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The s-d and p-d exchange interaction in $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$

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The exciton splitting induced by the s-d and p-d exchange interaction in $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ ($x<0.005$) was studied by polarized magnetoreflectance. Data were taken at 2 K in magnetic fields up to 5 T. Combining these results with magnetization data, a value $(N_0\alpha-N_0\beta)=2.1\pm0.4$ eV was obtained for the difference between the s-d and p-d exchange constants. Assuming that $N_0\alpha=+0.2$ eV, the p-d exchange is antiferromagnetic, with a magnitude $N_0\beta=-1.9$ eV.

I. INTRODUCTION

One of the most interesting features of diluted magnetic semiconductors (DMS's) is the strong exchange interaction between localized electrons (d or f) and delocalized electrons (s-like) or holes (p-like). This interaction leads to large conduction- and valence-band splittings in the presence of a magnetic field, which result in spectacular magneto-optical effects such as giant Faraday rotation.[1] The available data for the s-d exchange show that in II-VI DMS's this interaction is largely independent of the host lattice or the magnetic ion.[1] On the other hand, the p-d exchange varies strongly with both host lattice and magnetic ion. In particular for all DMS's with Mn, Fe, and Co the p-d exchange is antiferromagnetic, whereas for Cr-based DMS's it is ferromagnetic.[2–4] The strong variation of the p-d exchange results from the fact that this interaction is due to the kinetic exchange, which strongly depends on the energy separation between the p and d levels as well as on the overlap of the p and d wave functions (hybridization).[5–8]

During recent years substantial progress has been made in understanding the microscopic origins of the s-d and p-d exchange.[6–8] In particular, both the sign and the form of s-d and p-d exchange Hamiltonian for Mn-, Co-, and Fe-based DMS's were reproduced by theoretical calculations.[6] However, a detailed analysis of the chemical trends is still to be done. Moreover, for DMS systems with magnetic ions other than Mn the experimental data too are rather limited. For Fe-based DMS's, exchange parameters were reported only for $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Se}$,[9] $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Se}$,[10–12] and $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Te}$.[13] More complete data will be needed for testing future theoretical models. Here we report on a study of the s-d and p-d exchange in $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ crystals using free-exciton spectroscopy. Crystals of $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ were grown only recently.

II. THEORETICAL BACKGROUND

In the presence of an external magnetic field **B** both conduction and valence bands undergo strong, exchange-induced, splittings.[1,14] Free-exciton spectroscopy, which studies optical transitions directly affected by the band splittings, is a powerful tool for measuring the s-d and p-d exchange interactions. In the Faraday configuration (**B** parallel to the light wave vector) four exciton lines are visible: two of them in the σ^+ polarization (lines A and B) and the other two in the σ^- polarization (lines C and D). Assuming a Heisenberg form for the s-d and p-d exchange interactions, the energies of the exciton lines in a cubic crystal are given by[14]

$$E_A=E_0+3b-3a,\quad E_B=E_0+b+3a,$$
$$E_C=E_0-b-3a,\quad E_D=E_0-3b+3a,\qquad(1)$$

where E_0 is the zero-field exciton energy, $a=(1/6)N_0\alpha x(-\langle S\rangle)$, $b=(1/6)N_0\beta x(-\langle S\rangle)$, $N_0\alpha$ and $N_0\beta$ are exchange integrals for conduction and valence bands, respectively, and $\langle S\rangle$ is the average component of the spin of the magnetic ion along **B**. Lines A and D are three times more intense than B and C. The splitting of the strong lines A and D provides a direct measure of the difference between the exchange constants

$$E_D-E_A=(N_0\alpha-N_0\beta)x(-\langle S\rangle).\qquad(2)$$

The average spin $\langle S\rangle$ is obtained experimentally from the macroscopic magnetization M (per unit mass),

$$M=-\frac{\mu_B x}{m}\langle L+2S\rangle=\frac{\mu_B x}{m}\frac{(-\langle S\rangle)}{k},\qquad(3)$$

where $k=\langle S\rangle/\langle L+2S\rangle$, μ_B is the Bohr magneton, and m is the average mass of the $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ molecule. The parameter k is equal to 1/2 for a spin-only magnetic moment, but $k<1/2$ for the Fe^{2+} ion due to the contribution of the orbital angular momentum to the magnetic moment.[9,10] Combining Eqs. (2) and (3), the difference between the exchange parameters is given by[15,14]

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$$N_0\alpha - N_0\beta = \frac{E_D - E_A}{M}\,\frac{\mu_B}{mk}, \tag{4}$$

which is independent of Fe concentration x.[16] In the case of a strong exciton splitting all four lines are resolved and the $N_0\alpha, N_0\beta$ parameters can be obtained individually using the ratio of the strong and the weak exciton-line splittings

$$\frac{E_D - E_A}{E_C - E_B} = \frac{(\beta/\alpha) - 1}{\frac{1}{3}(\beta/\alpha) + 1}. \tag{5}$$

This procedure cannot be used when the exciton splitting is small compared with the exciton linewidth, because lines with the same polarization (A and B or C and D) are not resolved. In this case it is usually assumed that the excitonic structure observed with a certain polarization consists only of the strong exciton line (A or D) since the other line (B or C) is much weaker. Obviously this is only an approximation; an analysis based on this assumption may underestimate the $E_D - E_A$ splitting by 10–20 %.[2] When the weak lines are neglected, Eq. (5) cannot be used. The two exchange integrals can then be obtained individually only if one of them is determined by other means. Typically, spin-flip Raman scattering is used to obtain $N_0\alpha$.[17]

III. RESULTS AND DISCUSSION

The $Zn_{1-x}Fe_xTe$ crystals used in this work were grown by the modified Bridgman method. Single-phase crystals were obtained only for rather low Fe concentrations $x \leqslant 0.005$. Attempts to grow crystals with higher x resulted in ferromagnetic precipitates (presumably iron telluride), which manifested themselves as hysteresis loops in the magnetization curves. For the present study we selected two crystals with the smallest content of such precipitates. The Fe concentration was $x = 0.003$ and 0.004. For such low x the usual methods of concentration determination (e.g., electron microprobe or wet chemical analysis) could not provide a satisfactory accuracy. Instead, we estimated x from the magnetization of the sample (see Ref. 9 for details). As pointed out above, in connection with Eq. (4), the exact value of x does not enter into the determination of the exchange constants.

The exciton splitting induced by the s-d and p-d exchange was studied at 2 K by measuring the reflectance in a magnetic field up to 5 T. Typical reflectance spectra for the σ^+ and σ^- polarizations at 5 T are shown in Fig. 1(a). The exciton splitting is clearly visible, although even at this highest field the splitting is smaller than the excitonic-structure width. Because of the small splittings, the two lines for each polarization (lines A and B or C and D) are not resolved. Following the usual practice in such a situation, we ascribe the observed splitting between the σ^+ and σ^- components to the energy difference $E_D - E_A$ between the two strong lines (see Sec. II). Figure 1(a) shows that the σ^+ structure (ascribed to line A) is at a lower energy than the σ^- stucture (predominantly line D). The observed sign of the splitting between the σ^+ and σ^- components is typical for all Fe-, Mn-, and Co-based DMS's. It corresponds to a positive $(N_0\alpha - N_0\beta)$. In all DMS's studied thus far, $|\beta|$ is much larger than $|\alpha|$. Assuming this to be the case here, $N_0\beta$ is negative, i.e., antiferromagnetic p-d exchange.[1,14]

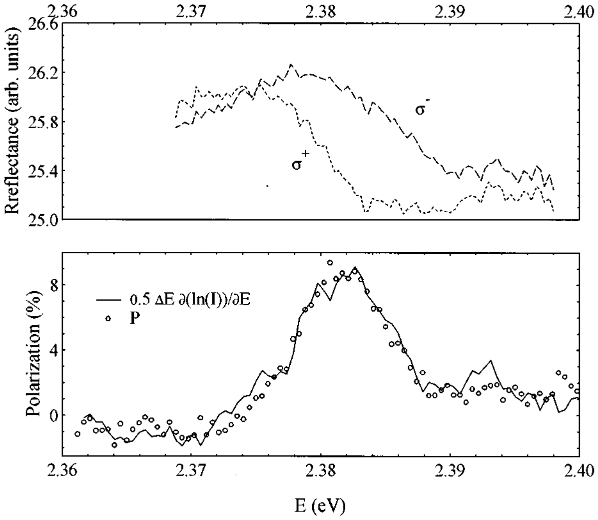

FIG. 1. (a) Reflectance spectra for $Zn_{1-x}Fe_xTe$, $x = 0.003$. (b) Degree of polarization $\mathscr{P}$ of the reflectance, Eq. (3), and the spectrum for $-0.5\Delta E\,\partial \ln I(E)/\partial E$. All the results are for $T = 2$ K and $B = 5$ T. The data for $\mathscr{P}$ were obtained by modulating the reflected light. The data in (a) are from a different experiment, with two fixed polarizations.

Because the splitting between the σ^+ and σ^- components was small, a direct determination of the magnitude of this splitting from the σ^+ and σ^- spectra was of rather poor accuracy. This was particularly true at low fields. A more precise determination of the magnitude of the splitting was obtained by measuring the degree of polarization $\mathscr{P}$ of the reflected light

$$\mathscr{P} = \frac{I(\sigma^-) - I(\sigma^+)}{I(\sigma^-) + I(\sigma^+)}, \tag{6}$$

where $I(\sigma^\pm)$ is the light intensity at a given polarization. Values of $\mathscr{P}$ were obtained by modulating the polarization of the reflected light.[18,3] The exciton splitting ΔE was obtained by combining the polarization and reflectance spectra using the equation[18]

$$\Delta E \approx \frac{2\mathscr{P}(E)}{-\dfrac{\partial}{\partial E}\ln I(E)}, \tag{7}$$

where $I(E) = \frac{1}{2}[I(\sigma^+) + I(\sigma^-)]$.

Figure 1(b) shows the spectrum of $\mathscr{P}$ versus E. The fact that this spectrum exhibits a peak, rather than a dip, in the middle of the excition energy range indicates that $E(\sigma^+) < E(\sigma^-)$. Of course this conclusion can be reached more directly from the spectra in Fig. 1(a).

Equation (7) is valid only when the σ^+ and σ^- spectra have the same shape and when the energy splitting is small, roughly no larger than the structure width. In such a situation the shapes of the spectra for $\mathscr{P}$ versus E and $-\Delta E\,(\partial/\partial E)\,[\ln I(E)]$ versus E should be the same. The splitting ΔE is then obtained from Eq. (7). If the forms of the σ^+ and σ^- spectra are different, the polarization spectrum

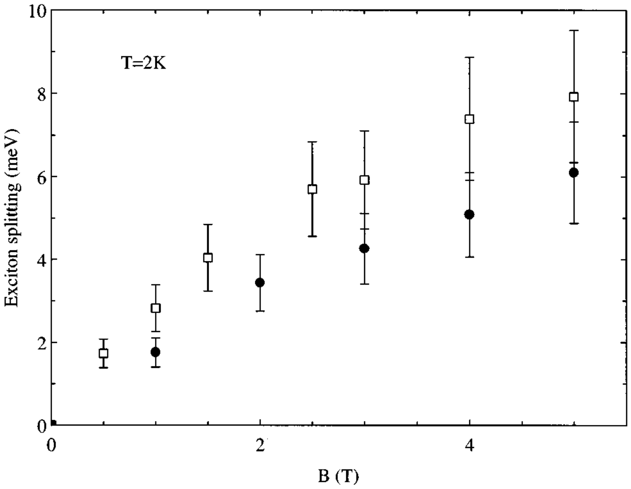

FIG. 2. Exciton splitting $E(\sigma^-)-E(\sigma^+)$ of $Zn_{1-x}Fe_xTe$, $x=0.003$ and 0.004, versus magnetic field B. These results were derived from data for $\mathscr{P}$ and for $-\partial \ln I(E)/\partial E$ using Eq. (7).

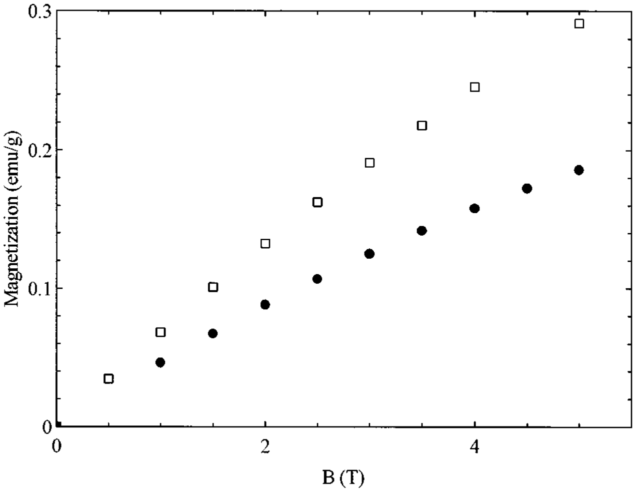

FIG. 3. Magnetization of $Zn_{1-x}Fe_xTe$, $x=0.003$ and 0.004, versus magnetic field B at $T=2$ K.

cannot be reproduced by a simple scaling of the logarithmic-derivative spectrum. The procedure based on Eq. (7) can then lead to substantial errors. In the present case both spectra are of the same shape, as shown in Fig. 1(b), which justifies the use of the method for $Zn_{1-x}Fe_xTe$. The exciton splitting was actually determined as the ratio of the heights of the peaks for both spectra. To obtain the peak height, a linear background was assumed and subtracted. This background correction was rather small. At the highest fields the splitting ΔE obtained directly from the energy separation between the σ^+ and σ^- spectra agrees with that derived from the polarization spectrum, within the experimental accuracy. To obtain the exchange contribution to ΔE, the splitting in pure ZnTe (Ref. 19) was subtracted. Figure 2 shows the exchange exciton splitting for the two $Zn_{1-x}Fe_xTe$ crystals as a function of magnetic field at 2 K. The error bars indicate the estimated overall accuracy. The field variation of the exchange exciton splitting in Fig. 2 is similar to that observed for other Fe-based DMS's.[20]

In order to estimate the exchange constants using Eq. (4), the magnetization of the very same samples was measured at 2 K using a superconducting quantum interference device magnetometer. The data [corrected for diamagnetic susceptibility of pure ZnTe: $\chi_d=-3.0\times10^{-7}$ emu/g (Ref. 21)] are shown in Fig. 3. The observed field variation is typical for Fe-based DMS's.[22]

The exciton splitting as a function of magnetization is displayed in Fig. 4. There is no difference between the data for the two samples, within the experimental error, indicating that the samples were reasonably homogeneous.[9] The data points seem to show a slight bending with increasing magnetization. However, the accuracy of the results is insufficient for concluding that this bending is significant. Therefore, the data were fit by a straight line, following Eq. (4). From the slope of this line, $\Delta E/M=32.5\pm7.3$ meV/(emu/g), the value $N_0\alpha-N_0\beta=2.1\pm0.4$ eV was obtained. Here we used the value $k=0.447$.[23] The present result for $N_0\alpha-N_0\beta$ is comparable to those reported for other Fe-based DMS's.[9–13]

Since in the present experiment the two exciton lines for the same polarization could not be resolved, the integrals $N_0\alpha$ and $N_0\beta$ could not be determined individually. Also, we are not aware of any other data for $Zn_{1-x}Fe_xTe$ that give the extra information needed for determining these exchange constants separately. On the other hand, as mentioned in Sec. II, the conduction-band integral $N_0\alpha$ is fairly independent of the magnetic ion and of the host lattice. In fact, the reported values of $N_0\alpha$ in II-VI DMS's are all in the range $0.2-0.25$ eV.[1] We therefore assumed $N_0\alpha=0.2$ eV for $Zn_{1-x}Fe_xTe$, which led to the estimate $N_0\beta=-1.9\pm0.45$ eV. This value for $N_0\beta$ is comparable to, but probably slightly larger than, those reported for other Fe-based DMS's: -1.27 eV for $Cd_{1-x}Fe_xTe$,[13] -1.60 eV for $Cd_{1-x}Fe_xSe$,[10,12] and -1.76 eV for $Zn_{1-x}Fe_xSe$.[9] All these values are negative, as is the case of Mn-based DMS's but in contrast to the positive $N_0\beta$ for Cr-based DMS's. The value of $N_0\beta$ in $Zn_{1-x}Cr_xTe$ is unusually large compared to the other Cr-based DMS's.[4] The present results show that this "anomaly" does not occur for $Zn_{1-x}Fe_xTe$.

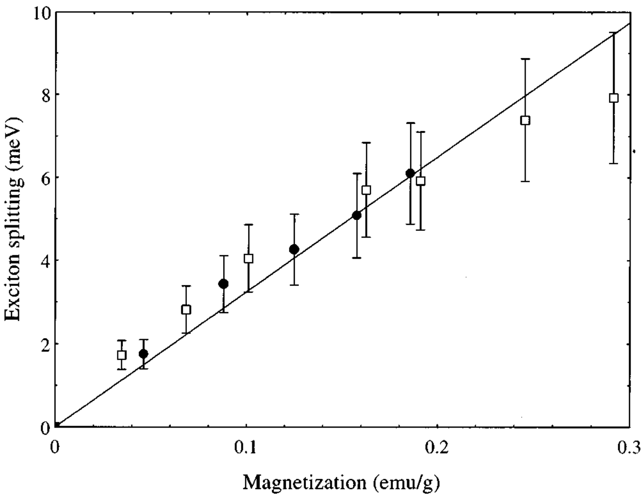

FIG. 4. Exciton splitting $E(\sigma^-)-E(\sigma^+)$ of $Zn_{1-x}Fe_xTe$, $x=0.003$ and 0.004, versus magnetization. The straight line corresponds to $(N_0\alpha-N_0\beta)$ = 2.1 eV.

Finally, we comment about possible spin-disorder effects.[24,25] Such effects are known to affect strongly the exciton splitting in crystals with low x and may lead to an overestimate of $N_0\beta$.[26] This problem results from the variation of $\Delta E/(x\langle S\rangle)$ with magnetic ion concentration. For instance, in the case of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{S}$ $N_0\beta$ determined from the ratio $\Delta E/(x\langle S\rangle)$ decreases about 40% from $x=0.001$ to 0.01.[24,25] Whether a similar situation occurs in the present work is not entirely certain at the present stage, since no appropriate calculations were done for $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$. For the present data no decrease of $N_0\beta$ was observed when x changed from 0.003 to 0.004 (Fig. 4), which could suggest that either spin-disorder effects are small for $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ or x was large enough for spin-disorder to be ineffective. One should, however, take into account that in the case of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{S}$ the expected decrease of $N_0\beta$ between $x=0.003$ and 0.004 is only about 6%. Such a decrease, if true for $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$, is below present experimental accuracy, which precludes pertinent conclusions about spin-disorder effects. Therefore appropriate calculations for $\mathrm{Zn}_{1-x}\mathrm{Fe}_x\mathrm{Te}$ are necessary to judge about possible spin-disorder correction for the evaluated $N_0\beta$ parameter.

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