New trends in the discussion of CMR-manganites and isostructural ferrites

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Abstract. Completing the Anderson and Hasegawa double exchange spin pair model by local spin quantization, ferrites as well as some Heusler alloys could be double exchange-supercoupling systems. This concept also adds a third interpretation to the Kondo-like resistivity anomalies found recently in FeSb₂.

1. Introduction

Recently, by adding the local spin quantization to the Anderson & Hasegawa calculation of a double exchange pair state it has been found that the first excited state to the metallic ferromagnetic double exchange (DE) ground state is an antiferromagnetic charge ordered insulating (CO) state [1]. This has two main consequences: (1) one can now view the ferrites which are isostructural to the CMR-manganites as well as the spinel-type ferrites as insulating CO systems with only the ground and first excited state changing roles [2] and (2) one can view semimetals which could have originated from a spontaneous valence decomposition as all-metallic DE-systems [3]. The latter comes about as follows: an insulating CO state can be viewed as electrons (e) and holes (h) localized periodically along the band edges (Fig. 1).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** A charge ordered lattice is molten to yield a normal semiconductor and then - following a configurational coordinate- undergoes a spontaneous valence decomposition by letting the gap value go to zero; a semimetal with equal charge carrier concentration \( n,p \) occurs, which might develop an excitonic quasi-particle gap at the Fermi-level \( E_f \) - for more details see text, for an example see CaFeO₃ under pressure [4].
Next, assuming some configurational coordinate change, the CO state could be molten, i.e. $e$ and $h$ now move into the near edge states, just like in ordinary semiconductors. In order to go over to a semimetal, one has to change the configuration again: for the occurrence of a spontaneous valence disproportion one has to let the electronic order parameter, i.e. the electronic gap, go through zero. The result is a semimetal with equal concentrations of electrons and holes $n,p$. All along the configurational changes, however, one can align the residual local spin moments either antiferromagnetically (AFM) or ferromagnetically (FM).

In this contribution we ask if this kind of DE-semimetals have unique excitations? While the doped CMR-manganites $R_{1-x}A_xMnO_3$ separate into electron and hole doped (quasiparticle-) regions, leaving the 1/2-1/2 compounds undecided, with a spontaneous valence decomposition, electrons and holes are excited simultaneously, opening the door for excitonic states, which, however, would have to be discriminated concerning their local spin array and which could also have a polaronic character because of the electron-spin-lattice subsystem coupling [5]. This yields in principle two kinds of (Frenkel-type, triangular) spin-excitons, one AFM (or spin frustrated) and the other spin parallel (Fig. 2)

![Figure 2](image.png)

**Figure 2.** Triangular FM and AFM spin-excitons are designed and taken out of a FM (a) and AFM (b,c) layered spin lattice; while both collision initiated transitions $a \rightarrow b$ and $c \rightarrow b$ are possible, the latter only involves a momentum exchange while the former involves both a momentum and energy exchange; for more details see text.

The triangular units are taken out of a FM and AFM (layer) lattice array. As in periodic lattices one has exciton bands, this taking out assumes some kind of exciton confinement. In a layer antiferromagnet, the extended exciton would at least be confined to one layer, not so for the FM exciton. As the collision probability increases with mobility, the AFM exciton should have the longer lifetime. Introducing a strain potential well, say via a foreign atom, both excitons could be localized, but the AFM one would be easier to localize, as one of the linear independent directions is already closed. Moreover, the AFM exciton has a defence mechanism against electronic charge as well as against phonon collisions: by flipping the spin at one corner, the spin state and with it the energy of the scattering center would not change, while the FM exciton would have to take up energy, i.e. the difference between the AFM and FM exciton energies [3] - under a spin-flip. So, the AFM center can exchange momentum only while the FM one can change momentum only if it takes up energy. Exciton lifetimes in metals are generally thought to be in the order of $10^{-15}$ s to $10^{-13}$ s and so usually the excitons are thought to decompose fast. If,
However, one or both spin exciton lifetimes could reach the phonon relaxation regime, $10^{-12}$ s, the (polaronic) excitons should show up in the resistivity versus temperature curves. There could even be a quasi-particle gap forming at the Fermi-level. In order to test the idea of a confinement enhanced lifetime, in what follows we have picked out three semimetallic compounds which also have random potentials, AFM or compensated spin order as well as resistivity anomalies, and FeSb$_2$.

2. Materials

If we now look for materials which might show such scattering effects, one should look for compounds which can be suspected to be valence decomposed, for example MnAs, $2x(+3) \rightarrow (+2)+(+4)$. In order to localize the exciton via (random) energy wells, we look for say, single crystals of MnAs$_{1-x}$P$_x$. Indeed, Fig. 3 shows unusual (Kondo-like) resistivity behaviour in the helical phase of the compound with $x = 0.11$, superimposed on spin disorder scattering.

![Figure 3](image-url)

**Figure 3.** La(Fe$_{1-x}$Al$_x$)$_{13}$ [6], MnAs$_{1-x}$P$_x$, ($x = 0.11$), [7] mixed crystals showing spin disorder scattering in the FM (canted, $x = 0.11$, dashed line) state and a resistivity anomaly in the AFM (helical, $x = 0.11$, 1,2 $B = 0, 0.8$ T) magnetic phase, in comparison with the resistivity anomaly observed recently in FeSb$_2$ [8].

This compound also shows a helical-canted-helical-paramagnetic magnetic phase sequence and a high spin-low spin transition in the paramagnetic range, both of which are typical for DE-superexchange (SE) mixed coupled systems. Moreover, Hall experiments [9] show that the $n = p$ condition is very closely fulfilled, bearing in mind that electrons and holes have different mobilities. The next candidate are mixed crystals based on the compound LaFe$_{13}$, i.e. La(Fe$_{1-x}$Al$_x$)$_{13}$; here, via mixing Fe and Al, we will get a distribution of magnetic couplings and this should bring about the largest static (magnetic) potential fluctuations. Indeed, these compounds show the Kondo-like behaviour even more dramatically, but again only in the spin compensated, magnetically ordered regime. Complex magnetic phase sequences are visible here only under co-doping with cobalt [10]. Recently, an even larger Kondo-like effect has been observed in single crystal FeSb$_2$ which at first sight does not contain random potentials at all. FeSb$_2$ has been described as narrow bandgap semiconductor [12] or as a Kondo-lattice insulator [11]. That compound has been tentatively identified as weak ferromagnet (canting?) with a (local?) moment.
of 1μB per Fe ion [11], so at least keeping within the possibilities of a double exchange band scenario. Note, however, that FeSb$_2$ shows a plateau between two drops, suggesting a two step process, just like the MnAs-derivate. So there are similarities between all three systems beyond the resistivity drop.

Viewing the three examples as the same or very similar phenomenon, we note that the Sommerfeld constant $\gamma$ of the MnAs-derivate $x = 0.09$ is too low for a Kondo-lattice (11.6 mJ/K$^2$mol [9]) and that the resistivity of the mixed crystals is too low for a semiconductor - about 180 $\mu$Ωcm for the LaFe$_{13}$ - derivates and $\rho_0$ of $x = 0.09$ is 33 $\mu$Ωcm - see Fig. 3, while the negative MR found in the MnAs-derivate could be linked to a H-field induced transformation of some of the AFM excitons into FM ones. Thus, there is still room for alternative ideas. In what follows we try to connect the AFM (or frustrated) excitonic states with the scattering situation in the three selected semimetals. Specifically, we present a calculation of the resistivity versus temperature curve, $\rho(T)$ to compare with experiment. Note, that while there might be a spin-flip scattering involved, we submit that the resistivity drop mainly results from the thermal/plasmonic destruction of the scattering centers on going to higher temperatures.

3. Calculation of the anomalous resistivity curve

In [2,13] a Matthiesen rule superposition of the anomalous, $\rho_\alpha$, and a phonon (or spin disorder) scattering $\rho_\phi$ with $\rho_\alpha \gg \rho_\phi$ in a $n,p$ semimetal (or semiconductor) has been assumed. In addition, a coexistence of free carriers - of initial concentration $n_0,p_0$ - and excitonic centers of number $N_{ko}$ is assumed, with the possibility of the centers to thermally decompose and thus add to the free carrier concentration:

$$n(T) = n_0 + \Delta n, p = p_0 + \Delta p$$

(1)

The decomposition was assumed to follow a chemical reaction, in particular:

$$\Delta n\Delta p = N_k^2 K$$

(2)

with $K = K_0 \exp(-\Delta E/kT)$ the reaction constant and $N_k$ the number of single excitonic scattering centers. Combining all this under the simplifications $n_0 = p_0$ and $\mu_{n0} = \mu_{p0}$, while setting aside the phonon or spin disorder contribution for a moment, yields:

$$\rho_0/\rho_k = (1/n_k + N_{ko}(K_0)^{1/2} \exp(-\Delta E/2kT)/n_0$$

(3)

where $n_k = N_k/N_{ko}$ the center density with $0 < n_k < 1$. If initially, the free carrier concentration is low against the center density, $1/n_k$ can be approximated by a cut-off constant, i.e.:

$$\rho_0/\rho_k = c + A \exp(-T_s/T)$$

for $T < T_s$, with $kT_s = \Delta E/2$ (3a)

and $A = N_{ko}(K_0)^{1/2}/n_0 \gg c$, while after the cut-off:

$$\rho_0/\rho_k = 1/n_k : T > T_s$$

(3b)

This unknown resistivity function (3b) we might obtain from the assumption that the single exciton centers surviving beyond $T_s$ undergo a decomposition process $C \rightarrow e + h$ for $T > T'_s$, i.e.

$$\Delta n\Delta p = N_k K'$$

(4)
In [13], it has been argued that this reaction is diffusion controlled - in this present contribution, we assume a reaction control. Taking $kT_s = \Delta E'$ and $\Delta n = \Delta p$ as before, for $T > T_s$ but now assuming that most of the free carriers have already been created, so that $\Delta n = (n - n_s) \approx (n^* - n_s)$, $N_k' = N_k$, $n^*$ high temperature carrier concentration, we obtain:

$$\frac{\rho_k}{\rho_s} = n_k = 2(n^* - n_s)^2 \exp(\Delta E'/k(T-T_{s^*}))/N_k K_0$$

for $T > T_{s^*}$. (5)

Note, that this approach offers an interpretation of the plateau which is found experimentally to occur between the two stages of the falling resistivity curve of MnAs0.9P0.1 and that of FeSb2 (Fig. 3). For $T_s < T < T_{s^*}$, $T_{s^*} = (T_s + T_{s^*})/2$, we then would have a transitional regime between single and double excitons, where a biexciton-exciton condensation/melting and with it critical phenomena may well occur. Actually, this plateau-like regime is the one of major interest for applications, as one can calculate the highest figure of merit for TEP cycles exactly here. For an example of the calculations see Fig. 4, where the normalization to $\rho_0$ is introduced using $\frac{\rho_k}{\rho_0} = (\rho_k/\rho_s)(\rho_s/\rho_0)$.

![Figure 4. An example of the resistivity function:](image)

For $T<T_{s^*} = \Delta E/2k$, $1/(1+9\exp(-1/t))$ with $t = T/T_{s^*}$; for $T > T_{s^*} = \Delta E'/k$, the function $0.003\exp(2/(t-1.5))$ takes over. For even higher temperatures the phonon (or spin disorder) resistivity takes over.

Unlike the mixed crystals, at first sight FeSb2 gives no indication of random potentials. With the mixed crystals, the exciton-polarons could well be itinerant or hopping between particular sites, while they should be more (exciton-) band like in FeSb2, - see also the differences along different crystal directions. As for the LaFe13 derivates one expects a distribution of exchange interactions, here one could speak of spin-frustration in a band scenario, eventually helped by SE-frustration. The helically magnetically ordered MnAs-derivates, with As, P having only an ionic size difference, should be closer to FeSb2.
4. Conclusions
In a more comprehensive view, the anomalous Kondo-like resistivity curves obtained in several mixed and pure single crystal systems, could be connected with spin transfer magnetism. Specifically, electrons and holes could, at low temperatures, build up AFM polaron-exciton Kondo-like scattering centers. Then, the resistivity drop with increasing temperature would be rather due to their thermal decomposition as to an increase of the Kondo-mobility with temperature which could be connected to the spin-flip scattering on those centers.

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