Materials 218/Chemistry 277: Cooperative magnetism in solids — examples of perovskites and spinels

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Coperative magnetism: Phenomenology, Curie paramagnetism and Curie-Weiss paramagnetism, the internal field:

- In a normal paramagnet, all the spins are non-interacting. At any finite temperature, there is a tendency for the spins to misalign, even in the presence of a magnetic field. Only at 0 K do the spins all line up in the presence of a magnetic field, and the magnetic *susceptibility* $\chi = M/H$ *diverges*. M is the magnetization, the number of magnetic dipoles formed per unit volume of sample, and H is the magnetic field. Divergence of the susceptibility arises when even an infinitessimally small field aligns all the spins. The system obeys the Curie law, and is called a Curie paramagnet, with:

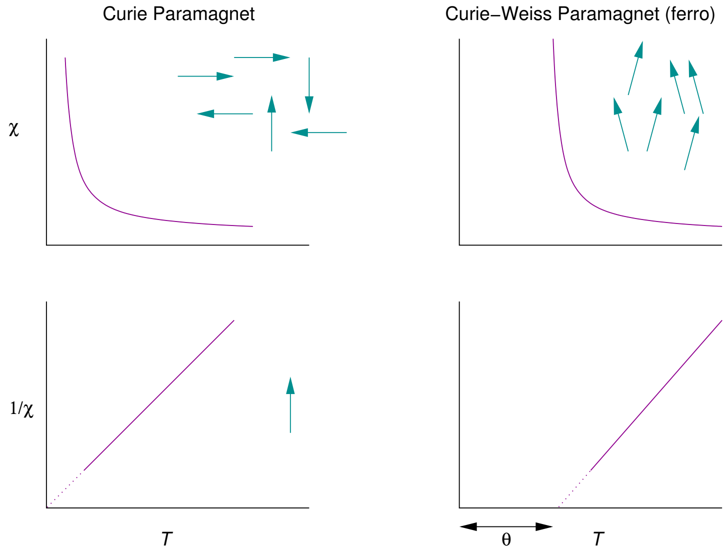
  $$\chi = \frac{C}{T}$$

  The Curie constant C is indicative of the number of magnetic spins per atom. Good examples of paramagnets are those containing magnetic ions in insulating solids[1] where the ions are far from one another. An example is the alum, $(NH_4)Cr(SO_4)_2{\cdot}12H_2O$, where the large number of water molecules in the crystal help isolate the magnetic Cr^{3+} ions.

  Ferromagnetic interactions between spins arise as a result of an internal field (the Weiss field). A system that is normally a paramagnet with ferromagnetic interactions, displays, as a result of the internal field, Curie-Weiss behavior in the paramagnetic regime:

  $$\chi = \frac{C}{(T - \theta)}$$

  As a result of the internal field tending to align the spins, the susceptibility diverges even at finite temperatures. The temperature at which the divergence occurs is called the Weiss constant θ and it is often (but not necessarily) the Curie temperature T_C for the paramagnetic to ferromagnetic phase transition.



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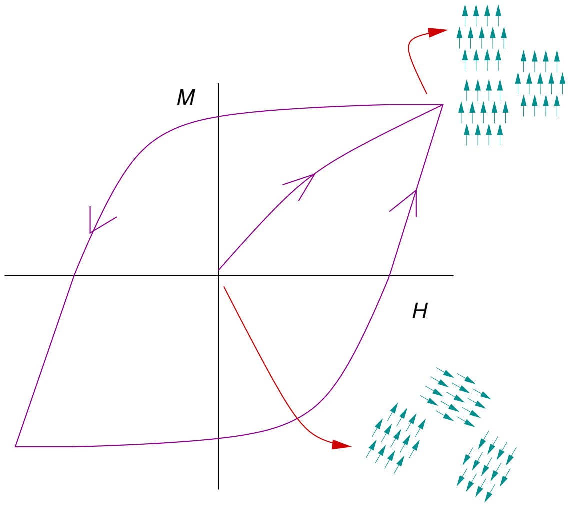
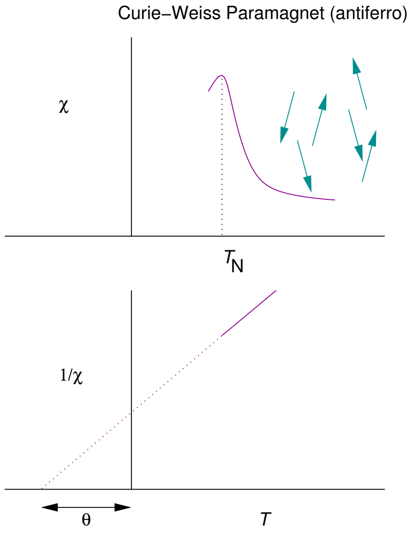
[1] In metallic solids, spins can communicate with one-another over long distances through the mediation of conduction electrons

Systems showing such Curie-Weiss behavior in the magnetic susceptibility are typical ferromagnets such as Fe, Co, Ni, CrO_2, CoS_2 *etc.*

In materials that are ferromagnetic, magnetic domains, which are regions of aligned spins, tend to form below the Curie temperature T_C. The domains themselves need not be all aligned. The application of an external magnetic field however, tends to ensure that the net spin of each domain is aligned with the magnetic field. One of the indicators of the presence of magnetic domains is the characteristic hysteresis loop of ferromagnets.



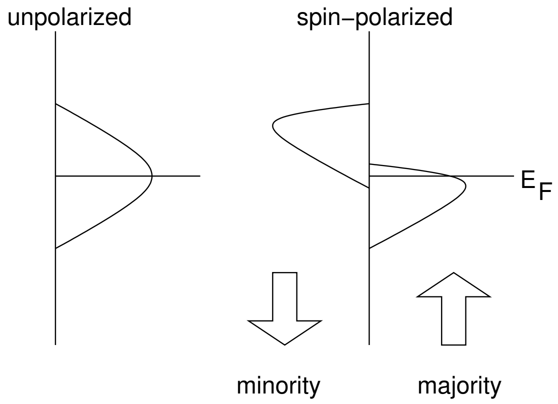
- In some systems, the internal field tends to antiallign spins. These systems are antiferromagnets. The Curie-Weiss plot is shifted so that θ is negative. In other words, even at 0 K, the spins cannot be lined up by applying a magnetic field. Only at some fictitious negative temperature will the spins all line up.



The intercept of the $1/\chi$ trace with the temperature axis is at some $\theta < 0$. In a well-behaved antiferromagnet, the phase transition from a paramagnet to an antiferromagnet takes place at the Néel temperature T_N and $T_N = -\theta$. Examples of antiferromagnets are Cr, Mn, Cr_2O_3, CoO, α-Fe_2O_3 . . .

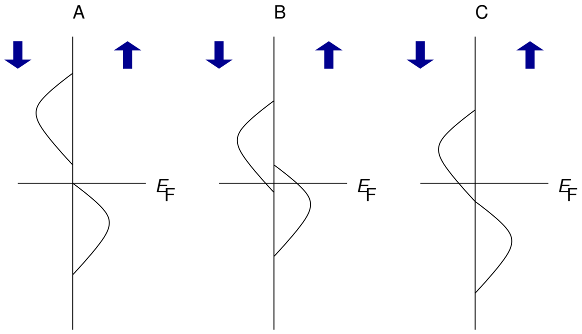
The origins of cooperative magnetism:

- Valence d and f orbitals are more contracted than valence s and p orbitals. As a result, systems with d of f valence electrons are often magnetic. Please see the handout. Also, please read a book like Kittel, if you wish to learn more.
- In a magnetic d electron compound, spin-polarization splits the densities of state:



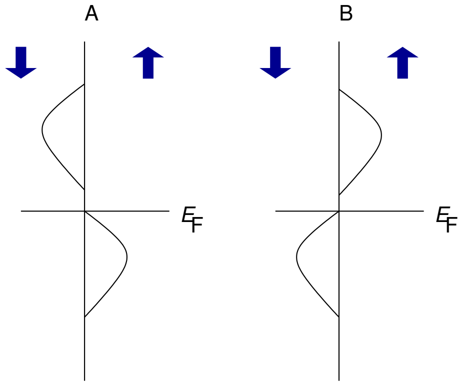
The states are usually called spin-up (↑) and spin down (↓), or alternately majority and minority. "Up" and "down" are not be thought of as actual directions in which the spins point.

- In a ferromagnet, all the spins on the magnetic (d) ions point in the same direction. On the d ion site, the DOS might look like:

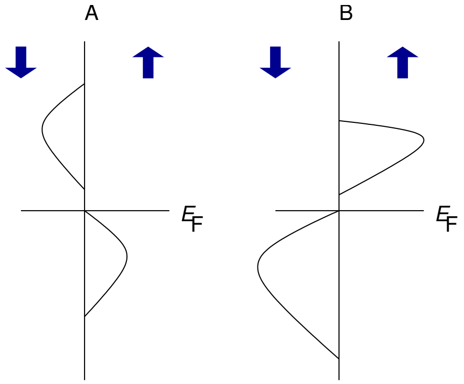


The figure shows the partial d-electron DOS of magnetic atoms in ferromagnets. **A** is a ferromagnetic insulator. These are quite rare. An example is the spinel $CdCr_2Se_4$. **B** is a typical ferromagnetic metal such as Fe. **C** is a ferromagnetic half-metal such as the pyrite compound CoS_2.

- Antiferromagnetic compounds have two identical magnetic atoms **A** and **B** distinguished by the sense of the spin. The partial *d* DOS on one of the atoms cancels (in the sense of spin) the partial *d* DOS on the other atom. In the scheme below are the **A** and **B** site *d* partial DOS in an insulating antiferromagnet.



- A ferrimagnet (example, the spinel $CoFe_2O_4$) is like an antiferromagnet, except the two sites **A** and **B** are both chemically and magnetically distinct. In the spinel $CoFe_2O_4$, **A** could represent the *d* DOS of the Co atoms and **A** could represent the *d* DOS of the Fe atoms.



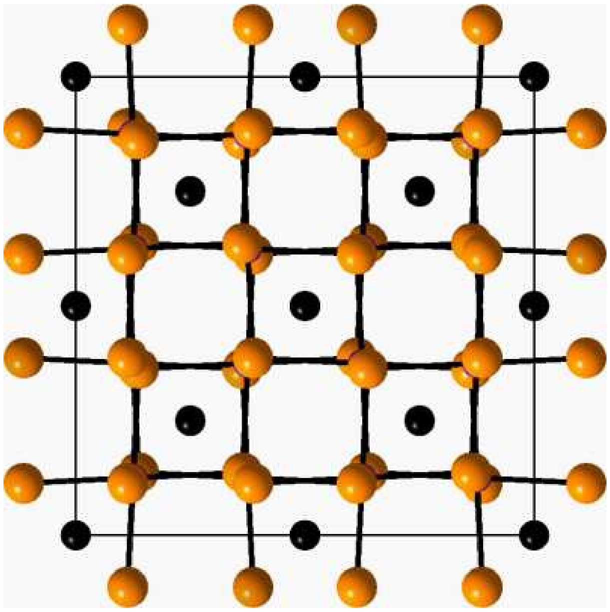
Examples of real systems: Ferrimagnetism in $Fe_{0.5}Cu_{0.5}Cr_2S_4$

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).

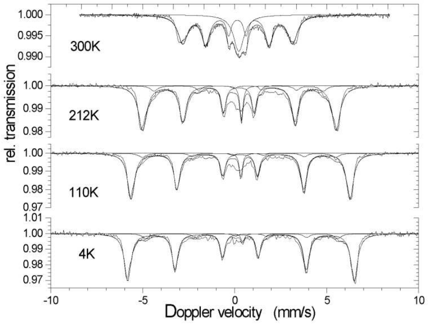
- What are the principle magnetic interactions – studied using Mössbauer spectroscopy, neutron diffraction and density functional electronic structure calculations.

- The compound is a spinel:



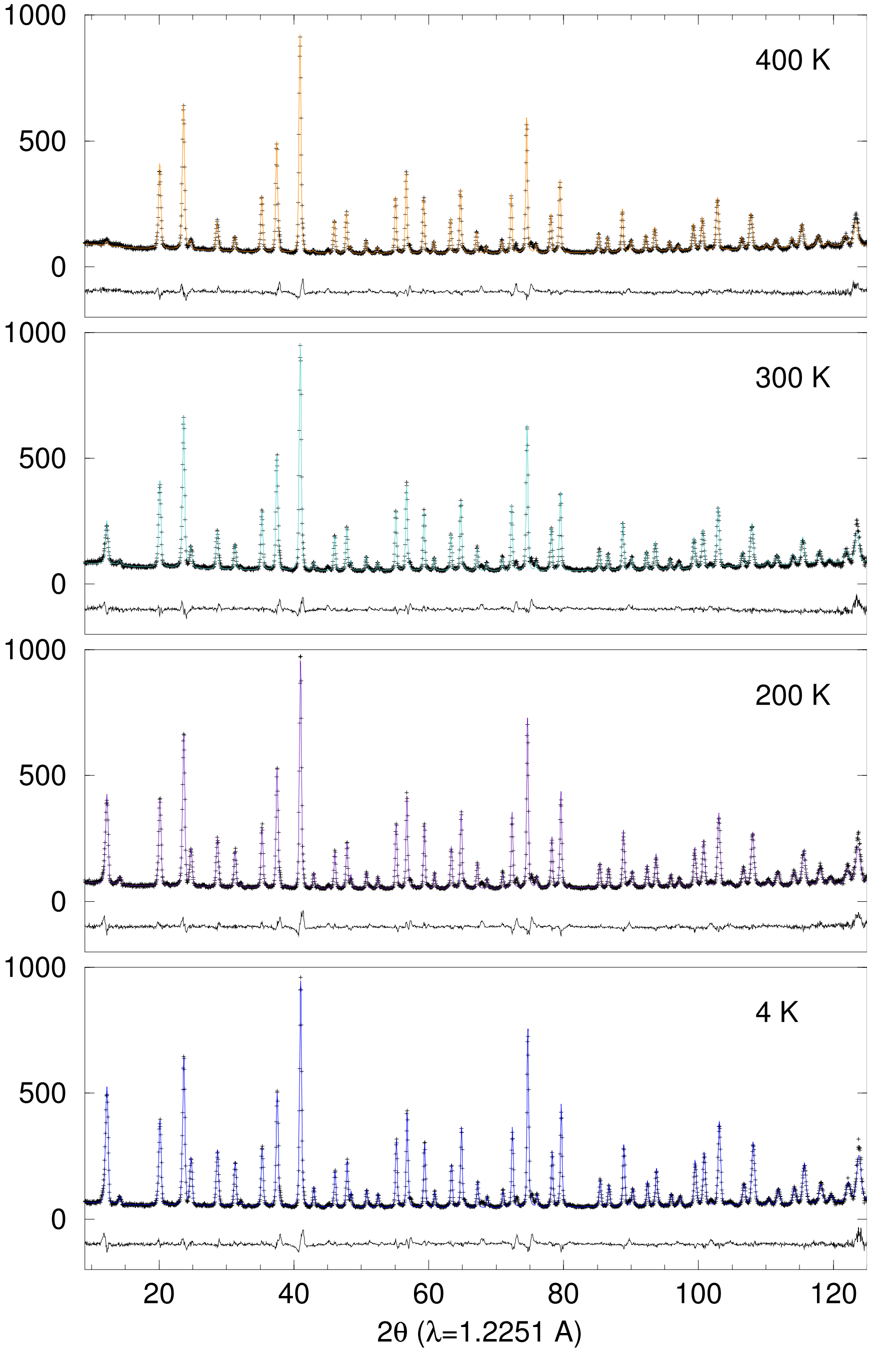
The atoms Cu, Fe and Cr occupy the various tetrahedral and octahedral sites in the crystal structure. How are they distributed ? What are their oxidation states ?

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



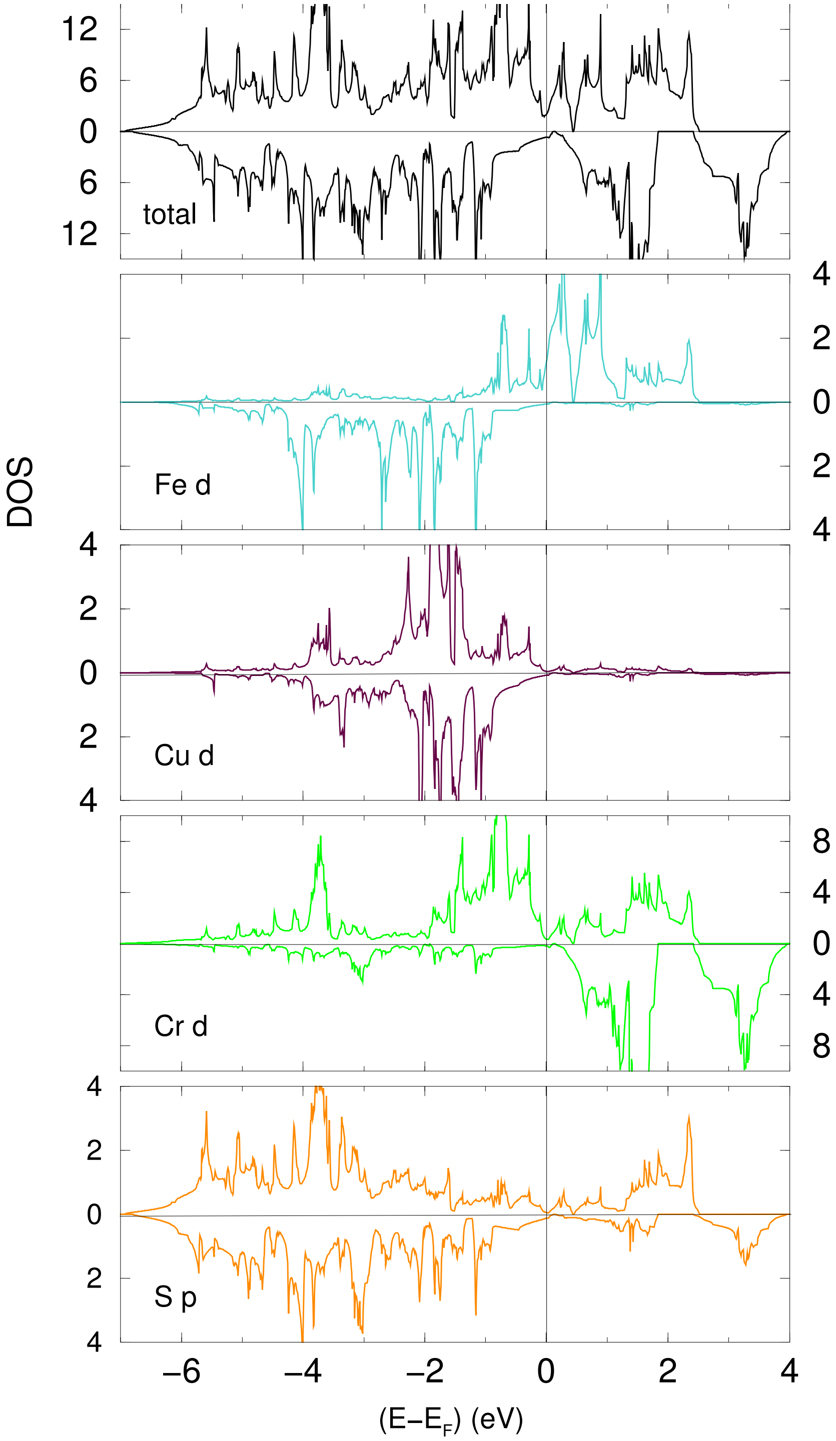
Note the changes in the nature of the Mößbauer spectrum at different temperatures, due to the changing internal fields in the magnetic system.

- 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: