Ferromagnetism in magnetic 4f-systems

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Abstract. In magnetic 4f-systems electronic and magnetic properties are carried by two different electron groups. They are ferromagnetic insulators and semiconductors respectively and have become important recently due to their applications in spintronics. For their realistic theoretical description the sf-model is used that contains the electron-magnon interaction in the form of an intraatomic exchange coupling between the itinerant conduction and the localized 4f-electrons. The sf-model is solved exactly in the zero bandwidth limit; it turns out that finite band occupations n reduce the saturation magnetization so that $m\ (T=0, n\ \neq 0) \leq S$. Furthermore, the Curie temperature T_C depends on band occupation n which is experimentally modeled by doping with suitable impurities. The theoretical calculations are shown to reasonably agree with experimental results.

1. Introduction

Magnetic 4f-systems are compounds containing rare earth atoms and their magnetic properties are due to only partially filled 4f-shells. The incompletely filled 4f-shell is responsible for a permanent magnetic moment that is strictly localized at the lattice site as 4f-wavefunctions of adjacent ions practically do not overlap. However, the two outer 6s-electrons become quasi-free conduction electrons that in metallic 4f-systems move through the entire lattice. An indirect exchange interaction (RKKY interaction) then causes the permanent magnetic moments to align spontaneously below a critical temperature; magnetic 4f-systems are therefore ferromagnetic or antiferromagnetic. Prototypes are the EuX, $X = O, S, Se, Te$ which are insulators or semiconductors respectively and the metallic Gd.

As electronic and magnetic properties of magnetic 4f-systems are caused by two different electron groups several interesting mutual effects are observed. On the one hand, the magnetic moment system is sensitive to changes to the conduction electron density. One consequence of this is that the saturation magnetization $m\ (T=0, n\ \neq 0) \leq S$. Here S denotes the spin quantum number of the partially filled $4f$-shell. In the case of Eu^{2+}-ions this quantum number is according to Hund's rules $S = {}^7/_2$. On the other hand, the Curie temperature T_C increases with increasing band occupation n and critical temperatures close to room temperature have been observed e.g. in magnetic semiconductors of the type $(Ga, Mn)As$ and in iron based superconductors [1,2]. Here a few percent of the Ga-atoms are replaced by magnetic Mn-ions and the effective coupling between the magnetic moments is similar to that observed in magnetic 4f-systems. This makes such specimen promising examples for the development of spintronic devices. Furthermore, due to the statistical distribution of the Mn-ions interesting phenomena are observed, e.g. spin glass and Kondo behavior, magnetic moment quenching, and a possible coexistence between magnetic order and intermediate valence states [3]. As the temperature dependence of the spin dependent density of states $\rho_\sigma\ (E)$ is in turn influenced by the magnetization of the 4f-moments drastic conduction band deformations and band splittings have been reported [4].

Magnetic 4f-systems are theoretically described by alternatively the Anderson model [5], a hybridized Kondo lattice model [6], or the sf-model [7]. It is shown in various references (see e.g. reference [8]) that the sf-model describes the coupling between the itinerant conduction electrons and the localized $4f$-moments and especially spin exchange processes between the two subsystems in a particularly realistic manner. The detailed understanding of these exchange interactions has recently gained renewed interest in connection with molecular magnetic materials [9]. Even though the sf-model defines a non-trivial many body problem, it can be solved rigorously in certain limiting cases. This provides for a further advantage of the sf-model as the accuracy of approximate solutions can be tested in these limiting cases.
The sf-model is introduced in the following section. In Section 3 both exact and approximate solutions to the many body problem are discussed. Numerical evaluations and corresponding results are presented in Section 4. The paper concludes with a short summary.

2. The Model

The sf-model describes the mutual effects between the two different electron groups in magnetic 4f-systems and is defined by the Hamiltonian

$$H = H_s + H_f + H_{sf}$$

$$H_s = \sum_{ij\sigma} T_{ij}\, c_{i\sigma}^{+}\, c_{j\sigma} + \frac{1}{2}\, U \sum_{i\sigma} n_{i\sigma}\, n_{i-\sigma} \tag{1}$$

Here $c_{i\sigma}^{+}$ denotes the creation operator for a σ-electron at lattice site R_i, $c_{i\sigma}$ is the corresponding annihilation operator. The operator for the occupation number is then

$$n_{i\sigma} = c_{i\sigma}^{+}\, c_{i\sigma}$$

H_s describes the system of itinerant conduction electrons that are treated as s-electrons and has the well known form of the Hubbard model. Note that the Coulomb interaction is only considered in its simplified intraatomic version, i.e. it only acts if there are two electrons with opposite spin present in the same Wigner-Seitz cell. U is the corresponding Coulomb matrix element: T_{ij} are the hopping integrals. The subsystem of localized magnetic moments is described in a realistic manner by the Heisenberg model

$$H_f = -\sum_{ij} J_{ij}\, S_i \cdot S_j \tag{2}$$

The spins at R_i and R_j interact via the exchange integrals J_{ij}. The two subsystems are coupled by an sf-exchange, i.e. a local interaction between the 4f-spin S_i and the conduction electron spin σ_i

$$H_{sf} = -g \sum_i \sigma_i \cdot S_i = -\frac{1}{2}\, g \sum_{i\sigma} (z_\sigma\, S_i^z\, n_{i\sigma} + S_i^\sigma\, c_{i-\sigma}^{+}\, c_{i\sigma}) \tag{3}$$

H_{sf} is an effective operator that simulates the electron-magnon interaction that is responsible for a spontaneous magnetization in magnetic 4f-systems; g is the intraatomic sf-exchange constant. A realistic parameter value for magnetic $4f$-systems would be $g = 0.2\ eV$ [8]. Note that the ratio g/W describes the relative strength of the sf-coupling with $g/W \rightarrow 1$ representing the strong and the limit $g/W \rightarrow 0$ the weak coupling limit.
The Hamiltonian of Eq (1) describes a non-trivial many body problem that is generally not exactly solvable. However, there are a couple of interesting exactly solvable limiting cases that are discussed in Section 3.

3. Exact and approximate solutions

The sf-model is rigidly solved in the zero bandwidth limit [10] and the case ($T = 0, n = 0$) describing one electron in an otherwise empty conduction band [11]. In the zero bandwidth limit the Bloch band degenerates to a single level T_0 that due to the sf-exchange interaction splits into four quasiparticle energies

$$E_1 = T_0 - g\,S$$
$$E_2 = T_0 + g\,(S+1)$$
$$E_3 = T_0 + U - g\,(S+1)$$
$$E_4 = T_0 + U + g\,S$$

with temperature and particle number dependent spectral weights $\alpha_{i\sigma}\,(T.n)$ describing the degeneracy of the energy levels E_i. For the general case of finite bandwidths W an alloy analogy may be applied where the alloy consists of four components E_m, $m = 1, \ldots..4$ with concentrations $c_m = \alpha_{m\sigma}\,(T,n)$ statistically distributed over the entire lattice. This leads to a many body problem that can be solved approximately but selfconsistently within the coherent potential approximation CPA [12]. The CPA calculates an ensemble average where the selfenergy

$$\Sigma_{k\sigma}\,(E,k) = \Sigma_{k\sigma}\,(E) \tag{4}$$

becomes wavevector independent. Within the CPA the one particle Green function

$$G_{k\sigma}\,(E) = \frac{\hbar}{E - \varepsilon\,(k) + \mu - \Sigma_{k\sigma}\,(E)} \tag{5}$$

has the typical form of an interacting electron system where the selfenergy represents many particle correlations not contained in a one particle theory. The quasiparticle density of states

$$\rho_\sigma\,(E) = -\frac{1}{\pi}\;\Im \int_{-\infty}^{+\infty} dx\;\frac{\rho_0\,(x)}{E - x - \Sigma_\sigma\,(E)} \tag{6}$$

is in turn calculated from an integral over the free Bloch density of states. Applying Eq (6) to magnetic 4f-systems yields quasiparticle density of states that are considerably deformed and split compared to the free Bloch band. This is discussed further in the next section.

4. Results

We first want to discuss metallic 4f-systems and therefore evaluate Eq (6) as a function of temperature at fixed band occupation n. For the Bloch density $\rho_0\,(E)$ a simple model version from the tight binding approximation [13] is used. The temperature dependence mainly results from the 4f-magnetization m that is regarded as a parameter and varies from near saturation at $T = 0\ K$ to $m\ (T = T_C\,) = 0$ according to the usual Brillouin function behavior. The calculation is done to roughly model Gd with $T_C = 238\ K$. The remaining set of parameters used are typical for moderate coupling, i.e, $g = 0.2\ eV, W = 1\ eV. S = {}^{7}\!/_{2}$. The corresponding results are plotted in Figure 1 below which shows the temperature and spin dependent quasiparticle density of states $\rho_\sigma\,(E)$.

The original Bloch band is for both $\sigma = \uparrow\downarrow$ split into two quasiparticle subbands. The splitting is a consequence of the sf-interaction, i.e. many particle correlations and their effect depends on the relative coupling strength ${}^{g}\!/_{W}$. With decreasing magnetization, i.e. increasing temperature the subbands start to merge until they finally coincide at $T = T_C$. These results imply that the influence of the 4f-moments on the itinerant conduction electrons vanishes above T_C. This view is, however, challenged by the authors of reference [14] who claim that a correlation based exchange splitting between the ↑ and ↓ densities of states persists in the paramagnetic phase.

On the other hand, for ferromagnetic insulators and semiconductors, e.g. EuX the Curie temperature $T_C\,(n = 0)$ for the empty conduction band was previously calculated within the mean field approximation of the Heisenberg model [15] and corresponding results are summarized in Table 1 below.

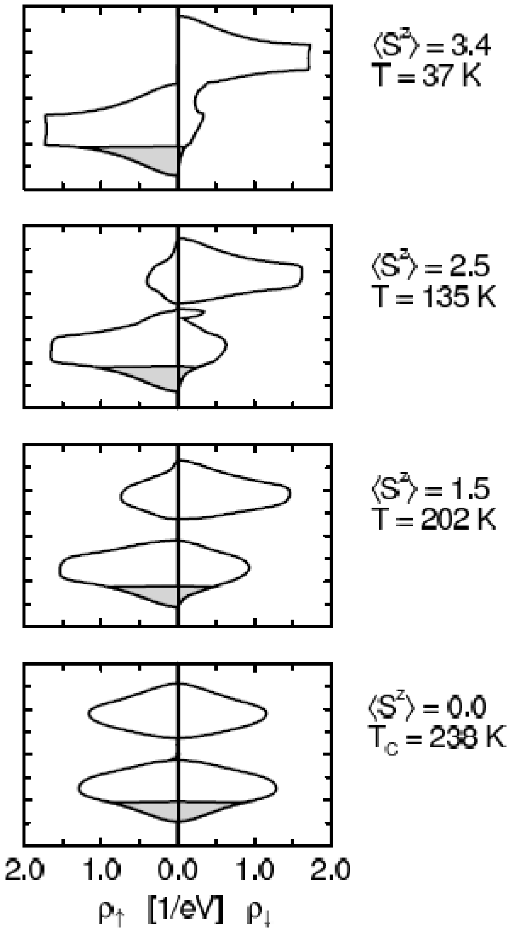

Fig 1: Quasiparticle density of states $\rho_\sigma\ (E)$ for four different values of the 4f-magnetization $m = \langle S^z \rangle$ and $\sigma = \uparrow\downarrow$.

Table 1: Experimental and theoretical values for the critical temperatures of EuX according to ref [15].

X	Exp value for critical temperature	Theoretical value for critical temperature	Type of magnetization
O	66.8 K	86.6 K	ferromagnetic
S	16.6 K	21.5 K	ferromagnetic
Se	4.6 K	$-$ 4.0 K	metamagnetic
Te	9.6 K	8.5 K	antiferromagnetic

While the calculated values from the MFA are slightly enhanced the Curie temperatures $T_C\ (n = 0)$ generally come out too low, especially with regard to possible applications in electronic devices.

However, with increasing band occupation n, the Curie temperature $T_C\ (n)$ increases according to the equation

$$\frac{T_C\ (n)}{T_C\ (n=0)} = 1 + \frac{S+1-n}{S+1} \quad n^{4/3} \tag{7}$$

Equation (7) is derived from a mean field approximation where the dependence of the exchange integrals on band occupation n is due to the RKKY-interaction [16]. Corresponding numerical results are plotted in Figure 2 below.

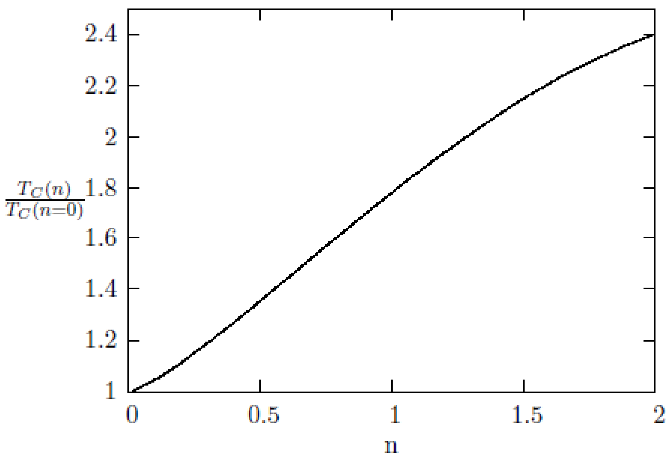

Fig 2: Curie temperature $T_C\ (n)$ from a mean field approximation of the sf-model.

With increasing band occupation n the Curie temperature T_C of the ferromagnetic 4f-system increases as the RKKY-interaction leads to an effective coupling between the permanent magnetic moments. This increase of T_C on n is experimentally modeled by doping with suitable impurities and similar results have been reported both experimentally [1,2] and theoretically [6, 17]. Furthermore, for large enough band occupations T_C is more than doubled compared to the corresponding value for the empty conduction band. The critical temperature thus becomes close to room temperature which is important regarding possible applications in spintronics. On the other hand, the saturation magnetization decreases from its $n = 0$ value $m\ (T = 0, n = 0) = S = {}^{7}/_{2}$ according to Figure 3 below.

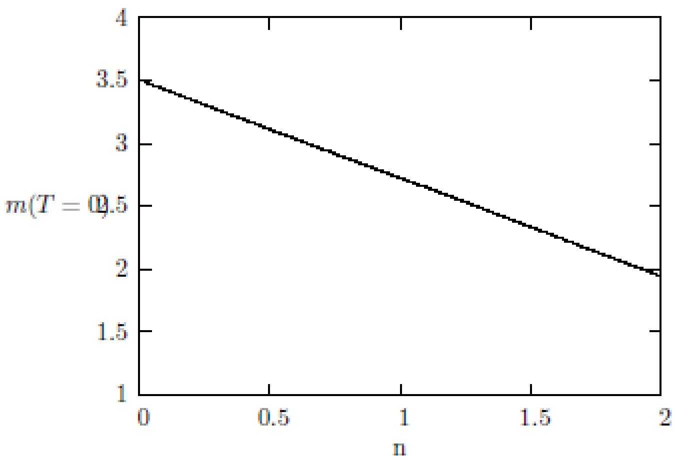

Fig 3: Saturation magnetization $m(T = 0)$ as a function of band occupation n.

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This result already follows from the exactly solvable zero bandwidth limit. A ↓-electron can even at $T = 0\,K$ exchange its spin with the then antiparallel localized 4f-spin. A bound state of the conduction electron with the spin wave is formed. The corresponding quasiparticle has an infinite lifetime and is known as the magnetic polaron [18]. The consequence of this is a saturation magnetization $m\,(T = 0, n) \leq S$ in contrast to the Heisenberg model where spin waves only occur at finite temperatures. Spin waves (magnons) are measured by neutron scattering experiments. The magnon-electron interaction on the one hand increases magnetic order, yet on the other hand contributes to the electrical resistivity of magnetic 4f-systems. The authors of reference [19] observe an increase in resistivity of $CeCuAl_3$ with temperature in the magnetically ordered phase in agreement with the theory developed in this paper.

5. Conclusions and Summary

In this paper it is shown that magnetic 4f-systems are reasonably well described within the sf-model that contains an exchange interaction between the localized 4f-spin and the itinerant conduction electron. Using an alloy analogy the spin system is solved within the coherent potential approximation CPA. As a result of correlation effects the conduction band structure becomes temperature dependent while the 4f-magnetization turns out to be sensitive to changes in the conduction electron density. The Curie temperature T_C is enhanced at finite band occupations n with T_C-values close to room temperature being obtained. This makes magnetic 4f-systems suitable for applications in spintronic devices.

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