_{ss} in this compositional range has $100 < T_N < 400K$. The natural samples also exhibited anomalously high coercive fields, such that "many do not demagnetize in alternating fields of 0.1T..."(Robinson, Harrison, McEnroe and Hargraves, 2002).

Exsolution lamellae are observed, in layers parallel to $(0001)_{hex}$ that range in thickness from macroscopic to a few atomic layers. High resolution transmission electron microscopy (HRTRM) studies of these samples (McEnroe, Harrison and Langenhorst, 2002; Robinson, Harrison, McEnroe and Hargraves, 2002) reveals multiple generations of lamellae, i.e: $\sim 2000nm$ thick Ilm_{ss}-lamellae that contain much finer Hem_{ss}-lamellae (Fig. 2); and Hem_{ss}-lamellae that have very thin Ilm_{ss}-lamellae in them. Clearly, their very high coercivities suggest that if one could synthesize Hem_{ss}-lamellae in Ilm_{ss} host, they would make excellent hard magnetic storage devices.

Robinson et. al. (Robinson, Harrison, McEnroe and Hargraves, 2002) proposed the "lamellar magnetism hypothesis" (LMH) to explain the anomalous magnetic properties (departures from bulk properties) of Hem_{ss}-lamellae in Ilm_{ss} host. The idea is that magnetic coupling in Hem_{ss} is FM within $(0001)_{hex}$ layers, but AF between nn $(0001)_{hex}$ layers, so any Hem_{ss}-lamella that has *an odd number of* Hem_{ss} *layers* will have a net ferrimagnetic (FiM) moment; i.e. the magnetism of "contact layers" [$(0001)_{Fe}$-layers in Hem_{ss}-lamella that are nn of $(0001)_{Ti}$-layers in Ilm_{ss} host, would be observable. The surrounding Ilm_{ss} host will be PM except at very low temperatures. Robinson et. al. (Robinson, Harrison, McEnroe and Hargraves, 2002) also postulated that there should be *charge ordering* of Fe^{3+} and Fe^{2+} in the "contact-layers" such that: (1) $Fe^{3+}O_6$ octahedra in the "contact-layer" share faces with $Fe^{3+}O_6$ octahedra in the Hem_{ss}-lamella, and with $[\,]O_6$ vacant octahedra in the nn $(0001)_{Ti}$-layer; (2) $Fe^{2+}O_6$ octahedra in the "contact-layers" share faces with $Ti^{4+}O_6$ in Ilm_{ss} host, and with $[\,]O_6$ octahedra in the Hem_{ss}-lamella; (3) Fe-ions in the Ilm_{ss} host are almost all Fe^{2+}. The zero Kelvin first principles (FP) electronic structure calculations described below, were used to search for evidence of this proposed charge ordering.

2. COMPUTATIONAL STUDIES

Possible Stability of Intermediate Phases

To study phase stability in hematite-ilmenite, spin polarized (SP) Vienna Ab-initio Simulation Package (VASP) (Kresse and Hafner, 1993; Kresse, 1993; Kresse and Hafner, 1994; Kresse and Furthmüller, 1996a,b) calculations were performed in the generalized gradient approximation (GGA; VASP-SPGGA), using soft (Vanderbilt, 1990) pseudopotentials. Total energy calculations were done for $\alpha - Fe_2O_3$, $FeTiO_3$, Ti_2O_3 and several 30-atom supercells with intermediate composition and various sequences of $(0001)_{Fe}$- (F) and $(0001)_{Ti}$-layers (T) (Fig. 3). For example, FTFFFT indicates a six layer sequence in which there are two $(0001)_{Ti}$-layers plus four $(0001)_{Fe}$-layers. All VASP calculations were fully relaxed with respect to both cell constants and atomic coordinates. Supercell formation energies, ΔE_{Str}, (relative to a mechanical mixture of $\alpha - Fe_2O_3$ and Ti_2O_3) are plotted in Fig. 3; units are kJ/mol, where one mol = Avogadro's number of $MO_{1.5}$ formula units; M = an Fe- or Ti-cation. Taken at face value, these results indicate that some intermediate phase(s) are stable. Of the structures for which VASP calculations were performed, only TFFFFF is a candidate ground state, because ΔE_{TFFFFF} is on the convex hull between $\alpha - Fe_2O_3$ and $FeTiO_3$. This makes it a ground-state of the system, unless ΔE_{Str} for some UN-studied configuration is low enough to remove ΔE_{TFFFFF} from the convex hull. Because phase separation between Hem_{ss} and Ilm_{ss}, is often observed in natural samples, and no intermediate phases have been reported, one expects all ΔE_{Str} for structures with bulk compositions between $\alpha - Fe_2O_3$ and $FeTiO_3$ to plot *above* the mixing line between $\alpha - Fe_2O_3$ and $FeTiO_3$. Either the collinear VASP-SPGGA treatment of the magnetic contribution to the total energy, ΔE_M, is not precise enough for correct predictions of hematite-ilmenite phase stabilities, or there are intermediate phases to be discovered.

Electronic Structure of the FTFFFT Supercell

The FTFFFT supercell was chosen as a first approximation for a lamellar magnetic system, because it is the smallest cell in which a 3-layer hematite block, with "contact-layers," coexists with a 3-layer ilmenite block. One would prefer a thicker ilmenite-block, and a more ilmenite-rich bulk composition, but the next smallest system is a 60 atom supercell. The essential constraints on supercell construction are: (1) each $(0001)_{hex}$ cation-layer must include at least two cations so that one FeO_6-octahedron in a "contact-layer" can share an octahedral face with a TiO_6-octahedron in the ilmenite-block; while the other FeO_6-octahedron in the "contact-layer" shares a face with an FeO_6-octahedron in the hematite block.

Table I: Columns 1-4 are a schematic $(11\bar{2}0)$ projection of the FTFFFT... supercell in spin configuration UuuDDUUDDddU; □ indicates an unoccupied O_6-octahedron; horizontal lines represent hexagonally closest packed oxygen layers. Columns 6 and 7 are LAPW results for total spin densities on Fe- and Ti-ions.

□	$Fe1\Uparrow$	$Fe8\Uparrow$	□		+3.258	+3.282
$Ti4\downarrow$	□	$Ti2\downarrow$	$Ti4\downarrow$		-0.066	-0.075
$Fe6\Downarrow$	$Fe7\Downarrow$	□	$Fe6\Downarrow$		-3.410	-3.446
□	$Fe4\Uparrow$	$Fe5\Uparrow$	□		+3.515	+3.514
$Fe3\Downarrow$	□	$Fe2\Downarrow$	$Fe3\Downarrow$		-3.354	-3.400
$Ti1\uparrow$	$Ti3\uparrow$	□	$Ti1\uparrow$		+0.134	0.132
□	$Fe1\Uparrow$	$Fe8\Uparrow$	□		+3.258	+3.282

Table II: FTFFFT supercell spin configurations and LAPW energies kJ/mol. relative to the lowest state that was calculated.

$Fe1$ 0.01‡	$Ti1$ 0.14	$Ti2$ 0.18	$Fe2$ 0.32	$Fe3$ 0.36	$Fe4$ 0.48	$Fe5$ 0.51	$Fe6$ 0.64	$Fe7$ 0.68	$Ti3$ 0.82	$Ti4$ 0.86	$Fe8$ 0.99	$\Delta E_M^{\dagger}$
U	u	u	U	D	U	D	U	D	d	d	D	9.58
U	u	u	U	U	U	U	U	U	u	u	U	9.55
U	u	u	D	U	D	U	D	U	d	d	D	9.12
U	u	u	D	D	U	D	U	U	d	d	D	3.64
U	u	u	D	D	U	U	D	D	d	d	U	0

† ΔE_M (M for the magnetic contribution to total energy) is in kJ/mol where one mole = 6.0225*10^{23} $MO_{1.5}$ formula units (M = Fe or Ti).
‡ Approximate cation z-coordinates; note Fe1 and Fe8 occupy the same cation layer.

Table III: A schematic $(11\bar{2}0)$ projection of the FTFFFT... supercell in spin configuration UddDDUUDDddU. Columns 6 and 7 are Dmol results for total spin densities on Fe- and Ti-ions.

□	$Fe1\Uparrow$	$Fe8\Uparrow$	□		+3.505	+3.513
$Ti4\downarrow$	□	$Ti2\downarrow$	$Ti4\downarrow$		-0.153	-0.143
$Fe6\Downarrow$	$Fe7\Downarrow$	□	$Fe6\Downarrow$		-3.532	-3.447
□	$Fe4\Uparrow$	$Fe5\Uparrow$	□		+3.515	+3.514
$Fe3\Downarrow$	□	$Fe2\Downarrow$	$Fe3\Downarrow$		-3.535	-3.448
$Ti1\downarrow$	$Ti3\downarrow$	□	$Ti1\downarrow$		-0.140	-0.159
□	$Fe1\Uparrow$	$Fe8\Uparrow$	□		+3.513	+3.505

All Electron Calculations

To investigate the charge ordering in "contact-layers" that Robinson et al. (Robinson, Harrison, McEnroe and Hargraves, 2002) postulated, two types of spin polarized all electron calculations were performed: (1) general potential linearized augmented planewave (LAPW) (Singh, 1994) calculations of densities of states (DOS) were done on an FTFFFT supercell with ionic positions that were relaxed in VASP-SPGGA calculations; (2) Fully relaxed Dmol (Delley, 1990, 2000) calculations of spin densities in $\alpha - Fe_2O_3$ and the FTFFFT supercell. Table I is schematic $(11\overline{2}0)_{hex}$ projection of the FTFFFT supercell that was used in LAPW calculations, in which the last two columns are calculated atomic spin densities.

LAPW Calculations

Fig. 4 is a plot of the total DOS which indicate that the FTFFFT supercell with spin configuration UuuDDUUDDddU: where lower case u and d indicate Ti-up and Ti-down spin orientations, respectively; U and D indicate Fe-up and Fe-down spin orientations, respectively. Configuration UuuDDUUDDddU is predicted to be a metal, which is probably not correct.

All cations in the FTFFFT supercell are symmetrically distinct, but as indicated by the spin densities in Table I the differences between some cations are vanishingly small (c.f. Fe1 and Fe8 Table I). Therefore, representative cation DOS are plotted in Fig. 5, from the top down:

- Ti1 is strongly ionic as expected for a Ti^{4+}-ion.
- Fe4 is at the center of the hematite block. This site exhibits: moderate crystal field splitting ($-3 < T2_g < -2eV$, $E_g \sim -1eV$); significant spin dependent Fe-O hybridization (low DOS peaks $< -3eV$); and clear ionic character.
- Fe3 is in the "contact-layer," and shares an $FeO_6 - TiO_6$ octahedral face. This is the "contact-layer" Fe that is predicted to be Fe^{2+} in the LMH. There is much less crystal field splitting than in the Fe1-site. Spin dependent Fe-O hybridization is significant, and it has some metallic character.
- Fe2 is the "contact-layer" Fe that is predicted to have Fe^{3+} character, in the LMH, but the DOS for this site are not significantly different from those of Fe3.
- Fe1 is at the center of the ilmenite block. The DOS indicate: strong crystal field splitting; spin dependent Fe-O hybridization; and metallic character.

Table II lists LAPW values for ΔE_M for five spin configurations in the FTFFFT supercell. Of the configurations considered, UuuDDUUDDddU is lowest in energy; it has AF-coupling within the central hamatite-block, DDUUDD, and AF-coupling between the hematite-block and the Fe1 and Fe8 sites in the ilmenite-block. All the LAPW calculations had significant residual forces, which suggest shortcomings in the VASP optimization. For example, residual forces for configurations UuuDDUUDDddU, UuuDDUDU-UddD, and UuuDUDUDUddD, are 24.54, 16.49, and 22.22 kJ/mol, respectively (mol = Avogadro's number of $MO_{1.5}$ formula units). This implies significant magnetoelastic coupling, of the order of ∼8 kJ/mol.

Small, but significant spin densities, $\sim 0.1e^-$, are predicted for Ti1 and Ti4 which are the Ti-ions that occupy TiO_6-octahedra that share faces with Fe3 and Fe6, respectively, in the hematite-block. This result hints at charge-ordering of a sort that is not predicted by the LMH; rather than reduction of the Fe3 and Fe6-ions, there is a slight reduction of the Ti-ions that face them across shared octahedral faces.

Dmol Results

Table III is a schematic $(11\bar{2}0)_{hex}$ projection of the FTFFFT supercell that was used in Dmol calculations, in which the last two columns are calculated atomic spin densities. The Dmol FTFFFT supercell spin density results are plotted in Fig. 5, and compared with those for Fe^{3+} in $\alpha - Fe_2O_3$. Curiously, calculated differences between Fe spin-densities in FTFFFT and those in $\alpha - Fe_2O_3$ are so subtle as to appear insignificant. Unlike the LAPW results, the Dmol calculations predict that all Ti-ions are slightly reduced, $\sim 0.15e^-$, not just those that share octahedral faces with Fe-ions in the "contact layers."

3. DISCUSSION AND CONCLUSIONS

Formation energies for supercells with bulk compositions intermediate between $\alpha - Fe_2O_3$ and $FeTiO_3$ suggest that some intermediate compound(s) should be stable at low T. There are no experimental data to support this prediction, and observational data suggest, but do not mandate, that such intermediate phase(s) do not form. Either the simple collinear magnetism VASP-SPGGA approximation is insufficient for such predictions, or there are intermediate phases to be discovered.

According to the LMH, one expects Fe1, Fe8, Fe3 and Fe6 (Table I), in the ilmenite block, to be more like Fe^{2+}; and Fe4, Fe5, Fe7 and Fe8 in the hematite-block, to be more like Fe^{3+}. Spin density calculations that were performed with the LAPW and Dmol codes do not support the LMH

with respect to charge ordering in "contact-layers." Predicted charge ordering does approximately follow the LMH predictions in a qualitative sense, but quantitatively, these effects are so subtle as to appear insignificant. Rather than $Fe^{3+} \rightarrow Fe^{2+}$ reduction, in Fe-ions that share octahedral faces with Ti-ions, a slight reduction of the Ti's, $\sim 0.1e^{-}$, is predicted (in Dmol calculations all Ti-ions are predicted to reduce by $\sim 0.15e^{-}$).

The LAPW DOS plots point to interesting trends and differences between Fe-ions that lie: 1) between Ti-layers, Fe1, Fe8; in contact-layers, Fe2 and Fe3; at the center of the hematite block, Fe4 and Fe5. Fe-ions at the center of the ilmenite block have more metallic character and greater crystal field splitting than those in the contact-layer or at the center of the hematite block (Fe4, Fe5). Fe2 and Fe3 in the contact-layer exhibit intermediate character: some metallic character and reduced crystal field splitting. All Fe-ions exhibit significant spin-dependent Fe-O hybridization, and analysis of the LAPW residual forces indicates significant magnetoelastic coupling, of the order of $\sim$8 kJ/mol.

It seems likely that the FTFFFT structure in spin configuration UuuD-DUUDDddU should not be metallic, as predicted by the LAPW calculations. A fully relaxed LAPW calculation, or some other lower-energy spin configuration, might exhibit a band-gap. It is also possible to generate a band-gap by the LDA+U (Bandyopadhyay, Sarker, Velev, Butler *et al.*, In press; Punkkinen, Kokko, Hergert and Väyrynen, 1999) approach for correcting spin-spin correlations, however, choosing U is somewhat arbitrary, and different values of U correspond to different changes in the DOS for Fe- and O-ions; which imply significant changes in ΔE_M.

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FIGURE CAPTIONS

Figure 1:
An empirically calculated phase diagram for the system $Fe_2O_3 - FeTiO_3$

Figure 2:
Fine Hem_{ss} lamellae in coarser Ilm_{ss} lamellae; micrograph courtesy of R. J. Harrison.

Figure 3:
Structure formation energies, ΔE_{Str}, for various supercells with bulk compositions that are intermediate between $\alpha - Fe_2O_3 - FeTiO_3$.

Figure 4:
Total density of states for the FTFFFT supercell in spin configuration UuuDDUUDDddU. Cell constants and atomic were relaxed in VASP-SPGGA calculations, but DOS were calculated with the LAPW code. Note that the system is predicted to be metallic.

Figures 5:
Densities of states for (a) the Ti1-ion and (b-e) the Fe1-Fe4 ions in the FTFFFT supercell in spin configuration UuuDDUUDDddU.

Figures 6:
Dmol results for ion spin densities in the FTFFFT... supercell: solid horizontal lines indicate spin densities in $\alpha - Fe_2O_3$; solid vertical lines indicate Ti-layers.

FIGURES

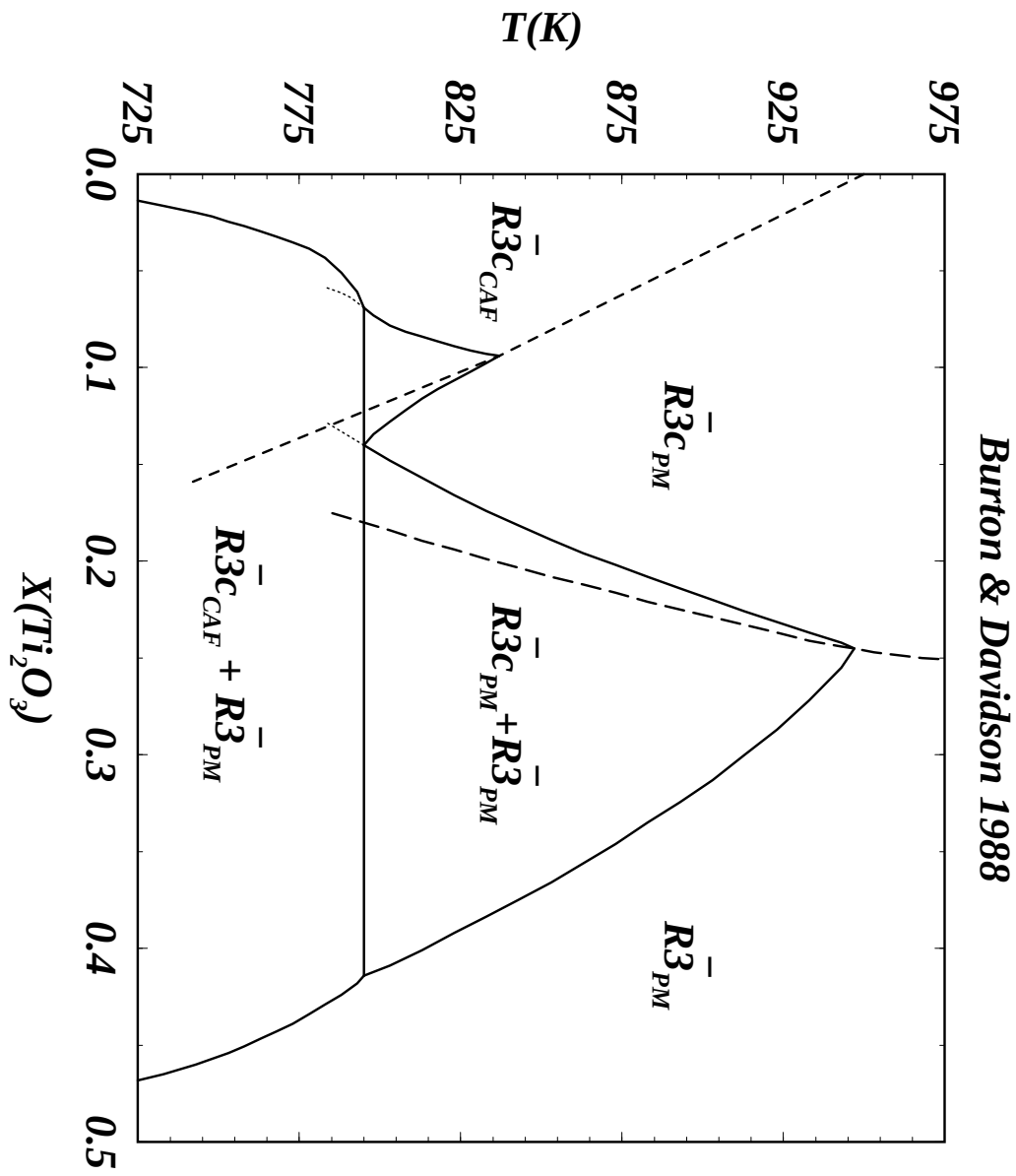

Figure 1: Calculated phase diagram for the system $Fe_2O_3 - FeTiO_3$.

Hematite ppts
RH0104 300.0KV X80K 100nm
Ilmenite Host

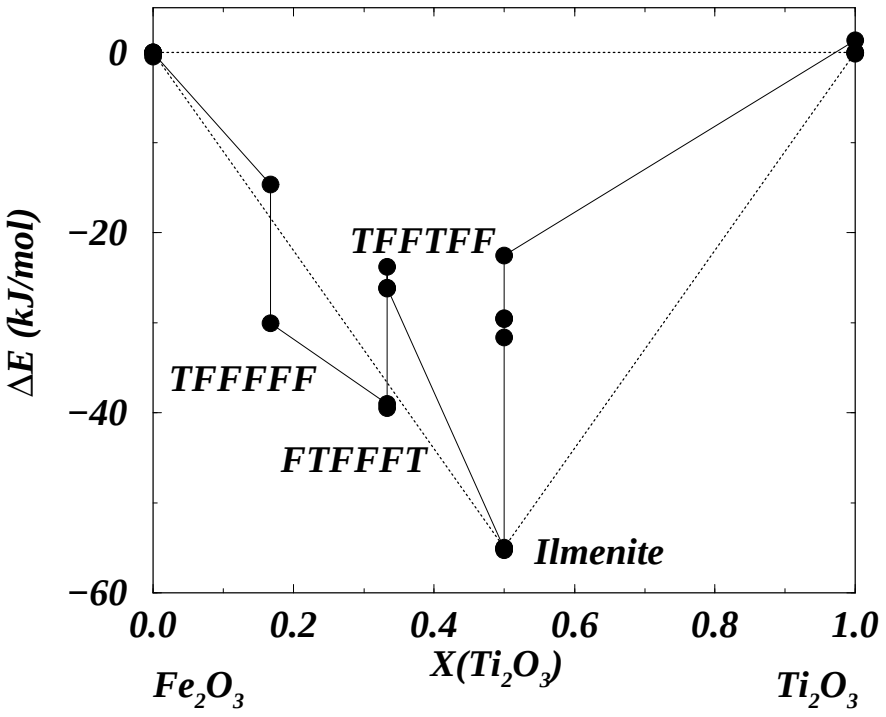

Figure 3: Structure formation energies, ΔE_{Str}, for various supercells with bulk compositions that are intermediate between $\alpha - Fe_2O_3 - FeTiO_3$.

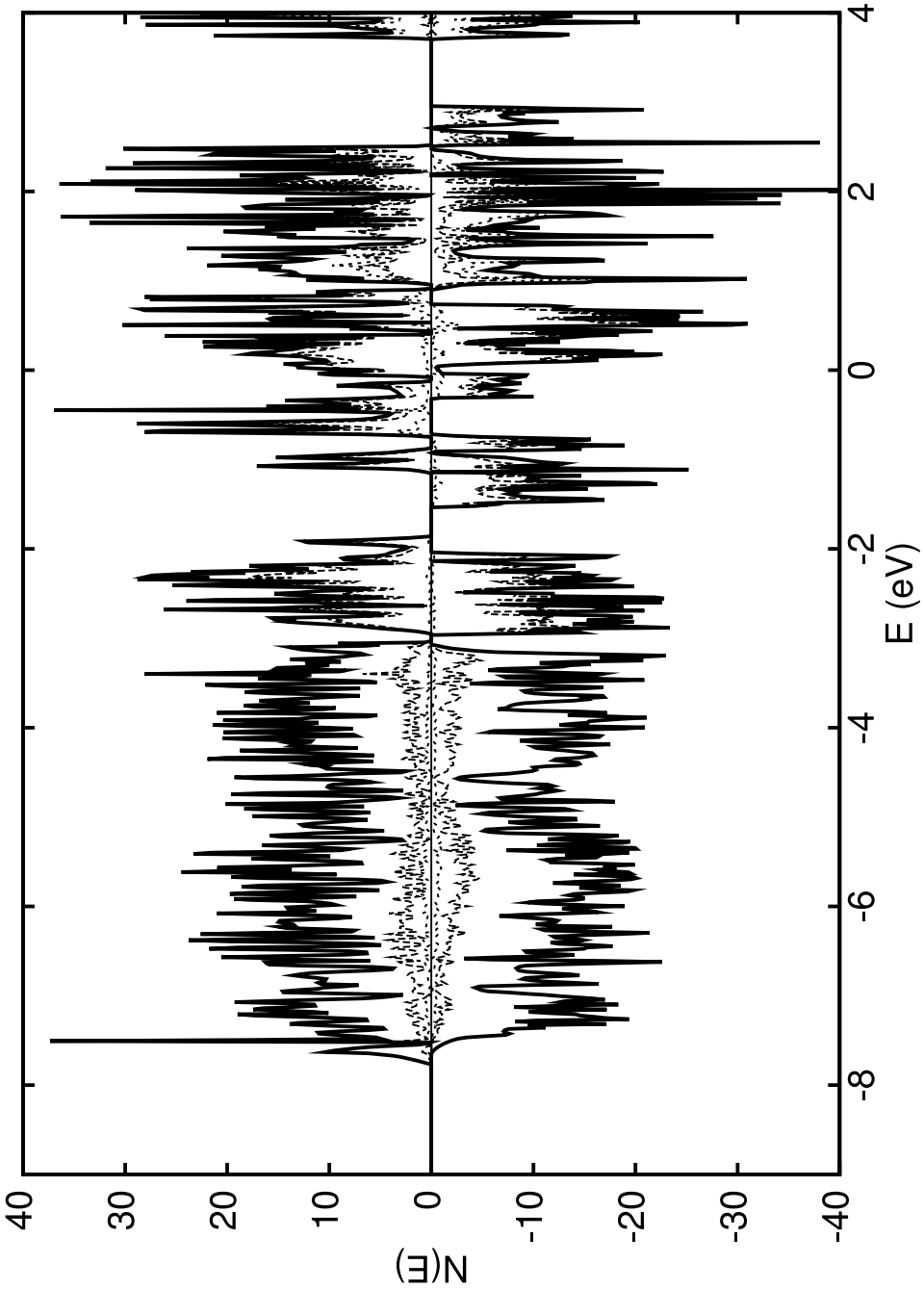

Figure 4: Total density of states for the FTFFFT supercell in spin configuration UuuDDUUDDddU. Cell constants and atomic were relaxed in VASP-SPGGA calculations, but DOS were calculated with the LAPW code. Note that the system is predicted to be metallic.

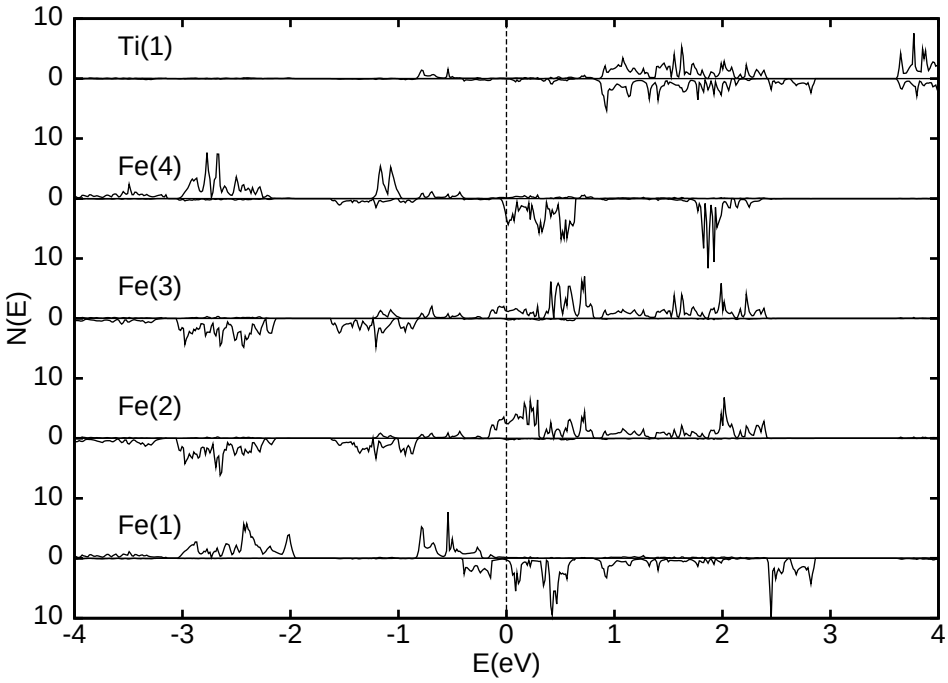

Figure 5: Densities of states for the Ti1-ion (top curves) and the Fe1-Fe4 ions (from the bottom up) in the FTFFFT supercell in spin configuration UuuDDUUDDddU.

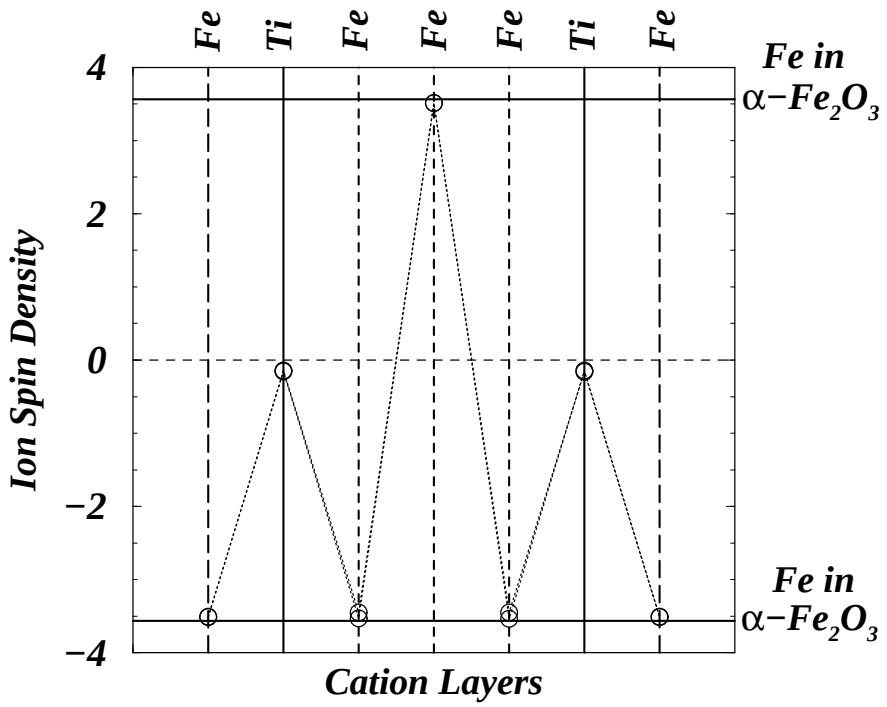

Figure 6: Dmol results for ion spin densities in the FTFFFT... supercell: solid horizontal lines indicate spin densities in $\alpha - Fe_2O_3$; solid vertical lines indicate Ti-layers.