Magnetoreflectance and magnetization of the semimagnetic semiconductor Zn$_{1-x}$Fe$_x$Se

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Magnetoreflectance measurements of excitonic interband transitions are used to study the exchange interaction between band electrons and localized Fe d electrons in cubic Zn$_{1-x}$Fe$_x$Se ($x < 0.06$) at $T = 1.9$ K and $B < 5$ T. Combining exciton splitting with the magnetization of the same samples, we determined the conduction- and valence-band exchange constants $N_0\alpha = 0.25$ eV and $N_0\beta = -1.76$ eV.

I. INTRODUCTION

The interesting magnetic and optical properties of semimagnetic semiconductors [SMSC's (Ref. 1)] result from the coexistence and interaction of two electronic subsystems in these materials: localized d electrons (giving rise to localized magnetic moments) and delocalized band electrons.[1] Fe SMSC's represent a special case, since Fe^{++} substitutional ions possess both spin and orbital momenta ($S = 2, L = 2$). This situation leads to the appearance of a field-induced magnetic moment associated with the Fe ion[2,3] (in contrast, Mn^{++} and Co^{++} can be considered as spin-only ions, characterized by permanent magnetic moments.[1]). The exchange interaction between d electrons and band electrons results in strong band splittings, which were reported for Cd$_{1-x}$Fe$_x$Se,[4-7] Cd$_{1-x}$Fe$_x$Te,[8] and Zn$_{1-x}$Fe$_x$Se.[9] The available exciton-splitting and magnetization data indicate that band splittings are parametrized by macroscopic magnetization, similarly as was for Mn SMSC's.[1,10] For Zn$_{1-x}$Fe$_x$Se this conclusion is, in fact, based on the results obtained for only one sample.[9] Moreover, the final value of the exchange constant in this case was underestimated due to the simple model used to describe the Fe ion.[9] We therefore thought it worthwhile to complete the data for this material. We studied the magnetoreflectance and magnetization of a new set of Zn$_{1-x}$Fe$_x$Se crystals with the aim of determining the exchange constants for the conduction and valence bands.

II. THEORETICAL BACKGROUND

The s,p-d exchange interaction between delocalized band electrons and localized d electrons of magnetic ions in SMSC's is usually described in a Heisenberg-type form:[1] $H_{\text{ex}} \sim \mathbf{S} \cdot \mathbf{j}$, where $\mathbf{S} = (S_x, S_y, S_z)$ is the magnetic

ion spin and $\mathbf{j} = (j_x, j_y, j_z)$ is the quasiangular momentum operator of a band electron. This simple form of the exchange Hamiltonian is only true in particular situations: an electron from the conduction band ($j = \frac{1}{2}$) interacting with *any* magnetic impurity, or a valence-band electron ($j = \frac{3}{2}$) interacting with a *special* magnetic ion, namely the ion with vanishing orbital momentum of the ground state (i.e., Mn^{++}). In all other cases non-Heisenberg terms should be included,[11] as a consequence of the fact that the dominant part of the p-d exchange originates from the strong hybridization between the valence band and t orbitals of the d-shell electrons.[12,13] Only in the case of single occupation of t orbitals can non-Heisenberg terms be neglected.[11] Actually, this is the case for Fe SMSC's ($d^6 = e_+^2 t_+^3 e_-^1 t_-^0$) as well as for Co SMSC's ($d^7 = e_+^2 t_+^3 e_-^2 t_-^0$). Therefore, for all these SMSC's, the Heisenberg Hamiltonian constitutes a good approximation of the s,p-d interaction. In the spirit of the mean-field theory and virtual-crystal approximation, the exchange Hamiltonian can be written in the following form:[1,14]

$$H_{\text{ex}} = -JN_0 x \langle \mathbf{S} \rangle \cdot \mathbf{j} , \qquad (1)$$

where J is the exchange constant, N_0 is the number of unit cells in unit volume, and x is the Fe concentration.

It was shown[5,6] that even in the case of the Fe^{++} ion, which has nonvanishing orbital momentum, the mean spin of an Fe ion $\langle S \rangle$ is proportional to the magnetic moment $\langle M \rangle = \langle L + 2S \rangle$: $\langle S \rangle = k \langle M \rangle$, where $k = 0.447$ for Zn$_{1-x}$Fe$_x$Se, whereas, for the spin-only case, $k = \frac{1}{2}$. The smaller k value (with respect to the spin-only case) reflects the contribution of nonvanishing orbital momentum to the magnetic moment. We notice that this contribution is rather small ($\approx 10\%$), since it results from the admixture of the excited ^5T term.[15] The

coefficient k depends slightly on temperature as well as on magnetic field, but its variation is far below the typical experimental accuracy of exciton splitting, and we therefore assume a constant k value in further considerations.

A similar analysis performed for an Fe-Fe pair[16,5] shows that also in this case, spin is proportional to the pair magnetic moment (with the coefficient $k=0.462$ for $Zn_{1-x}Fe_xSe$). The difference in k for isolated ions and pairs is irrelevant and, therefore, one can assume that macroscopic magnetization measures $\langle S \rangle$ (at least for dilute systems) and that the proportionality factor k is practically the same as for a single ion. Under this assumption, we get for the magnetization

$$M_m = \langle M \rangle (\mu_B x/m) = (\langle S \rangle /k)(\mu_B x/m) , \qquad (2)$$

where

$$m = (1-x)m_{Zn} + xm_{Fe} + m_{Se} = m_{mole}/N_{av}$$

is the mass of a SMSC molecule, and μ_B is the Bohr magneton (we have also neglected the opposite directions of M_m and S).

The band structure of SMSC's is obtained by diagonalization of the well-known band Hamiltonian[17,18] augmented by the exchange Hamiltonian (1). For details of the calculations, we refer to Refs. 18 and 5.

The resulting band structure of $Zn_{1-x}Fe_xSe$ is shown in Fig. 1. We note linear splitting of the conduction band $E_c = E_g \pm \tau$ and $j = \frac{3}{2}$ valence band $E = \pm \delta$, where E_g is the energy gap, $\tau = \frac{1}{2}(N_0\alpha)x\langle S \rangle$, $\delta = \frac{1}{2}(N_0\beta)x\langle S \rangle$, and $\alpha = \langle S|J|S \rangle, \beta = \langle X|J|X \rangle$ are exchange integrals for the conduction and valence bands, respectively.[14] Consequently, optical transitions from the valence band to the conduction band can be used for the determination of $N_0\alpha - N_0\beta$:

$$\Delta E = E_D - E_A = (N_0\alpha - N_0\beta)x\langle S \rangle$$
$$= (N_0\alpha - N_0\beta)mkM_m/\mu_B , \qquad (3)$$
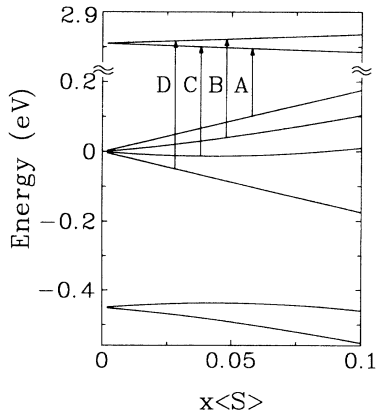

FIG. 1. Calculated diagram of energy levels of the conduction and valence bands of $Zn_{1-x}Fe_xSe$ as a function of $x\langle S \rangle$. The following parameters were used: $\Delta = 0.15$ eV, $E_g = 2.81$ eV, $N_0\alpha = 0.25$ eV, and $N_0\beta = -1.76$ eV. The arrows indicate observed optical transitions.

where E_D and E_A are energies of the optical transitions A and D denoted in Fig. 1.

III. EXPERIMENT

Our $Zn_{1-x}Fe_xSe$ crystals were grown by the modified Bridgman (high-pressure) method. The crystalline structure was cubic. The actual Fe concentration of the samples was determined by microprobe analysis. It was found that the Fe concentration can vary by 10–15 % of the actual concentration along the sample. For the samples for which no microprobe checking was performed, we estimated x from the zero-field exciton energy versus concentration dependence. We note that this procedure provides only local concentration checking. The full specification of our samples is presented in Table I.

We measured free-exciton magnetoreflectance in the Faraday configuration (light wave vector parallel to the magnetic field) for circularly polarized light (σ^+, σ^- polarizations) at $T=1.9$ K and magnetic field $B=5$ T. The magnetic field was oriented along the (110) direction. The reflectance was measured on cleaved surfaces and neither mechanical polishing nor chemical etching was performed.

The magnetization was measured by means of a superconducting-quantum-interference-device (SQUID) magnetometer. The data were obtained on the same samples on which magnetoreflectance was measured. Previous investigations of Fe SMSC's [$Cd_{1-x}Fe_xSe$,[19] $Zn_{1-x}Fe_xSe$,[9] and $Zn_{1-x}Fe_xS$ (Ref. 20)] suggested the existence of some paramagnetic impurities in the crystals other than Fe^{++}. The concentration of these impurities was estimated at about 1% of the actual Fe^{++} content.[20]

IV. MAGNETIZATION

In Fig. 2, we show examples of magnetization (per unit mass) data for $Zn_{1-x}Fe_xSe$: $x=0.014$ (No. 1), 0.03 (No. 3), 0.037 (No. 4), and 0.059 (No. 9) at $T=1.9$ K as a function of magnetic field. The presented data reveal features typically observed for Fe SMSC's (Ref. 3) and characteristic for a field-induced magnetic moment.

We recall that the ground state of the Fe^{++} free ion

TABLE I. Conduction- and valence-band exchange-constant differences for samples studied.

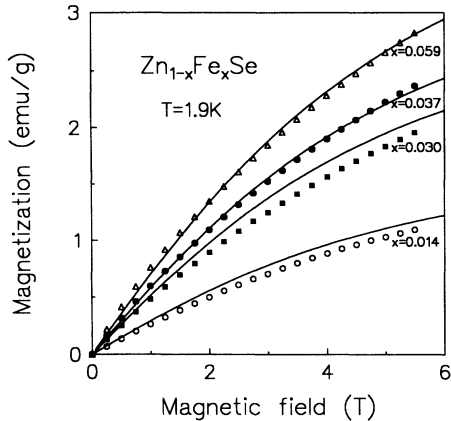| Sample no.	x	$N_0\alpha - N_0\beta$ (eV)
1	0.014±0.001	2.29±0.05
2	0.014±0.002	2.27±0.05
3	0.03±0.004	1.88±0.05
4	0.037±0.01	1.66±0.02
5	0.042±0.006	1.63±0.02
6	0.040±0.005	2.09±0.06
7	0.051±0.006	1.94±0.04
8	0.058±0.002	2.53±0.07
9	0.059±0.002	1.82±0.04
10	0.06±0.01	1.93±0.04
11	0.06±0.01	2.05±0.03

FIG. 2. Magnetization of $Zn_{1-x}Fe_xSe$ at $T=1.9$ K for B parallel to the (110) direction. The solid lines show calculated magnetization as described in Sec. IV.

(^5D) is split by a tetrahedral crystal field into a ^5E orbital doublet and a higher-lying ^5T orbital triplet (separated from ^5E by $10Dq \approx 3000$ cm^{-1}, where Dq is the crystal-field parameter). Spin-orbit interaction splits the ^5E term into a singlet A_1, a triplet T_1, a doublet E, a triplet T_2, and a singlet A_2 (the energy separation between these states is approximately equal to $6\lambda^2/10Dq$, where λ is the spin-orbit parameter).[21,15,22,23] Thus, the ground state is a magnetically inactive singlet A_1. Field-induced mixing between the ground and the excited (magnetically active) states results in Van Vleck–type paramagnetism.[15,22]

Magnetic properties (magnetization, specific heat, susceptibility) of Fe SMSC's are usually described using the "crystal-field model".[15,16] In this model one assumes that the Fe-ion system can be factorized into Fe-Fe pairs coupled by principally long-range interaction [the so-called extended nearest-neighbor pair approximation (ENNPA) (Refs. 24 and 25)]. Calculations (for both cubic and hexagonal structures) showed that the long-range interaction is not as relevant for Fe-based SMSC's as it was for Mn-type SMSC's and, therefore, the ion system can be factorized into NN pairs and isolated (i.e., having no magnetic NN) ions only.[3,16] Moreover, in our field range the Fe-Fe pairs contribution is typically smaller by two orders of magnitude than the isolated ions contribution.[5] Finally, magnetization per ion can be described by isolated ions only:

$$M = \mu_B \langle M \rangle_s P_s(x) , \qquad (4)$$

where $\langle M \rangle_s$ is the magnetic moment of an isolated ion and $P_s(x)$ is the probability that the ion has no magnetic NN. $P_s(x)=(1-x)^{12}$, assuming random distribution of Fe ions in the crystal. $\langle M \rangle_s$ can be evaluated using eigenstates of Fe^{++} ions. For details of the calculations we refer to Refs. 5 and 26.

In our case, the Hamiltonian matrix is parametrized only by two material parameters: Dq and λ. The resulting energies can be thus used for estimation of these parameters. For that, we used measured energies of optical transition $A_1 \rightarrow T_1$ [15.8 cm^{-1} (Ref. 29)] and $A_1 \rightarrow T_2$

[46.2 cm^{-1} (Ref. 29)], as well as the zero-phonon-line energy for the $^5E \rightarrow {}^5T$ transition [2738 cm^{-1} (Ref. 30)]. The best fit was found for $Dq=294.3$ cm^{-1}, $\lambda=-92.8$ cm^{-1} (calculated energies: 14.4, 46.6, and 2738 cm^{-1}).

Numerical solutions of the Fe-ion Hamiltonian are used for calculating magnetic moment $\langle M_z \rangle$. Finally, macroscopic magnetization (per unit mass) reads

$$M_m(x)=\mu_B(x/m)\langle M \rangle_s P_s . \qquad (5)$$

In Fig. 2, we show results of magnetization calculations for some of our crystals. We find satisfactory matching with the experimental data even for $x=0.059$, which is a rather high concentration. We note that the proposed model is limited to low concentrations, typically $x < 0.04$, where contributions from large clusters can be neglected.[5] Reasonable matching in our case, even for higher concentrations, results from a rather limited field range, where antiferromagnetically coupled clusters (pairs, triples, etc.) contribute negligibly to the magnetization.[3,5] Contributions from the clusters is clearly demonstrated for still-higher x ($x > 0.1$) or at higher fields.[3,31]

Nevertheless, we point out that for a limited field range and concentration ($x < 0.05$), the overall shape of the magnetization is the same for all the samples, and the magnetization scales with concentration [scaling factor $x(1-x)^{12}$]. We also note that observed deviations between experimental data and theory for $x=0.014$ and 0.03 can be accounted for by concentration uncertainty (cf. Table I).

V. MAGNETOREFLECTANCE

Exciton magnetoreflectance was measured in the range of fundamental energy gap and optical transitions A,B (σ^+, Fig. 1) and C,D (σ^-, Fig. 1) were observed. In Fig. 3 we present examples of the variation of exciton energies with magnetic field for $x=0.051$ (No. 7).

In Fig. 4 we plot exciton splitting $\Delta E = E_D - E_A$ versus mkM_m/μ_B, as suggested by Eq. (3), for some of
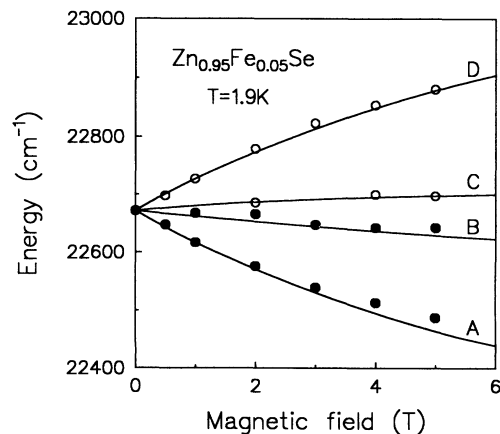

FIG. 3. Energies of the exciton lines [A,B (σ^+); C,D (σ^-)] in $Zn_{0.949}Fe_{0.051}Se$ (No. 7) at $T=1.9$ K for $B\|(110)$. The lines show results of theoretical calculations with $N_0\alpha=0.25$ eV and $N_0\beta=-1.76$ eV and experimental magnetization.
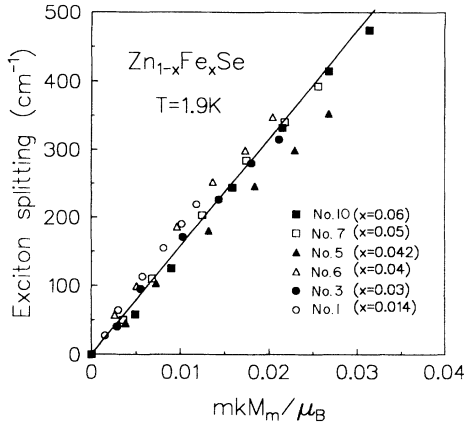
FIG. 4. Exciton splitting $(E_D - E_A)$ of $Zn_{1-x}Fe_xSe$ vs magnetization expressed in mkM_m/μ_B. $T = 1.9$ K and $B \| (110)$. The straight line shows theoretical dependence for $N_0\alpha - N_0\beta = 2.01$ eV.

our samples. We find that exciton splitting is proportional to the magnetization for each sample with reasonable accuracy. We evaluated $N_0\alpha - N_0\beta$ for each sample by fitting a straight line for each data set (Table I). We note rather large differences in $(N_0\alpha - N_0\beta)$ for different samples. We believe that this situation results from a variation of local Fe concentration along the samples. Magnetization as measured by us is a volume average and is therefore characteristic for the average concentration of the sample. On the other hand, exciton reflectance probes the local (near-surface) x value. The difference between the average and local x results in different slopes, although exciton splitting is still proportional to magnetization due to the fact that the overall shape of magnetization is only weakly x dependent (Sec. IV). Finally, we take the average value 2.01 ± 0.08 eV for $N_0\alpha - N_0\beta$, which is very close to the value 2.00 eV resulting from the previous data[9] [we note that originally in Ref. 9 the value $N_0\alpha - N_0\beta = 1.79$ was given, assuming $k = \frac{1}{2}$ (Ref. 21) instead of $k = 0.447$ (see Sec. II)]. This should be considered a fortunate coincidence, in view of the scattering of the data for different samples (Table I). The present value is more reliable, since it is based on measurements on a large set of samples. Similarly as in $Cd_{1-x}Fe_xSe$,[5] the correction for paramagnetic impurities present in our crystals is smaller than the experimental error and was therefore neglected.

The individual values of $N_0\alpha$ and $N_0\beta$ can be evaluated

with the help of splittings of exciton lines B and C, since[14]

$$\beta/\alpha = (r + 1)/(r - \tfrac{1}{3}) , \tag{6}$$

where $r = (E_C - E_B)/(E_D - E_A)$. Utilizing the value $\beta/\alpha = -7.0 \pm 0.7$ resulting from all the investigated samples we obtained

$$N_0\alpha = (0.25 \pm 0.03) \text{ eV} , \tag{7}$$
$$N_0\beta = (-1.76 \pm 0.09) \text{ eV} .$$

Using these values, one can calculate precisely the band structure with the experimental magnetization as a parameter. The result is exemplified in Fig. 3 (we stress that no further fitting procedure was performed). We find reasonable agreement between experimental data and our model, which shows that band splittings are, in fact, parametrized by macroscopic magnetization, as predicted in Sec. II. Finally, we comment on chemical trends of the exchange interactions observed for SMSC's. We notice that the obtained exchange constants are very close to the values reported for $Cd_{1-x}Fe_xSe$ [$N_0\alpha = 0.25$,[4] 0.26,[6] $N_0\beta = -1.45$,[7] -1.53,[6] and -1.6 (Ref. 5)]. The valence-band constant is substantially higher for Fe SMSC's than was reported for Mn SMSC's [typical value -1 eV (Ref. 1)], which indicates stronger p-d hybridization for Fe SMSC's. It is expected that stronger hybridization (monitored by $N_0\beta$) is correlated with stronger d-d coupling. Such a correlation is indeed observed for SMSC's. Typical d-d exchange constants for Mn SMSC's are $8 \text{ K} < |J_{dd}| < 16 \text{ K}$,[1] whereas for Fe SMSC's, $|J_{dd}|$ is about 20 K.[3] A detailed analysis of chemical trends in d-d and p-d exchange requires further study, in particular the superexchange theory for Fe SMSC's must be developed [see K. Hass in Ref. 1(b)] and information about the location of d levels must be gathered.

VI. CONCLUSIONS

We have confirmed the earlier observation for cubic $Zn_{1-x}Fe_xSe$ that conduction- and valence-band splittings are parametrized by macroscopic magnetization. Combining free-exciton splitting data with the magnetization results, we evaluated the exchange integrals for conduction and valence bands. We have also shown that for limited Fe concentration and magnetic-field range ($x < 0.05$, $B < 5$ T) the major contribution to the magnetization results from the noninteracting Fe ions, which is well described in the simple crystal-field model.

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