Transition Metal Oxides for Spintronics:

Calculated Electronic Structures

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CrO$_2$ has the Rutile Structure
(cubic with 2 formula units/cell)

CrO$_2$ may be an important spintronic material. It is the only material demonstrated to have near 100% spin polarization at surface.
CrO$_2$ is a Ferromagnet and a half-metal.

- Calculated Moment: $2\mu B$/Cr
- CrO$_2$ has been prepared as an epitaxial film by CVD and LPE on TiO$_2$ (100).
- It appears to have a half-metallic (100) surface as well as bulk.
TiO$_2$ is a non-magnetic insulator that also occurs in the Rutile structure.

CrO$_2$ has been grown epitaxially on TiO$_2$, but apparently not vice versa. Simple theory would predict an infinite Tunneling Magnetoresistance for a CrO$_2$-TiO$_2$-CrO$_2$ sandwich. Calculations use density functional theory in GGA approximation and underestimate the band gap.
Solid Solutions of Ilmenite (FeTiO$_3$) and $\alpha$-Hematite (Fe$_2$O$_3$) are also possible spintronic materials. They appear to be ferrimagnetic semiconductors.

- Hematite has corundum structure.
- Replacing alternate layers of Fe atoms by Ti yields Ilmenite.
- Continuous solid solutions of composition: $(1-x)$(FeTiO$_3$)$\cdot x$ (Fe$_2$O$_3$) can be grown.
- Disorder on cation lattice affects magnetic and electrical properties.
Magnetic Structure of $\alpha$-Hematite

- Below ~260K the moments are aligned along the (111) direction. Alternate layers are aligned in opposite directions.
- Above ~260K the moments are in the (111) planes.
- Symmetry does not require moments a and b to be anti-parallel in presence of spin-orbit coupling.
- Slight canting leads to ~0.002 $\mu_B$/molecule (in plane).
- First-principles calculations yield ferromagnetic planes coupled antiferromagnetically in agreement with experiment.
- Calculations yield correct (T=0) anisotropy and a magnetic moment of approximately 4$\mu_B$.

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First-Principles LSDA calculations predict that $\alpha$-Hematite is an anti-ferromagnetic insulator. The majority DOS for an Fe atom equals minority DOS for Fe atom on neighboring layer. Calculated moment is $\sim 4\mu_B$/Fe.
Electronic and Magnetic Structure of Fe$_3$TiO$_6$

Total Moment: 3.95$\mu_B$

Transport in Fe$_3$TiO$_6$ is predicted to be strongly spin-dependent.
Ilmenite-Hematite Solid Solutions from supercell calculations

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Integrated DOS for Fe_{11}TiO_{18}

Ti impurity adds $4\mu_B$ and 1 electron.
The calculated maximum net moment of $4\mu_B/Ti$ agrees qualitatively with experiment for ordered ilmenite-hematite solid solutions.

Bozorth et al. 1957
Where does the extra electron reside?

- "carrier" is polarized oppositely to the net moment
- "carrier" is relatively delocalized residing on neighboring cation layers
- Fe$^{+2}$ resides on cation layers not occupied by Ti even though in-plane Fe neighbors are closer
Impurities in $\alpha$-Fe$_2$O$_3$. The following elements were substituted for Fe in a 30-atom Fe$_2$O$_3$ supercell.

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Note that number of majority electrons is constant for substitutions to the left of Fe and number of minority electrons remains constant for impurities to right of Fe.
Summary

• TiO$_2$ and CrO$_2$ crystalize in rutile structure and seem to offer opportunity for large TMR.
• The ilmenite-hematite, (1-x)FeTiO$_3$•xFe$_2$O$_3$, solid solution system is part of a very large family that will offer the opportunity for modification of properties by substitution.
• Electronic structure calculations predict moment of 4µ$_B$ and 1 n-type carrier per Ti substituted for Fe in Fe$_2$O$_3$.
• Calculated structural and magnetic properties seem to agree well with experiment.
• Details of electronic structure (e.g. band gaps) and transport properties may be affected by dynamic correlation effects that are not treated accurately by Density Functional Theory.