Materials 218/UCSB: Class XIII: Some more cooperative magnetism

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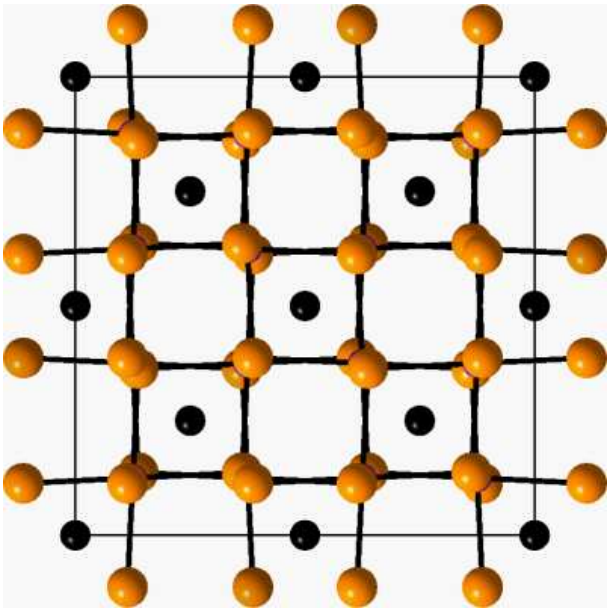
Examples of real systems: Ferrimagnetism in $Fe_{0.5}Cu_{0.5}Cr_2S_4$

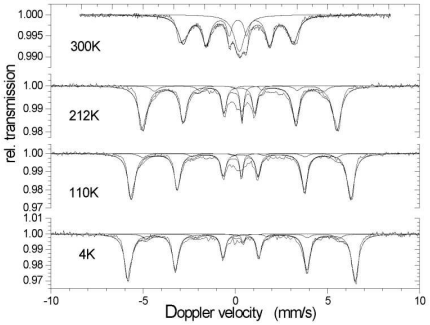
From: O. Lang, C. Felser, R. Seshadri, F. Renz, J.-M. Kiat, J. Ensling, P. Gütlich and W. Tremel, Magnetic and Electronic Structure of the CMR Chalcospinel $Fe_{0.5}Cu_{0.5}Cr_2S_4$, *Adv. Mater.* **12** (2000) 65.

- $Fe_{0.5}Cu_{0.5}Cr_2S_4$ 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:



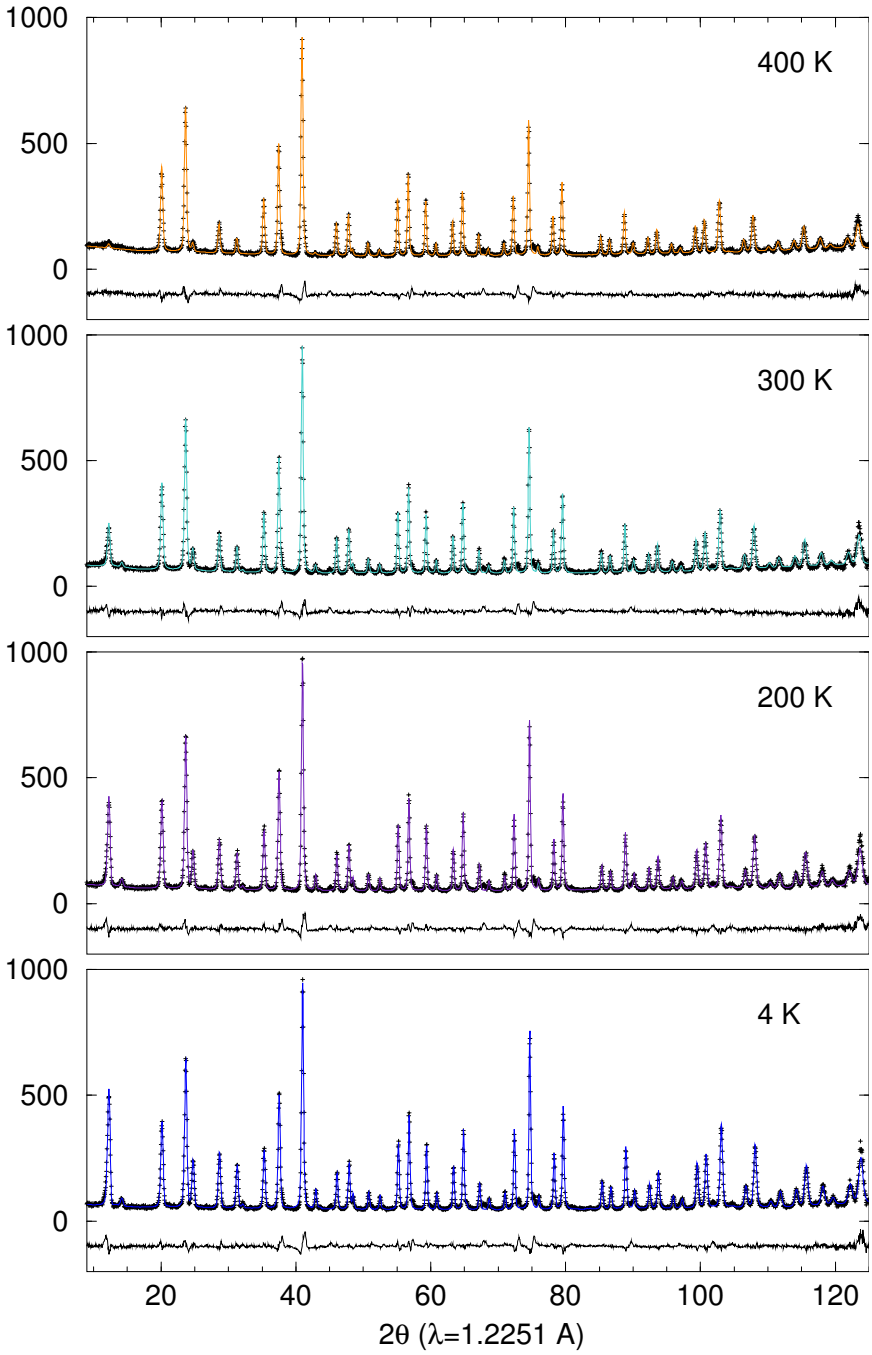
The atoms Cu, Fe and Cr occupy the various tetrahedral and octahedral sites in the crystal structure. How are they distributed ? What are their oxidation states ?

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



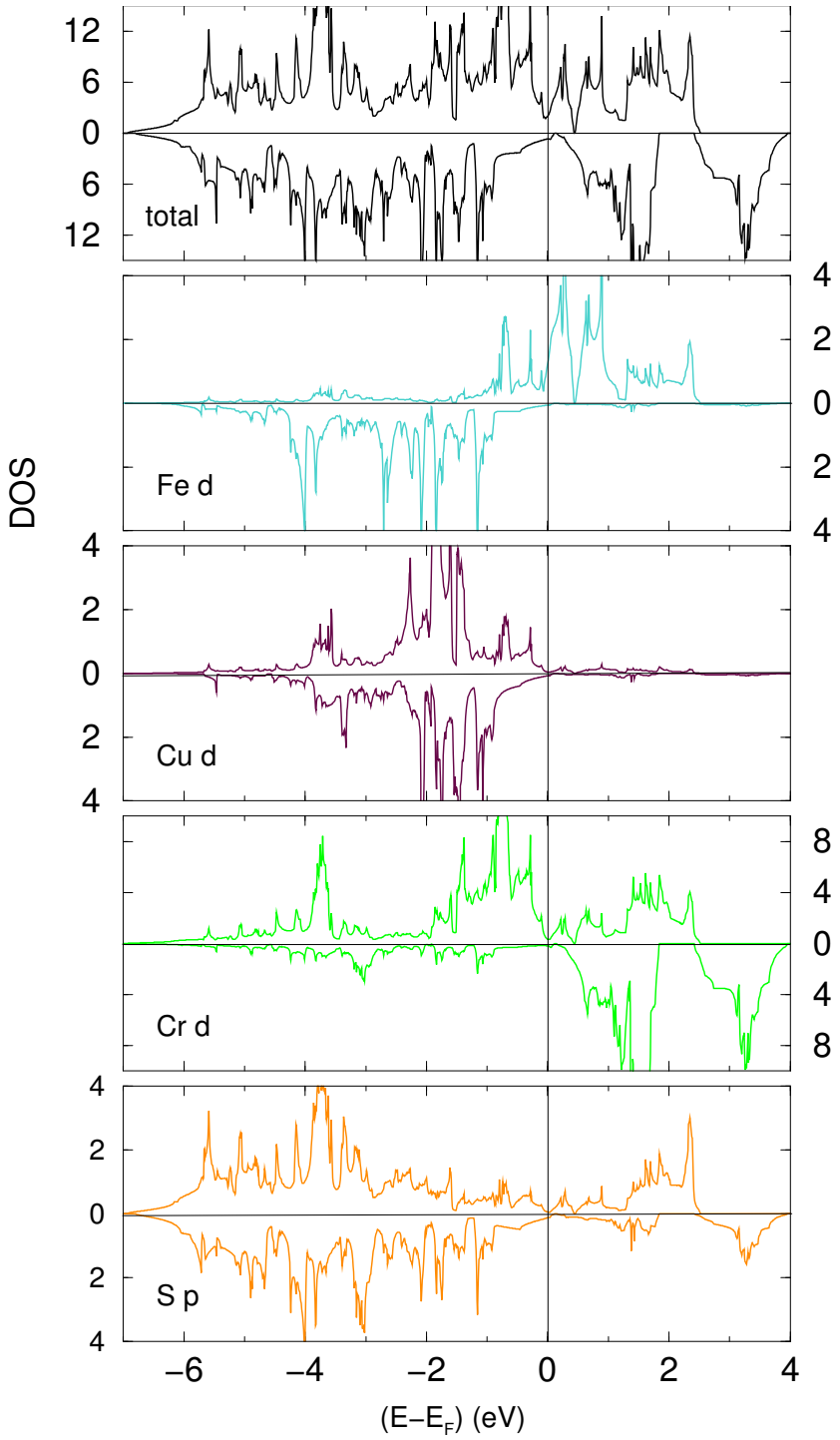
Note the changes in the nature of the Mößbauer spectrum at different temperatures, due to the changing internal fields in the magnetic system.

- 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: