Exchange interactions

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1. POTENTIAL AND KINETIC EXCHANGE INTERACTIONS

It is well known that the direct dipole-dipole interaction between magnetic moments is much too weak to explain the typical magnitudes of spin dependent interactions between electrons. It is convenient to single out two spin exchange mechanisms accounting for the magnetic properties of solids, discussed in detail in the context of in a number of reviews, particularly in the context of diluted magnetic semiconductors [1–3].

The driving force behind the potential exchange is the Pauli exclusion principle which precludes two electrons with the same spin to appear simultaneously in the same location. Accordingly, the magnitude of the Coulomb potential energy is lower for such a pair, comparing to the case of two electrons with anti parallel spins. The potential exchange is ferromagnetic and accounts for the Hund's rule, intra-atomic *s-d* exchange interaction, and exchange interactions between spins of carriers occupying the same band.

The kinetic exchange occurs between two electrons residing at different sites. One of these electrons can visit the site occupied by the other provided that its spin has the orientation matching a relevant empty level. Such a quantum hopping, or in other words hybridisation of states, enlarges the localisation radius and, hence, lowers the electron kinetic energy. The kinetic exchange leads usually, but not always, to an antiferromagnetic interaction between the spin pair in question. In compounds containing transition metals, the *p-d* kinetic exchange couples the spins of carriers occupying anion p-like bands with the spins of electrons residing in open *d* shells of magnetic cations. Typically, in the considered TM compounds the kinetic exchange – if symmetry allowed – is much stronger than the potential exchange. The opposite situation occurs in the case of rare earth doped materials, where the *spd-f* hybridisation is usually weak.

Obviously, the way by which the above mechanisms lead to the spatial ordering of the spin polarisations depends on whether the *d* electrons remain localised on parent ions or undergo an insulator-to-metal transition and, therefore, contribute to the Fermi volume. In the former case, and in the absence of carriers, the spins of magnetic ions are coupled by the mechanism known as the superexchange. In metals or extrinsic semiconductors, where either conduction or valence *sp* bands are only partly occupied, a carrier-mediated spin-spin coupling emerges, known as the *sp-d* Zener or Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. If doping of a magnetic insulator results in the appearance of electrons in the upper or holes in the lower Hubbard band, the so-called double-exchange mechanism can operate. Finally, for sufficiently large overlap between *d* wave functions the Mott-Hubbard transition will take place, so that the Stoner mechanism of ferromagnetism in an itinerant carriers systems will dominate. We will now briefly describe these mechanisms.

II. SUPEREXCHANGE

As a result of the aforementioned *sp-d* exchange interaction, the valence band electrons will be either attracted to or repulsed by the adjacent magnetic ions, depending on the mutual orientation of the itinerant and localised spins. This results in a spatial redistribution of spin-down and spin-up valence band electrons, the total energy of the system attaining a minimum for an antiferromagnetic arrangement of neighbouring localised spins, as shown on Fig.1. This indirect *d-d* coupling is known as superexchange. Indeed, most of magnetic insulators are antiferromagnets or ferrimagnets (if ions with differing spin states co-exist), with Néel temperatures reaching 523 K in the case of NiO and Curie temperatures approaching 800 K in ferrimagnetic spinel ferrites $(Zn,Ni)Fe_2O_4$.

However, the case of europium chalcogenides (e.g., EuS) and chromium spinels (e.g., $ZnCr_2Se_4$) implies that the superexchange is not always antiferromagnetic and that ferromagnetism is not always related to the presence of free carriers, even though the Curie temperature T_C does not exceed 100 K in these compounds, despite the large magnetic ion concentration. In the case of rock-salt Eu compounds, there appears to be a competition between antiferromagnetic cation-anion-cation and ferromagnetic cation-cation superexchange [4]. The latter can be traced back to the ferromagnetic *s-f* coupling, and the presence of *s-f* hybridisation, which is actually stronger than the *p-f* hybridisation due to symmetry reasons [1,4]. In such a situation, the lowering of the conduction band associated with the ferromagnetic order enhances the energy gain due to hybridisation. The Cr-spinels represents the case, in which the *d* orbitals of the two cations are not coupled to the same *p* orbital, resulting – in agreement with the Goodenough-Kanamori rules – in a net ferromagnetic superexchange.
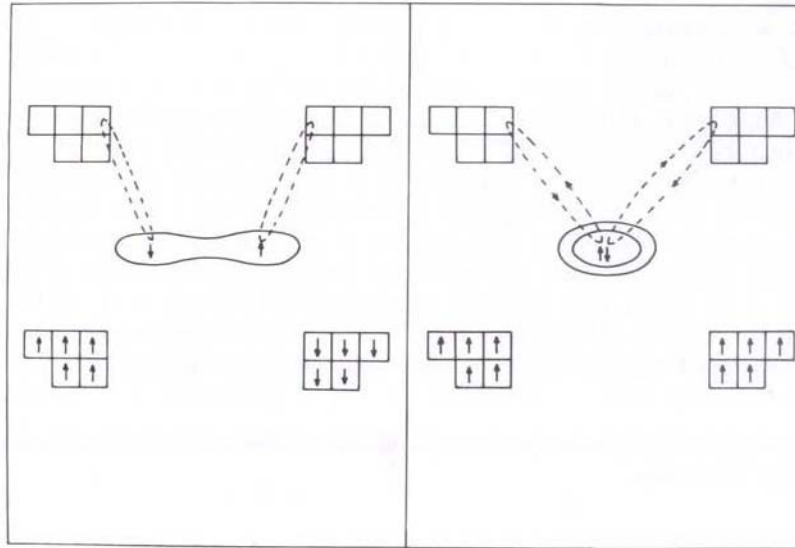

FIG. 1: Schematic illustration of the antiferromagnetic superexchange between localised Mn spins mediated by entirely occupied anion orbitals. The spin-dependent shift of anion orbitals, sizable for the antiferromagnetic arrangement of neighbouring Mn spins, enhances the lowering of the system energy associated with the *p-d* hybridisation.

IV. *sp-d* ZENER/RKKY MODELS

When an *sp* band is partly filled by carriers but the electrons in the open magnetic shells

remain localised, the sp-d interaction causes the appearance of spin-polarised carrier clouds around each localised spin. Since the spins of all carriers can assume the same direction if the band is only partly filled, a ferromagnetic ordering can emerge, as noted by Zener in the 1950s in the context of magnetic metals. This ordering can be considered as driven by the lowering of the carriers' energy associated with their redistribution between spin subbands that are split apart in energy by the sp-d exchange interaction with localised spins, as shown schematically in Fig. 2 for the case of a p-type DMS. Typically, the intra-band potential exchange enhances the magnitude of the resulting T_C.

A more detailed quantum treatment indicates, however, that the sign of the carrier-mediated interaction between localised spin oscillates with their distance according to the
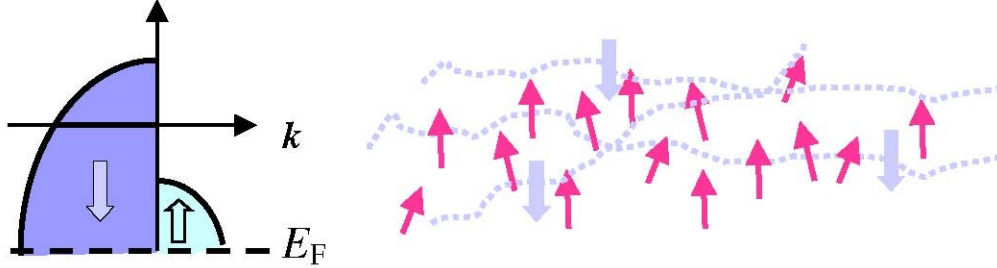

FIG.2: Pictorial presentation of carrier-mediated ferromagnetism in p-type diluted magnetic semiconductors, a model proposed originally by Zener for metals. Owing to the p-d exchange interaction, ferromagnetic ordering of localised spins (red arrows) leads to the spin splitting of the valence band. The corresponding redistribution of the carriers between spin subbands lowers energy of the holes, which at sufficiently low temperatures overcompensates an increase of the free energy associated with a decrease of Mn entropy associated with the spin ordering.

celebrated Ruderman-Kittel-Kasuya-Yosida (RKKY) model. The RKKY and Zener models lead to the same values of T_C in the mean-field approximation [5] as long as the carrier concentration is smaller than that of the localised spins, usually the case of DMSs. If the carrier and spin concentrations are comparable, either ferromagnetic or antiferromagnetic coupling prevails, depending on the ratio of the distance between localised spins to the inverse of the Fermi wave vector. Finally, if the carrier density is much greater that that of the localised spins –like in diluted magnetic metals – a random sign of the interaction results in a spin-glass phase. Interestingly, the p-d Zener model explains the origin of ferromagnetism in double perovskite compounds, such as Sr_2CrReO_6, where the magnitudes of T_C attain 625K [6].

A. Double exchange

This mechanism operates if the width V of a partly occupied band is smaller than the energy of the exchange interaction of carriers with localised spins. Such a situation occurs if magnetic ions with differing charge states coexist. Here, a ferromagnetic spin ordering facilitates the carrier hopping to an empty neighbour d orbital. Thus, since V is proportional to the hopping rate, the ferromagnetic order is driven by a lowering of the carrier energies due to an increase in V. Accordingly, in such systems the spin ordering – either spontaneous or generated by an external magnetic field – is accompanied by a strong rise of the conductivity, or even by an Anderson-Mott insulator-to-metal transition, leading to colossal negative magnetoresistance. This is the case of manganites, like $(La,Sr)MnO_3$, where Sr doping introduces holes in part of the Mn d states. The ferromagnetic order, surviving up to 350 K, is brought about by the double-exchange

interaction involving the on-site Hund's ferromagnetic spin coupling and hopping of d electrons between neighbour Mn^{3+} and Mn^{4+} ions.

V. STONER FERROMAGNETISM

As already mentioned, the potential exchange interaction favours a ferromagnetic ordering of the carriers in a band. However, such an ordering would mean that carriers occupy only one spin subband, so that their Fermi energy, and thus their kinetic energy increases. For typical values of the sp band width this increase hampers the onset of ferromagnetism. However, the existence of the potential exchange leads to a band-gap narrowing in doped semiconductors and enlarges — by the Stoner enhancement factor or, equivalently, by the Landau's Fermi liquid parameter $A_F > 1$ — the Pauli susceptibility of normal metals. The same parameter rises the Curie temperature in correspondence to the RKKY/Zener mechanism of localised spins' ordering, $T_C \to A_F T_C$ [5].
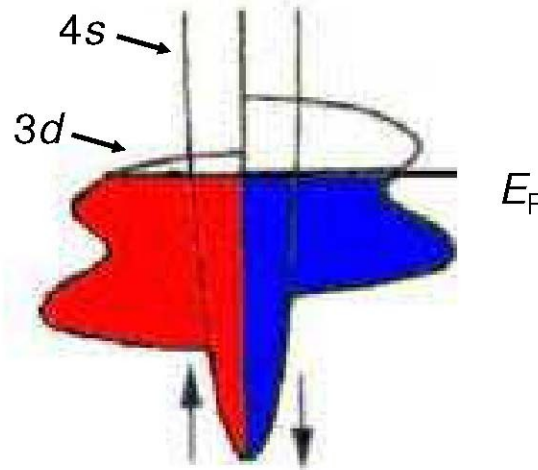
FIG. 3: Pictorial presentation of the Stoner mechanism accounting for ferromagnetism of itiner-ant magnetic moments. Owing to the Mott-Hubbard insulator-to-metal transition the 3dorbitals become delocalised and form bands. As long as these bands remain narrow, an increase of kinetic energy associated with redistribution of electrons to the majority spin subband does not overcompensate a lowering of the Coulomb energy occurring if electrons are spin polarised.

An interesting situation occurs if an overlap between TM d orbitals leads to a Mott-Hubbar d insulator-to-metal transition resulting in the itinerant character of the d electrons. As shown in Fig. 3, if the d band formed in this way is sufficiently narrow, the lowering of the potential energy associated with ferromagnetic ordering is not overcompensated by a change in the kinetic energy. This Stoner mechanism accounts for the ferromagnetism of, *e. g.* elemental ferromagnets, leading to a T_C as high as 1390 K in the case of Cobalt.

Acknowledgments

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