ESM2009

Magnetism of free eelctrons

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There are two simplified, limiting models of magnetism. One is the model of localized electrons, where the electrons are localized in a shell on the atomic site. There may be strong coulomb correlations among them which are responsible for Hund's first two rules. The 3*d* ions can be regarded as spin-only ions, for which S is the good quantum number, whereas the magnetic moment and angular momentum of the 4*f* ions are given by J. The 3*d* electrons may be significantly hybridized their their neighbours (ligand field interaction) without losing the localised character of the magnetism, which is described by an occupation of magnetically-split energy levels given by Boltzmann statistics. This leads to the Brillouin treatment of Curie-law paramagnetism,

$$\chi = n\mu_0\mu_B^2/k_BT$$

varying as 1/T, and molecular-field theory in its localized form. All the ions have the same $3d^n$ configuration, and there are no charge fluctuations.

At the other extreme is the magnetism of metals, which was first considered by Stoner in the context of the free-electron gas. In an applied magnetic field, there is a tiny splitting of the chemical potential of ↑ and ↓ electrons (1.5 K per tesla), which creates an imbalance in the two populations, and gives rise to Pauli paramagnetism,

$$\chi_P = 2\mu_0\mu_B^2\mathcal{D}_{\uparrow,\downarrow}(\varepsilon_F)$$

which is two orders of magnitude smaller than Curie paramagnetism at room temperature, and is temperature-independent. Here $\mathcal{D}_{\uparrow,\downarrow}$ is the density of states, for one spin, at the Fermi level. There is another temperature-independent term in the susceptibility, the Landau diamagnetism, which is one third as large.

Another quantity which depends only on the density of states at the Fermi level is the Sommerfeld coefficient γ of the electronic specific heat.

$$\gamma = (\pi^2/3)k_B{}^2\,2\mathcal{D}_{\uparrow,\downarrow}(\varepsilon_F)$$

The ratio χ_P/γ should be a constant *R*, independent of material, if the model were correct. It works for monovalent alkalai metals, where there is a half-filled *s* band with weak electronic correlations. This means that instantaneously the configurations s^0, $s^{1\uparrow}$, $s^{1\downarrow}$, and s^2 are all equally likely.

Coulomb correlations among the electrons make the unoccupied and doubly occupied configurations less probable, thereby enhancing the Pauli susceptiblity. The ratio χ_P/γ becomes greater as the correlations become stronger, reaching about 10*R* in the case of palladium, a metal which is on the verge of ferromagnetism.

The coulomb correlations lead eventually to Stoner ferromagnetism in a *d* band, with degenerate orbitals, and to the Mott transition when there is no place for the costly polar states within the band of allowed energies (bandwidth). It is hardly an exaggeration to say that everything that is interesting in solid-state physics is a result of electronic correlations.

The onset of Stoner ferromagnetism can be described by molecular field theory, in the spirit of Weiss. However, the molecular field has to produce a splitting equal to the occupied bandwidth, which is several thousands of degrees. T_C is never that high! * What happens is that the correlations persist within an atom above T_C, as if there were a localised, but disordered moment.

* An exception may be the spin-split impurity band, which could account for d^0 ferromagnetism