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Survey of the Field of Magnetic Semiconductors

Abstract: Magnetic semiconductors are materials with good band conductivity as well as magnetic order. Since each phenomenon requires a different description of the relevant electron states, the band structure of these materials is very complicated, containing band states as well as localized states. An important condition for strong interaction between the magnetic and the conducting electrons appears to be the existence of high densities of states at the Fermi energy, providing large carrier polarizations in the magnetized state.

Introduction

Nearly one-half of all elements in the periodic table are transition or rare-earth elements with partially filled inner d or f shells. Transition-element and rare-earth compounds represent the largest but least understood group of solid-state materials. Their most remarkable property is the strong interaction between the d or f electrons. This may make these materials magnetic but it simultaneously tends to suppress the electrical conduction predicted by band theory for all materials with partially filled energy bands.

For many decades, the magnetic properties of transition elements and their compounds have been investigated and interpreted in many details, and this field is represented now by one of the larger sections in the literature of solid-state physics. The "Magnetism" section is separated rather fundamentally from another big section, "Semiconductors," because the two begin with nearly opposite assumptions in attacking the many-body problem of the solid state.

Magneticians usually like to start with the many-electron model of the single atom because the magnitude and g factor of the atomic magnetic moment can be obtained readily from the Russell-Saunders coupling scheme and the Hund rules. The solid-state environment is considered to modify somewhat the configuration of the electron spins and ground-state orbitals through the electrostatic crystal fields or covalent ligand fields, but not to change the basically local character of the "magnetic" electrons. Difficulties arise where the exchange interaction between neighboring atoms and long-range magnetic order have to be explained. For metals, at this point, one runs into vehement discussions about localized vs itinerant electron models. In nonconducting materials, such as ferrites, garnets, perovskites, etc. the molecular field and superexchange theories are still doing a satisfactory job. But the situation becomes increasingly difficult when electrical transport phenomena are to be explained. The localized, many-electron model provides for each cationic state a well-defined energy level derived from the lowest multiplet term of the single atom. Where there is an integral number of electrons per equivalent cation, the motion of an electron from one atom to the equivalent neighbor actually requires a local increase of the valence state at one cation and a decrease at the other, which requires an activation energy. Generally the transferred electron remains bound to the hole it left behind, which explains why the ground state is insulating in many magnetic compounds with partially filled d bands, such as NiO, MnS, etc. If excess holes or electrons are introduced by suitable doping or by deviations from stoichiometry, conductivity is observed, but this is described by a thermally activated "hopping" of the charge carriers through the lattice.

In semiconductor physics, on the other hand, one prefers to use the band model because it gives an excellent description of the transport phenomena. The interaction between electrons associated with neighbor atoms is assumed to be strong compared to the spherical potential of a single atom. If the overlap between electron orbitals at neighboring atoms is sufficiently large, the electrons can move so fast and screen one another so well against local Coulomb potentials that charge carriers can move everywhere without activation energy. Unfortunately, the neglect of electron-electron interactions in the spherical potential of individual atoms also eliminates the reason

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for formation of magnetic moments. Good and simple semiconductors are never magnetic.

The gap in solid-state physics between magnetic and conducting phenomena is hard to close without confrontation with extremely complicated many-body problems. It is even doubtful that situations with intermediate character could exist in reality. It is conceivable that the magnetic and the itinerant electron states are two thermodynamically different states to which an electron cannot belong at the same time. In this case one expects the occurrence of an abrupt Mott transition from the magnetic to the conducting state as soon as the orbital overlap between neighboring atoms, with the associated electron-electron screening, exceeds a critical value. This overlap may be altered by experimental conditions, such as pressure, heat, etc. The studies of such effects in transition element compounds are still quite preliminary.

A long history of electrical measurements on magnetic 3d compounds, mainly oxides, had converged in the opinion that hopping is here the most common conducting mechanism. Since most applications of semiconductors require large charge-carrier mobilities, more detailed study of transport phenomena in magnetic compounds had only weak motivations. In recent years, however, the situation has changed drastically. It began with the discovery that even the classical example for hopping conductivity, the Li-doped NiO, is a narrow band conductor if studied as a single crystal or a carefully prepared ceramic. The hopping properties were only simulated by dirty grain boundaries. Then evidence was found that in chalcogenides of the rare earths and Cr a rather good band conductivity with mobilities of about 10 $\text{cm}^2/\text{V-sec}$ coexists with magnetic ordering.[1–3] Such "magnetic semiconductors" are of special interest, since magnetic ordering and electrical and optical properties show strong interdependencies that bring new aspects not only to the problem of electrons at the border between the magnetic and the conducting states, but also to the technical application of magnetically controlled semiconductors or electrically controlled magnets.

The simplest model of a magnetic semiconductor is a material having free carriers in the presence of strictly localized atomic moments. The concentration of free carriers can be varied, as is usual in semiconductors, by optical or thermal excitations, carrier injection, etc. The carriers, i.e., electrons in a conduction band or holes in a valence band, are supposed to become spin polarized to a certain extent by intra-atomic exchange of the localized magnetic electrons with the itinerant conduction electrons. The charge-carrier polarization produces long-range interactions between the localized magnetic moments of the atoms and orders them below a certain transition temperature. This situation is well described for metals by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) theory, which gives, for a lattice of atomic moments J with lattice parameter R, the following expression for paramagnetic Curie temperature:[1]

$$\theta = \frac{N}{E_{\mathrm{F}}} A^2 (g-1)^2 J(J+1) \sum F(2k_{\mathrm{F}}R),$$

where N, E_{F}, k_{F} are the density, Fermi energy and Fermi wave number of the itinerant electrons, respectively, and A is the intra-atomic exchange constant for coupling between itinerant and localized electrons, which may have a magnitude around 0.5 eV. $F(2k_{\mathrm{F}}R)$ is the Ruderman-Kittel function representing the decay of screening of a local magnetic field by conduction electron polarization as a function of distance R. The RKKY interaction is expected to be quite weak in most broad-band semiconductors, in which a few relatively fast conduction carriers become only weakly polarized by intra-atomic exchange. It is doubtful whether this interaction can be enhanced sufficiently so that the variations in carrier concentration that are feasible in semiconductor technology can produce useful magnetic variations around and above room temperature, as is desired for many technical applications. In order to strengthen the coupling, large densities of states are probably required at the Fermi energy, i.e., at the bottom of the conduction band in n-type semiconductors or at the top of the valence band in p-type semiconductors. Since the band structure does not generally comply with this special condition, this consideration also explains why most materials from the large multitude of semiconducting transition-element and rare-earth compounds show no conductivity-induced magnetism and only weak changes in semiconducting properties with magnetic order. However, the introduction of large densities of states and of Fermi levels, with a smaller energy separation from a band edge than the intra-atomic exchange splitting, eliminates much of the simplicity of the theoretical model, which is only applicable to fast Bloch electrons with intra-atomic exchange scattering as a small perturbation. All presently known materials for which the paramagnetic Curie temperature can be changed markedly by variations in conductivity show very large magnetoresistance effects in the neighborhoods of their Curie temperatures. Those effects are often larger by orders of magnitude than the spin-disorder resistance predicted by scattering theory.

Additional complications come from the fact that indirect exchange via itinerant carriers is, in presently known materials, never the only reason for long-range magnetic order: the carrier-free, insulating compound already shows magnetic order. This is particularly true of transition-metal compounds, because the magnetic d electrons are not too strongly localized and therefore contribute substantially to covalent bonding, which produces regular superexchange via the nonconducting anion electrons in the filled valence band. The situation is, in this respect, much simpler in rare-earth compounds, because the magnetic 4f electrons are, in principle, so well screened by the filled 5s and 5p shells of the Xe core that f-f interactions between neighboring atoms are quite small. But even the insulating Eu chalcogenides show magnetic ordering below Curie temperatures ranging from 76°K to 4°K. Therefore localized-electron exchange effects cannot be disregarded. These effects may result from the covalency of the 4f electrons, from polarization of the filled 5s and 5p shells or from superexchange via covalency of the f-d exchange-coupled 5d shell. It is also conceivable that mixing of the magnetic 4f electrons into empty conduction band states produces a type of "virtual" RKKY exchange.

Since the story of localized vs itinerant electrons is the topic of Honig's paper,[29] and Kasuya[30] discusses in detail the exchange between 4f electrons in magnetic semiconductors, we leave these topics now and survey some typical experimental properties of magnetic semiconductors.

Conductivity-controlled ferromagnetic exchange

Following the sensational discovery in 1950 by Jonker and van Santen[4] that the perovskite $LaMnO_3$ becomes strongly ferromagnetic, up to room temperature, when made conductive by oxygen deficiency or by replacement of La^{3+} by Sr^{2+} or Cr^{2+}, Zener[5] suggested the "double-exchange" mechanism which relates to the occurrence of metallic conductivity. The essential idea is that, since electrons hop without a change of spin, the hopping of electrons between atoms of different valence is easier when the atomic spins are aligned parallel to one another. Anderson and Hasegawa, Anderson, and deGennes[6] have extended this concept, which is a form of indirect exchange via mobile carriers when the intra-atomic exchange A is large compared to E_F and kT. The ferromagnetic interaction in $(La,Ca)MnO_3$ was interpreted to be due to the hopping of electrons between Mn^{3+} and Mn^{4+} ions. Later Jonker[7] and Goodenough[8] gave experimental evidence for a ferromagnetic Mn^{3+}-O^{2-}-Mn^{3+} interaction in rhombohedral perovskites that was not due to hopping conductivity, since it occurred in insulating compounds with ions of equal valence. The important condition was, rather, the removal of the Jahn-Teller distortion of the perovskite lattice by suitable chemical substitutions. This ferromagnetic Mn^{3+}-O^{2-}-Mn^{3+} interaction is due to superexchange, as was suggested by Goodenough.[8] The simultaneous existence of antiferromagnetic superexchange and ferromagnetic double exchange of $(La, Ca)MnO_3$ having a Jahn-Teller distortion produces a spin canting not explainable by superexchange alone.[6]

In 1956 Heikes and the group at Westinghouse made an intensive search for ferromagnetic exchange via charge carriers in 3d compounds with NaCl type structure. Only the composition $Li_{0.1}Mn_{0.9}Se$ showed ferromagnetism[9] (T_c = 110°K) and this disappeared again below 70°K. Spin cantings occur at other Li concentrations. The interpretations by Heikes[9] and deGennes[6] related ferromagnetism and spin canting to ferromagnetic clusters in an antiferromagnetic host lattice, double exchange being confined to the manganese atoms neighboring a Li^+ ion at which the mobile holes are trapped. Karpenko and Berdyshev[10] describe the ferromagnetism in $Li_xMn_{1-x}Se$ as an example of indirect exchange via free conduction carriers produced by thermal excitation. The disappearance of ferromagnetism at low temperature is a consequence of the exponential freeze-out of carriers with decreasing temperature. Goodenough,[8] however, has pointed out that the observation of ferromagnetism for certain Li concentrations in MnSe can be explained by the rules of superexchange, which predict ferromagnetic exchange between Mn^{2+} and Mn^{3+} in the low-spin state. The case of Li-doped MnSe is not yet closed.

In 1964 Lotgering[11] reported that the normal spinels $CuCr_2S_4$, $CuCr_2Se_4$ and $CuCr_2Te_4$ are p-type metals (ρ about 10^{-2} to 10^{-4} Ω-cm at room temperature) and show ferromagnetic order below Curie temperatures of 420, 460 and 365°K, respectively. The first explanation was again by double exchange between ambivalent Cr ions in $Cu^+Cr^{3+}Cr^{4+}X_4$. In Goodenough's alternative interpretation,[12] the p-type conductivity comes from the partially filled t_{2g}^5 orbitals at the Cu^{2+} ions which mix sufficiently with the anionic p orbitals to form band orbitals. The spin polarization of this band would be antiparallel to the localized Cr^{3+}-ion spins and could produce ferromagnetic RKKY exchange. Whatever the mechanism of interaction between conductivity and spin order, it is not the only reason for the observed ferromagnetism: The insulators $Cd(Cr_2^{3+})X_4$ and $Hg(Cr_2^{3+})X_4$ are also ferromagnetic. The spinels with the highest Curie temperature known for nonmetallic ferromagnetics are the insulators $CuCr_2Se_3Br$ and $CuCr_2Te_3I$.[13] This ferromagnetism is due to a strong ferromagnetic 90° Cr^{3+}-X-Cr^{3+} interaction. Different models have been proposed to interpret the spiral and ferromagnetic properties of various Cr^{3+} thio- and seleno-spinels. These are based on strong ferromagnetic 90° Cr-X-Cr superexchange between near neighbors and weaker antiferromagnetic superexchange interactions between more distant Cr pairs.[3] The large flexibility of the spinel lattice for chemical substitutions makes the $A(Cr_2)X_4$ spinels an ideal system for studies of magnetic, electric and optical properties as functions of chemical composition.

The clearest response of magnetic order to variations in electrical properties is found in EuO and some other rare-earth chalcogenides. The Th_3P_4-compounds Gd_2Se_3 and Gd_2S_3 change without variation of lattice constant from antiferromagnetic to ferromagnetic, with T_c up to

100°K, if made conductive by introducing trivalent rare-earth cations into the holes of the defective cation lattice.[14] A somewhat smaller, but better investigated, change of Curie temperature with charge-carrier concentration is the increase with n-type conductivity found in NaCl-type Eu chalcogenides having a partial replacement of Eu^{2+} by trivalent rare-earth ions such as Gd^{3+}. The Curie temperature increase depends neither on the magnetic properties of the impurity ions nor on their concentrations, but only on the conduction-electron concentration.[15] This was demonstrated by distilling-off metallic Eu in vacuo, thus reducing the conductivity while the Gd^{3+} concentration remained constant. The largest Curie temperature increase, from 76°K to 137°K, has been found in EuO made n-type conductive by forcing Gd^{3+} ions into it.[16] Two models have been suggested for the conductivity-induced increase of the Curie temperature: (1) RKKY exchange via conduction electrons[14] that are removed from, or very loosely bound to, their donors; and (2) the impurity model of Kasuya and Yanase.[17] Here the electrons are assumed to remain bound to the donors by an energy of about 0.5 eV, thus forming an impurity state that really extends to only the 12 nearest Eu neighbors. Compared to usual impurity states in nonmagnetic semiconductors, the "magnetic" impurity state has as an additional feature: the exchange interaction of the bound electron with the localized-ion spins. Therefore the energy and radial extension of the impurity state vary with the degree of order in the spin lattice. This energy variation is responsible for the Curie temperature increase within the "molecule" of Eu ions around the donors. Above the magnetic Curie temperature the ferromagnetic order disintegrates, but ferromagnetic spin clusters around the donors survive at much higher temperatures. Whether the mobile electrons, which contribute to the ferromagnetic coupling, are itinerant or donor-bound has to be determined from electrical measurements.

Magnetically modified conductivity

The electrical properties of the 3d oxides are very complex, because the radial extension of the magnetic 3d orbitals relative to the cation-cation distances is in an intermediate region in which the transition between localized and conducting states can occur under the influence of many parameters. The qualitative and quantitative significance of each of these is often difficult to identify, and one finds a wide spectrum of materials from ferromagnetic metals to antiferromagnetic insulators. Some materials exhibit abrupt transitions from insulating to metallic states. These may occur at a magnetic ordering temperature, but they are nearly always accompanied by crystallographic deformations or transformations. It is hard to decide whether the crystallographic transformations are primary and modify the magnetic order or whether it is the other way around. Recent surveys of transition-metal oxides have been given by Adler[18] and by Goodenough,[8] and the topic is covered in this issue by several papers.[29,31]

The paper of deGennes[6] on double exchange gives a very stimulating discussion of the behavior of itinerant electrons in antiferromagnetic lattices. The Zener electrons have two "choices": They can try to keep their freedom, but then they have to cant all spins in the crystal an equal amount by the double exchange they produce; this requires an energy proportional to R^3. Or the electrons can give up some kinetic energy (proportional to R^2) in order to reduce the number of spins that have to cant. Since the latter case requires less energy, the Zener electrons are self-trapped in the cloud of parallel spins they produce by their own double-exchange mechanism. The spin-dressed electrons now have a very high effective mass and move only slowly through the crystal. Since the interactions with phonons and magnons are very strong, the dressed electrons fall quickly into bound states at defect or impurity sites. The spin cluster around the occupied impurity sites provides a magnetic activation energy for hopping from an occupied donor site to an empty impurity site without a spin cluster. The motion of Zener electrons through an excited spin lattice at finite temperatures is extremely complicated by the feedback of the electron properties in the statistical behavior of the spin lattice. At high temperatures, at which kT is comparable to the trapping energy, the electrons become free again.

The Cr and Eu chalcongenides have unusually large peaks in electrical resistivity at their ferromagnetic Curie temperatures. It is reasonable to expect such large magnetoresistance effects in magnetic semiconductors exhibiting Curie-temperature variation with mobile-electron concentration because these effects reflect the strong carrier polarization that is necessary for an RKKY interaction of notable magnitude. The largest magnetoresistance peak has been observed[19] in slightly doped EuS and EuSe with about 10^{18} carriers-cm^{-3}. In such materials the resistivity increases near the Curie temperature by a factor of more than 10^7 above the room temperature value, dropping sharply at lower temperatures with the onset of ferromagnetic order. For perfect ferromagnetic spin alignment, the resistivities are lower than the room temperature value. The peak resistivity near T_c decreases sharply with forced spin alignment in applied magnetic fields. With electron concentrations in excess of 10^{18} cm^{-3}, the resistivity peak reduces to dimensions that can be described by the theory of critical scattering of itinerant electrons by disordered spins in a ferromagnetic lattice.[20]

Interpretation of the "giant" magnetoresistance effect at small electron concentrations (beyond critical scattering) can take several approaches depending on the opinion one has about the mechanism of the electron-induced Curie temperature increase:

1) The mobile electrons are assumed to be essentially free and itinerant, but the splitting of their energy levels by intra-atomic exchange is comparable to or larger than E_F. Then, in contrast to the antiferromagnetic case, the electron mobility is not hindered by magnetic ordering at low temperature, because in the perfect ferromagnetic lattice the spins have the same periodicity as the ions. As the magnetic order decreases with increasing temperature, the conducting states break up into spin-up and spin-down areas. If the exchange splittings are larger than both kT and E_F, the electrons cannot move from one area to another without a spin flip. Therefore the electrons become trapped in spin clusters where short-range order is maintained by the RKKY interaction against thermal agitation. The spin-dressed pseudo-particles, or "spin polarons," move slowly through the lattice, and their effective mass may be further increased by electrostatic polaron effects. Thus they are caught quite easily by lattice defects such as impurities or vacancies. Since the spin dressing is larger the larger the magnetic susceptibility, the effect has its maximum at the ferromagnetic Curie temperature.

2) The impurity model[21] keeps the excess electrons trapped in the neighborhood of the donor levels, which lie deeper than kT below the conduction band. The conductivity is an impurity-hopping phenomenon with a magnetic activation energy that is derived from the differences in local spin order around occupied and empty impurity sites. The magnetic activation energy disappears in the ferromagnetic lattice, and impurity banding occurs. At high temperatures the resistivity decreases exponentially, as kT begins to override the magnetic activation energy or excites impurity electrons into the conduction band.

3) Optical measurements show that ferromagnetic order can be accompanied by a red shift to lower values of the energy gap between the conduction and valence bands. Therefore, it is conceivable that the impurity states into which the electrons condense with decreasing temperature merge with the widened conduction band in the ferromagnetic state. This effect would account only qualitatively for the observed temperature dependence of the resistivity. In contrast to experiment, the activation energy and the Hall effect would be expected to be temperature dependent.

Since recent photoconductivity measurements[22] in EuO, EuS and EuSe show the same resistivity dependence on spin ordering as do the doped samples, one tends to attribute to the impurities less significance than is required by model 2). But we should not anticipate here the discussion of the transport properties of the Eu chalcogenides by von Molnar.[32]

The spinels $CdCr_2S_4$ and $CdCr_2Se_4$ can be made p-type conducting,[2,3] with mobilities of about 30 cm^2/V-sec, by Au or Ag doping. The n-type conductivity, which has much lower mobility, is obtained with Ga or In doping. Whereas the p-type materials show no major irregularities around the ferromagnetic Curie temperature, n-type materials exhibit strong magnetoresistance effects. Haas[2] has shown that they can be well described by critical scattering theory, with some contributions by mechanism 2).

Compared to the wide variety of electrical properties shown by 3d transition-metal oxides, it is surprising that the Cr spinels and Eu chalcogenides, two material groups that have nothing obvious in common, behave so similarly. Quantitative differences are seen only in the region of small carrier concentrations, which have been obtained in EuS and EuSe but not thus far in the Cr spinels. The requirements for the simultaneous existence of ferromagnetism and semiconductivity seem to be so stringent that, in the rare case where it occurs, not too many free parameters are left for variations in electrical and optical properties.

Magnetic modifications of electronic band structure and optical properties

What are the specific details in the electronic structure of magnetic semiconductors from which the cross effects between conductivity and magnetism evolve? There is justifiable skepticism towards the application of usual band structure calculations to magnetic semiconductors because the one-electron approximation is invalid for localized magnetic electrons.[23] The fundamental difficulty and challenge is the suitable introduction of electron-electron interactions, responsible for the occurrence of magnetic moments and their ordering, into the one-electron picture, which provides the appropriate description of electronic transport phenomena. Since this problem has not yet been solved with sufficient generality, the discussion of electronic structure in magnetic semiconductors requires considerable intuition. By weighing chemical, crystallographic, magnetic, optical and electrical data against one another, one tries to design qualitative energy-level schemes that use a liberal mixture of one-electron band states and localized or molecular many-electron orbitals in order to obtain optimum agreement with experimental facts.[24] Figure 1 shows a typical diagram for a semiconducting compound that has a valence and a conduction band formed by well overlapping s and p wave functions, and localized many-electron $3d^n$ and $3d^{n+1}$ quasiparticle states, which are separated from one another by Coulomb repulsion. They can be further split by intra-atomic exchange and spin-orbit interaction or by the ligand field into states with different spin configurations of the $3d^n$ or $3d^{n+1}$ electrons, corresponding to the multiplet terms of the free atom. In Fig. 1 we have

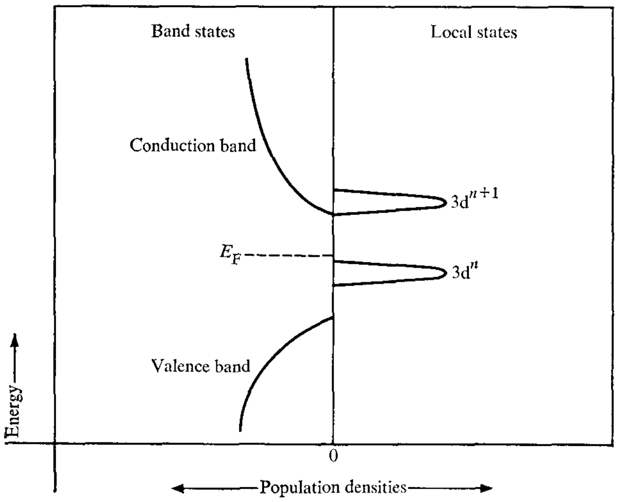

Figure 1 Schematic energy level diagram of an n-type magnetic semiconductor.

assumed that $3d^n$ is the last occupied level and $3d^{n+1}$ the first empty level and that these are separated by the Fermi energy, which is derived from the filling of the valence band and many-electron states by the number of electrons available in the material. The material in question is a semiconductor because the Fermi energy lies in the forbidden gap and the $3d^n$ levels are filled and therefore do not sustain conductivity in a stoichiometric compound with all cations of the same valence. The quasiparticle states are broadened by resonance between neighboring cations as the neighbors come sufficiently close together for overlap of their $3d^n$ wave functions. As long as the level broadening remains smaller than the multiplet separation, the hopping probability is spin dependent and produces double exchange. When the level broadening becomes comparable to the electronic Coulomb repulsion, a Mott transition to a metallic state occurs.

We have argued that the condition for strong interactions between conductivity and magnetism must be a high density of states at E_F, in order to have optimal spin polarization of the carriers. This can be obtained if the empty $3d^{n+1}$ states merge with the band states at the bottom of the conduction band. Therefore the material represented in Fig. 1 is an n-type magnetic semiconductor if E_F is brought to the bottom of the conduction band by doping, light radiation, thermal excitation, etc. A p-type doping with acceptors would bring holes into the occupied $3d^n$ states and change the magnetic moment. If the $3d^n$ states are narrower than the multiplet separation, i.e., the magnetic moments are close to the crystal-field theoretical value, we expect the holes to move from cation to cation by activated hopping and to introduce double exchange. On the other hand, a material having the $3d^n$ levels merged with the top of the filled valence band would be a p-type magnetic semiconductor. This is the case in the spinels $\mathrm{Cu(Cr_2)Sr_{3+x}Br_{1-x}}$, for example, although it is not yet clear whether it is the Cu:$3d^{10}$ or Cr:$3d^3$ levels, or both, that are at the band edge.[12]

In Eu chalcogenides the game has to be played with the $4f^7$ states as well as with the empty 5d states. The 4f electrons have stronger Coulomb repulsion and more widely separated $4f^n$ levels than the 5d electrons. They are probably too localized for measurable contributions to the carrier mobility of about 10 cm^2/V-sec observed in doped samples. Therefore, the empty 5d states with t_{2g} symmetry at the bottom of the conduction band must provide the high density of states required for n-type doping. Since p-type doping[25] reduces the magnetic $4f^7$ moments but does not produce p-type conductivity, it may be concluded that the position of the occupied $4f^7$ levels is in the forbidden gap above the valence band.[26] This assumption is in agreement with optical absorption and magneto-optical measurements, and also with recent APW calculations of the band structure, that consider the strong interactions of the 4f electrons with one another.[27]

We do not discuss here further details about how optical absorption spectra are used to verify proposed energy level schemes, because Dimmock[33] has included this topic in his paper. Additional magneto-optical measurements are helpful to identify optical transitions from and into spin-polarized electron states. Recent studies of the photoelectron emission from Eu chalcogenides give the absolute energies of the electron levels with respect to the work function.[28]

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