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Cr-BASED II-VI SEMIMAGNETIC SEMICONDUCTORS*

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We review the magnetic and optical properties of recently grown Cr-based II-VI semimagnetic semiconductors. We focus on two features of these materials which distinguish them from other semimagnetic semiconductors: the particular magnetic behaviour of these crystals, resulting from the Cr^{++} ion energy structure determined by a strong, static Jahn-Teller effect, and a ferromagnetic p - d exchange interaction, which is unique for II-VI semimagnetic semiconductors.

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1. Introduction

Semimagnetic semiconductors (SMSC) are mixed crystals based on classical semiconductors (such as CdTe, ZnSe or InAs), in which a controlled fraction of nonmagnetic cations is substituted by magnetic ions (such as Mn, Fe or Co) [1]. SMSC have attracted considerable attention during the last two decades, since they bridge the physics of semiconductors and magnetics. One of the most spectacular features of these materials is a strong exchange interaction between localized d electrons of magnetic ions and delocalized electrons of conduction (s - d exchange) and valence bands (p - d exchange) [1]. The p - d exchange is also crucial for coupling between magnetic ions, since the superexchange seems to be the driving force behind the d - d exchange [2-4].

So far most of the research on SMSC was focused on II-VI compounds with Mn, Co and Fe as magnetic ions. The magnetic behaviour of these SMSC is characteristic for either Brillouin-type paramagnets (multiplet ground state, no closely lying excited states) or Van Vleck-type systems (singlet ground state, yielding a field induced magnetic moment) [4]. On the other hand, for all the materials investigated so far, the s - d exchange was found to be ferromagnetic (F), while the p - d exchange — antiferromagnetic (AF) [1]. Let us recall that s - d exchange represents a so-called direct exchange, while p - d exchange is dominated by p - d hybridization. At the centre of the Brillouin zone only d electrons of t -type symmetry hybridize

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effectively with p -type electrons of the valence band. Therefore the occupancy of t -type orbitals of magnetic ions is crucial for the p - d exchange [2, 3]. It turns out that for Mn (d^6 electronic configuration), Fe (d^6) and Co (d^7) ions the occupancy of t -type orbitals is the same: all spin-up orbitals are occupied and all spin-down orbitals are empty (Mn: $d^5 = e_+^2 t_+^3 e_-^0 t_-^0$, Fe: $d^6 = e_+^2 t_+^3 e_-^1 t_-^0$ and Co: $d^7 = e_+^2 t_+^3 e_-^2 t_-^0$, where the subscript denotes the spin and superscript — occupancy of the orbital). This means that only spin-down electrons from the valence band can jump onto the d levels of magnetic ions, which eventually yield the AF coupling observed for Mn-, Co- and Fe-SMSC.

In contrast, the Cr^{++} ion with its d^4 configuration ($d^4 = e_+^2 t_+^2 e_-^0 t_-^0$) represents the ions with partially filled spin-up t -type orbitals and offers a new possibility: hopping of both spin-up and spin-down electrons from the valence band is possible in this case. The new exchange channels can yield F exchange. Moreover the energy structure of the Cr^{++} ion is, to some extent, reversed in respect to Fe^{++} ion, i.e. the ground crystal field term of the Cr ion is an orbital triplet 5T_2 , which suffers strongly the Jahn–Teller distortion [5, 6]. Consequently the ground state of the ion is a semidoublet, followed by another closely lying doublet and a singlet [5, 6]. Such an energy structure should result in a paramagnetism intermediate between Brillouin-type and Van Vleck-type [7, 8].

In view of this we review the magnetic and optical properties of Cr-based II–VI SMSC*.

2. The crystals

The Cr-based SMSC family is at present limited to $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ (cubic), $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ (hexagonal) and their mixture: $\text{Zn}_{1-x}\text{Cr}_x\text{Se}_{1-y}\text{S}_y$. Moreover, single phase crystals are available only for $x < 0.01$. Attempts to grow bulk crystals with higher concentrations resulted in precipitations of Cr_ySe_z or Cr_yS_z . Hopefully epitaxial techniques (MBE) could provide the crystals with higher Cr concentrations.

3. Cr ion energy structure

The energy structure of the Cr^{++} dopant was investigated already in the seventies, by EPR and IR spectroscopy [5, 6, 9–11]. It was shown that a conventional crystal field model provides a reasonable description of the data, if a static, tetragonal Jahn–Teller (JT) distortion of the Cr centre is taken into account.

The ground term of a free Cr^{++} ion is an orbital quintet 5D . A tetrahedral crystal field splits this term into an orbital triplet 5T_2 and an orbital doublet 5E (Fig. 1a). The static, tetragonal JT distortion (along the $\langle 100 \rangle$ direction) splits 5T_2 into an orbital singlet 5B_2 and an orbital doublet 5E , while the upper 5E state is split into two orbital singlets: 5B_1 and 5A_1 [12]. The spin–orbit interaction yields further splittings, in particular the 5B_2 level is split into a semidoublet Γ_1, Γ_2 , a doublet Γ_5 and a singlet Γ_4 (Fig. 1a). The effect of a magnetic field strongly depends on the magnetic field orientation relative to the axis of the JT distortion

*For the Cr-based IV–VI SMSC situation is essentially different: Cr^{++} ion is octahedrally coordinated and resembles tetrahedrally coordinated Fe^{++} (its ground state is 5E instead of 5T_2).

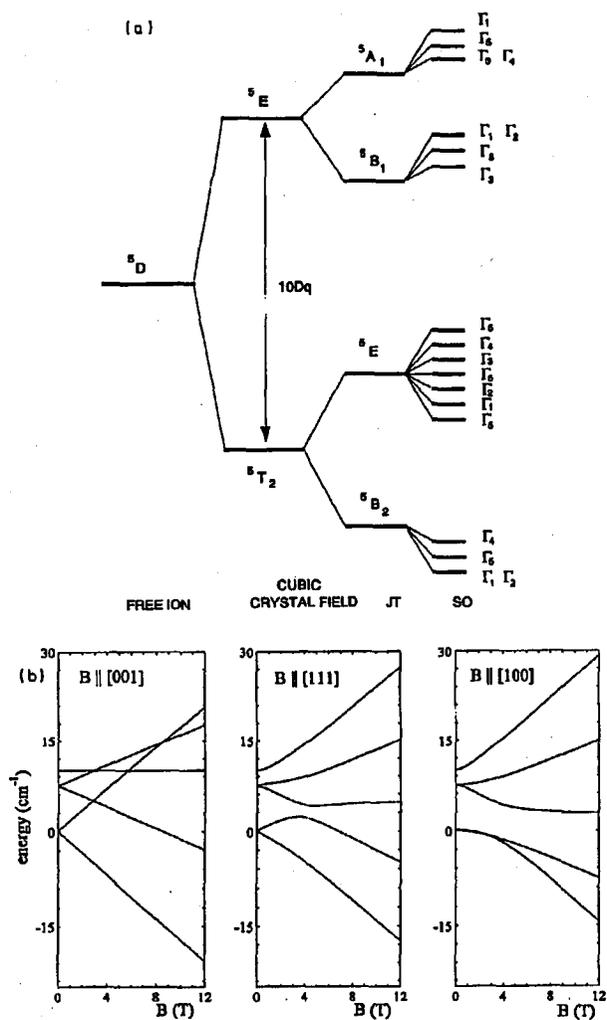


Fig. 1. Energy levels of the Cr^{++} ion, (a) energies in the absence of magnetic field (energy distances are not to scale), (b) the five lowest-energy Cr^{++} levels, calculated as a function of magnetic field B along the [001], [111] and [100] directions. The static Jahn-Teller distortion is along [001]. The parameters used correspond to Cr^{++} in ZnSe (after [8]).

(Fig. 1b). In general, the direction of the JT distortion forms an easy axis, while the direction perpendicular to the distortion — a hard axis [7, 8]. For a real crystal, there are three equivalent $\langle 100 \rangle$ directions, which means that for a given field direction there are three, in general nonequivalent, Cr centres.

The transitions between the levels of the 5B_2 state were observed for doped

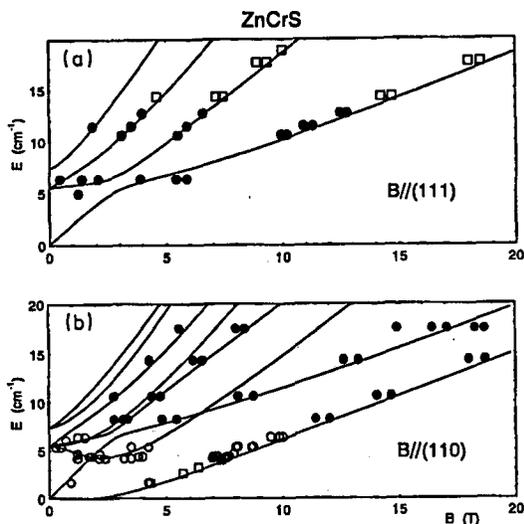


Fig. 2. Transmission energy versus magnetic field for: (a) $B \parallel$ sixfold axis, (b) $B \parallel (110)$. The lines show the calculated energy patterns of different Cr centres (after [14]).

crystals and at low fields in EPR [6]. Recently far infrared laser experiments were performed for ZnCrSe [13] and ZnCrS [14] at high magnetic fields. The characteristic transitions for different Cr centres are well visible. The field dependence of the energy level spectra is quite well described by a simple crystal field model (Fig. 2) [13, 14].

4. Magnetic properties

The low energy level structure of Cr ions is reflected in low temperature magnetic properties, such as specific heat and magnetization. Representative magnetic specific heat data are shown in Fig. 3 for ZnCrS. In the absence of a magnetic field a typical onset of Shottky-type anomaly may be observed, indicating the existence of an energy gap (of the order of a few K) between the ground and the excited levels. A similar situation was encountered in the case of Fe-SMSC [4]. However, the application of a magnetic field results in a strong increase in the specific heat, in contrast with Fe-SMSC, but similar to Mn- and Co-SMSC [1, 4]. Such a behaviour indicates that the ground state is a multiplet.

Typical magnetization data are presented in Fig. 4 for ZnCrSe. The field variation of magnetization is faster than observed for Van Vleck-type Fe-SMSC, but — contrary to Mn-SMSC — magnetization does not saturate at the lowest temperatures. Anisotropy of the order of 10% is observed at the highest fields and the lowest temperatures, with the $\langle 100 \rangle$ easy axis. The anisotropy decreases with increasing temperature. For $T > 20$ K magnetization is practically isotropic.

Both specific heat and a magnetization scale with Cr concentration, which indicates that the interaction between Cr ions is unimportant for the reported

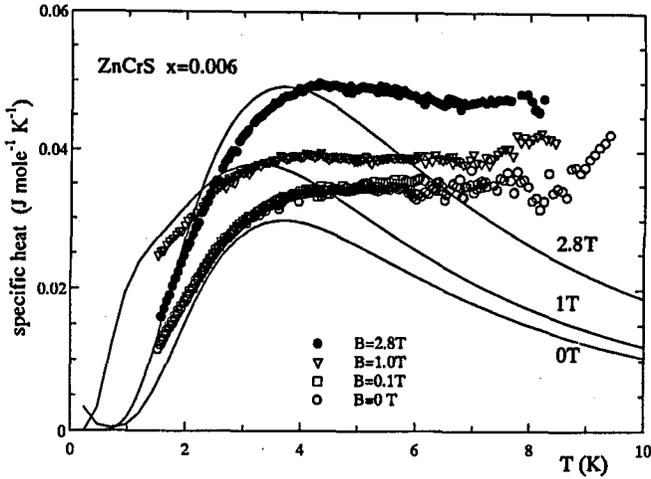


Fig. 3. Magnetic specific heat of $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ ($x = 0.006$) for $B = 0, 0.1, 1$ and 2.8 T ($B \parallel \langle 111 \rangle$). The solid lines show calculated specific heat for a cubic crystal with $B \parallel \langle 111 \rangle$, as described in the text. The curve for $B = 0.1$ T is practically the same as for $B = 0$ and therefore is not shown (after [8]).

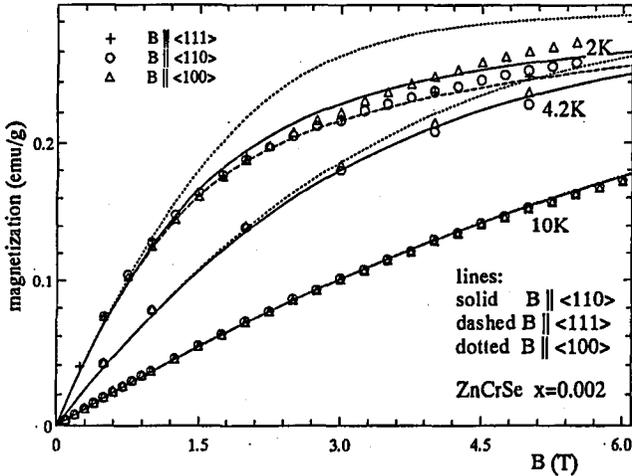


Fig. 4. Anisotropy of the magnetization of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ ($x = 0.002$) at various temperatures. The lines show the magnetization calculated according to the equilibrium model, as discussed in the text (after [8]).

crystals [4, 15]. This behaviour results from the low Cr concentrations and means that the model assuming a system of noninteracting Cr ions should be adequate for a description of the data.

The model describing magnetic properties must account for three different

Cr centres present in the crystal. In the presence of a magnetic field the centres are in general nonequivalent and any macroscopic quantity, such as magnetization or specific heat, is some average of the contributions of different centres. The difficulty is in assigning proper weights to these contributions. So far two extreme thermodynamic situations were considered [7, 8]. The first one (called "nonequilibrium") assumes that there is no redistribution of the number of the various centres, even if a magnetic field is applied. This situation corresponds to infinite potential barriers between different centres. In the opposite model (called "equilibrium") there are no barriers at all, which means that the population of the centres is governed by the equilibrium condition. Both models give the same results at temperatures higher than about 20 K, but differ significantly at low T . It was found that the equilibrium model describes reasonably well the observed specific heat (Fig. 3) and the magnetization (Fig. 4). For the magnetization, the magnetization anisotropy is described only qualitatively (Fig. 4), which suggests a deviation from the true equilibrium distribution of the Cr centres [8].

5. Optical properties

The s , p - d exchange interaction in SMSC yields strong energy band splittings. For Mn-, Co- and Fe-SMSC the exchange can be expressed in a simple Heisenberg form (resulting from the mentioned single occupancy of t -type orbitals) [16, 17]:

$$\mathcal{H} \propto \mathbf{S} \cdot \boldsymbol{\sigma},$$

where $\mathbf{S} = (S_x, S_y, S_z)$ is the spin operator of the magnetic ion and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is the spin operator of the band electron. Summing the interactions over randomly distributed magnetic ions one finds that the total conduction-valence band splitting reads [16]

$$\Delta E = (N_0\alpha - N_0\beta)x\langle S \rangle,$$

where $\langle S \rangle$ is the thermodynamic average of the ion spin and $N_0\alpha$, $N_0\beta$ are exchange parameters for conduction and valence bands, respectively. The band splittings can be studied in a straightforward way by free exciton spectroscopy [18]. Since for Mn-, Co- and Fe-SMSC $N_0\alpha > 0$ and $N_0\beta < 0$ [1], ΔE is always positive, which means that the exciton line components visible in σ^+ polarization are observed at lower energies than σ^- components. For Cr-SMSC the situation is essentially different: the sense of exciton splitting is reversed [19, 20], as exemplified in Fig. 5 for ZnCr(Se,S). This is true for all Cr-SMSC studied so far and indicates that $\Delta E < 0$ and $N_0\alpha - N_0\beta < 0$. Faraday rotation experiments performed for ZnCrSe gave results compatible with this observation [21]. Although $N_0\alpha$, $N_0\beta$ cannot be determined separately, since — due to low Cr concentrations — exciton splittings are rather small and not all the exciton lines can be resolved, the s - d parameter is expected to be positive (typical for direct exchange). Consequently $N_0\beta > 0$, which means that p - d exchange is ferromagnetic. We notice that the Cr ion is the only dopant known so far revealing F p - d exchange in SMSC.

The band splitting ΔE was found to be proportional to the macroscopic magnetization (Fig. 6) [19, 20], similarly as for the other SMSC [22, 1]. This

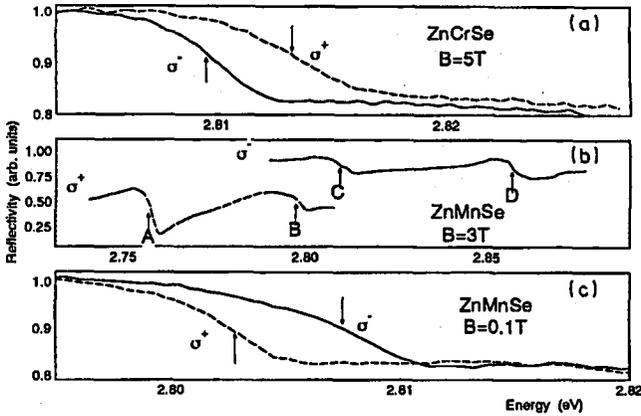


Fig. 5. Reflectance spectra of ZnCrSe and ZnMnSe at $T = 1.9$ K. (a) $\text{Zn}_{0.996}\text{Cr}_{0.004}\text{Se}$ at $B = 5$ T, (b) $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{Se}$ at $B = 3$ T, (c) $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{Se}$ at $B = 0.1$ T. The arrows indicate exciton energies and σ^+ , σ^- denote circularly right and left polarization of light (after [19]).

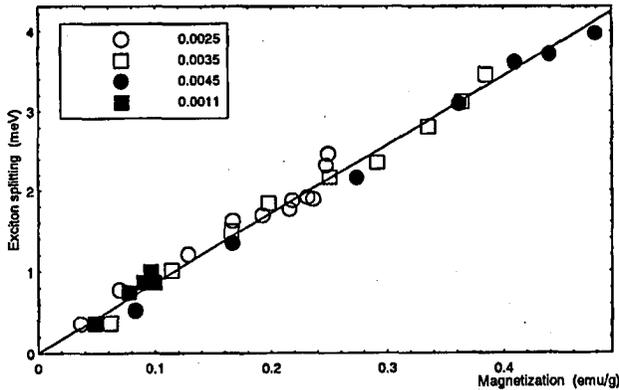


Fig. 6. Exciton splitting versus magnetization of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ for $x = 0.0011, 0.0023, 0.0035$ and 0.0045 . The straight line represents $N_0\alpha - N_0\beta = -0.9$ eV (after [19]).

suggests that the exchange interaction can be approximated by a simple Heisenberg Hamiltonian. Effectively the non-Heisenberg terms, predicted in Ref. [17] can be neglected.

Detailed calculations show that the average spin of a Cr ion (S) is measured by the magnetic moment (M) ($\langle M \rangle = 1.87\langle S \rangle$ [8, 19]) and subsequently by macroscopic magnetization. Therefore $N_0\alpha - N_0\beta$ can be evaluated from the exciton splitting versus the magnetization plot. This was done for ZnCrSe ($N_0\alpha - N_0\beta = -0.65$ eV [19]), ZnCrSe $_{0.95}$ S $_{0.05}$ ($N_0\alpha - N_0\beta = -0.63$ eV [20]) and ZnCrS ($N_0\alpha - N_0\beta = -0.37$ [20]). Since $N_0\alpha \approx 0.2$ eV for all the SMSC studied

so far [1], it was reasonable to adopt this value also for Cr-SMSC and obtain the estimates for $N_0\beta$: $N_0\beta$ (ZnCrSe) = +0.9 eV, $N_0\beta$ (ZnCrSe_{0.95}S_{0.05}) = +0.8 eV, $N_0\beta$ (ZnCrS) = +0.6 eV. The observed trend of decreasing $N_0\beta$ from ZnSe to ZnS is in contrast with the expected increase in the exchange parameter with decreasing lattice constant (the ZnS lattice constant is about 5% smaller than the ZnSe one), since a smaller anion-cation distance means increasing overlap of p and d wave functions [3, 17]. It is therefore very likely that p - d exchange, at least for the reported materials, is dominated by the variation of the Cr d -level position relative to the valence band in ZnSe _{y} S _{z} . Photoemission experiments would be very helpful in shedding some light onto this problem.

6. Conclusions

The novel features of Cr-SMSC can be summarized as follows:

- The magnetic behaviour of these materials is an intermediate one, between Brillouin-type, typical for Mn- and Co-SMSC, and Van Vleck-type observed for Fe-SMSC. The reason of such a behaviour is a strong, static Jahn-Teller distortion suffered by the ground term of Cr ions. A simple crystal field model taking into account the JT effect provides a reasonable description of the experimental data, although the low temperature thermodynamics of the Cr ion system is not well understood.

- The relation between conduction and valence band splittings, and macroscopic magnetization seems to be the same as for all the other SMSC (i.e. the band splittings follow the magnetization). This strongly suggests that s , p - d exchange interaction can be assumed in a simple Heisenberg form. The exchange parameters of Cr-SMSC are however unique: ferromagnetic p - d exchange was not observed in any other II-VI SMSC. Whether the sign of p - d exchange results from the new exchange channels present for Cr ions, or the particular location of the Cr d -level relative to the valence band, remains an open question.

In view of F p - d exchange one cannot exclude F coupling (d - d exchange) between Cr ions (which would be very important for possible applications of SMSC). One should however remember that the final character of d - d exchange will result from F and AF contributions, since the latter is still effective in the Cr case. Experimental verification of the d - d exchange sign is necessary. This will however be difficult without the crystals with higher Cr concentration. Hopefully the epitaxial techniques (MBE) could solve the problem.

Finally we notice that the new aspects of exchange interaction observed for Cr-SMSC should also be present in materials with other transition metal ions with a less than half filled d shell (Sc, Ti, V). We believe that the new phenomena found in Cr-SMSC will stimulate the understanding of the nature of both p - d and d - d exchange in SMSC.

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