Examples of real systems: Ferrimagnetism in Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$


- Fe$_{0.5}$Cu$_{0.5}$Cr$_2$S$_4$ is a ferrimagnetic metal that displays giant magnetoresistance – when a magnetic field is switched on, the electrical resistivity decreases significantly (many tens of a percent).
- What are the principle magnetic interactions – studied using Mössbauer spectroscopy, neutron diffraction and density functional electronic structure calculations.

- The compound is a spinel:

![Diagram of the spinel structure](image)

The atoms Cu, Fe and Cr occupy the various tetrahedral and octahedral sites in the crystal structure. How are they distributed? What are their oxidation states?

- Mössbauer spectroscopy confirmed the oxidation state of Fe was III and that the Fe was tetrahedral:

![Mössbauer spectrum](image)

Note the changes in the nature of the Mössbauer spectrum at different temperatures, due to the changing internal fields in the magnetic system.
• The neutron structure refinement at 400 K (when the system is paramagnetic) also suggested that the octahedral site is purely Cr while Cu and Fe are tetrahedral. The Cu was found to be non-magnetic so we assign to Cu, the oxidation state of I \( (d^{10}) \). Note that in neutron diffraction, the relative scattering lengths of Fe, Cu and Cr are respectively 0.95, 0.76 and 0.352:

The neutron diffraction pattern also shows the emergence of a low angle line as the sample is cooled. This is due to the onset of collective magnetism. Analysis of the low-T patterns suggested that Cr and Fe spins are aligned in a ferrimagnetic manner (actually, the Fe spins are canted in addition).
Density functional calculations of the magnetic/electronic structure using the LMTO method, and the neutron crystal structure as an input supported the picture of Cu(I) and Fe(III) and Cr(III). The DOS are shown:
The neutron moments (circles) and the calculated moments (squares) match quite nicely on both sites:

![Graph showing neutron moments and calculated moments for Fe and Cr](image-url)