Zeeman splittings of optical transitions at the L point of the Brillouin zone in semimagnetic semiconductors

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Magnetoreflectivity measurements for optical transitions at the L point of the Brillouin zone have been performed on $Zn_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$ alloys. Zeeman splittings of the transition labeled E_1 have been determined for both compounds. Furthermore, we have determined (for the first time in any semimagnetic semiconductor) Zeeman splittings of the $E_1+\Delta_1$ transition in $Hg_{1-x}Mn_xTe$. In $Zn_{1-x}Mn_xTe$, as in previously studied $Cd_{1-x}Mn_xTe$, it was necessary to introduce a variation of the ion-carrier exchange parameter with wave vectors in order to explain the data. The splitting of the $E_1+\Delta_1$ feature in $Hg_{1-x}Mn_xTe$ has been found to have the opposite sign and the equal absolute value as the splitting of the E_1 feature, consistent with the prediction of Ginter *et al.* [Solid State Commun. **48**, 849 (1983)].

INTRODUCTION

Strong ion-carrier exchange interaction in semimagnetic (diluted magnetic) semiconductors results in giant magneto-optical effects, especially at low temperatures.[1] In large gap semimagnetic semiconductors such effects have been studied in detail for interband transitions in the fundamental absorption-edge region. Zeeman splittings of band electron states at the center of the Brillouin zone have been measured and ion-carrier exchange constants determined for a number of compounds, mostly of zinc-blende and wurtzite structures.

For electron states far from the center of the Brillouin zone the situation is very much different, the exchange effects being much less spectacular than at the Γ point. This has been first reported by Dudziak *et al.*,[2] who performed magnetoreflectivity measurements on $Cd_{1-x}Mn_xTe$ alloys in the vicinity of the E_1 reflectivity feature originating from interband transitions at the L point of the Brillouin zone (above 3 eV). Since the width of the structure studied is large (about 100 meV at liquid-He temperatures) and the observed splittings small (a few meV), the authors (as well as their followers) used a polarization modulation technique to determine the splitting values.

A partial explanation of the observed difference in Zeeman splittings between the Γ and L points has been offered by Ginter *et al.*[3] They performed magnetoreflectivity measurements on $Cd_{1-x}Mn_xTe$ for three composition values, $x=0.028$, 0.05, and 0.10, and determined the ratio of the splitting value at the L point to that at the Γ point to be $\Delta E_L/\Delta E_\Gamma=\frac{1}{26}$. In order to relate exchange splittings at different points of the Brillouin zone, they proposed a simple tight-binding model. A calculation based on an assumption of wave-vector-independent ion-carrier exchange constants[4] α and β yielded $\Delta E_L/\Delta E_\Gamma=\frac{1}{4}$, much larger than the experimentally observed value.

The as yet most systematic magneto-optical study of interband transitions at the L point of the Brillouin zone has been performed by Coquillat *et al.*[5] on $Cd_{1-x}Mn_xTe$ in a wide range of alloy compositions ($0.01<x<0.39$) and temperatures ($4.5<T<100$ K). The results of Ref. 5 lead to a single value of the reduction factor $\Delta E_L/\Delta E_\Gamma=\frac{1}{16}$, independent of magnetic field, temperature, or alloy composition. The major part of the difference between Refs. 3 and 5 does not come from the experimental results, but from an omission in Ref. 3 of a factor of $\frac{1}{2}$ in the equation relating the measured degree of polarization to the logarithmic derivative of the reflectivity spectrum [see Eq. (1) in Sec. II, below]. However, even taking this into consideration, the reduction of $\Delta E_L/\Delta E_\Gamma$ calculated by Ginter *et al.*[3] is still much too small to account for the experimental data. Coquillat *et al.*[5] suggest a wave-vector dependence of the ion-carrier exchange integrals as a possible reason of the observed difference.

Some other papers may qualitatively add support to this idea. Bylsma *et al.*[6] and Gaj *et al.*[7,8] have linked temperature and composition variation of the energy gap in semimagnetic semiconductors to the fluctuations of the magnetic ion system. In order to explain the experimental data, the authors[6–8] introduce a strong variation of the ion-carrier exchange interaction as a function of the wave vector within the Brillouin zone.

Since the measured magneto-optical effects at the L point are small (the measured degree of polarization may be well below 1%), only the transition known as E_1 has been studied so far. The next reflectivity feature occurs at an energy $E_1+\Delta_1$, higher by the value of the spin-orbit splitting of the valence band at the L point (about 0.5 eV in II-VI tellurium compounds). Ginter *et al.*[3] predict for the $E_1+\Delta_1$ transition a Zeeman splitting equal in magnitude and opposite in sign to that of the E_1 transition. Since that prediction appears to be more general than the simple tight-binding model used in Ref. 3, it is particularly interesting to test it experimentally.

The purpose of this paper is to obtain and analyze experimental data on the Zeeman splittings at the L point of the Brillouin zone in $Zn_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$, materials not studied before in this respect. In particular we shall extend the measurements to the $E_1+\Delta_1$ transition in $Hg_{1-x}Mn_xTe$.

MATERIALS AND EXPERIMENT

The $Zn_{1-x}Mn_xTe$ and $Hg_{1-x}Mn_xTe$ crystals have been prepared by the Bridgman method at the Laboratoire de Physique des Solides of the Centre National de la Recherche Scientifique, Meudon, France ($Zn_{1-x}Mn_xTe$) and at Purdue University ($Hg_{1-x}Mn_xTe$). They were cut with a wire saw, polished, and etched in a solution of bromine in methanol directly before measurements. The composition of each sample was determined by microprobe analysis.

The thickness of the samples was of the order of 1 mm; the other dimensions were of a few mm. They were not oriented; in most cases the plane of the sample was the easy cleavage plane (110).

The homogeneity of the samples was different for different materials; since optical measurements integrate over the surface of the sample and magnetization results represent a volume average, the only significant inhomogeneity is that across the thickness of the samples. We estimate it to be smaller than $x=0.01$ for $Hg_{1-x}Mn_xTe$, whereas for the other compounds it is much better.

Magnetoreflectivity measurements were performed in the Faraday configuration. The sample was placed in a magneto-optical cryostat (Société des Matériels Cryogeniques) with a split superconducting coil with magnetic field ranging up to 5.5 T. The measurements were carried out at temperatures $4.5<T<100$ K. The source was a tungsten filament lamp, with the light depolarized using a polarization scrambler.

Magnetoreflectivity measurements of the exciton structure at the Γ point were performed in the Faraday configuration using both circular polarizations. The σ^+ and σ^- reflected beams were selected by a circular polarizer setup formed by a polaroid filter and two achromatic Fresnel rhombohedrons.

At the L point, the reflectivity was measured by means of a chopper with a frequency of 23 Hz. At the same time the polarization signal I^+-I^- was measured by means of a Hinds photoelastic modulator with a frequency of 50 kHz (Fig. 1). The two signals were detected by two separate lock-in amplifiers working at respective modulation frequencies, and fed into a Hewlett-Packard HP85B microcomputer which controlled the whole experiment. The measurements were done typically at 2 Å intervals, with a time constant of 0.3 s. The system was adjusted to cancel any polarization modulation signal which might exist in the absence of magnetic field throughout the spectral range of interest.

In order to determine the reflectivity spectra, reference measurements were carried out with a mirror replacing the sample under the same experimental conditions.

In order to reduce the influence of the noise, some measurements were averaged over a number of runs. A smoothing procedure has been also applied.

The three signals: reference I_0, total intensity $I=I^++I^-$ and modulation I^+-I^- were used to calculate the degree of polarization $P=(I^+-I^-)/(I^++I^-)$, and the reflectivity $R=I/I_0$ spectra. The latter has been numerically differentiated.

It was found, similarly as in Refs. 5 and 6, that the polarization spectra reproduced quite well the form of the logarithmic derivative of the reflectivity (Fig. 2). This shows that the magnetic field splits the reflectivity spectrum into two components of equal magnitude, observed in the σ^+ and σ^- circular polarizations, respectively, without changing the form of the spectrum. In such a situation the splitting ΔE between the two components may be determined from the following equation:[5]

$$P=\tfrac{1}{2}\Delta E\frac{d(\ln R)}{dE}\ . \tag{1}$$

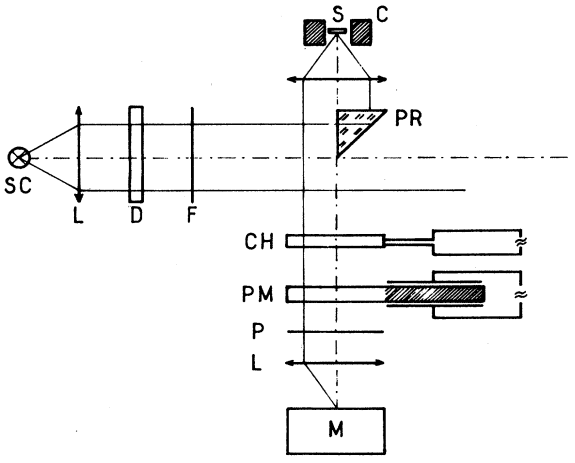
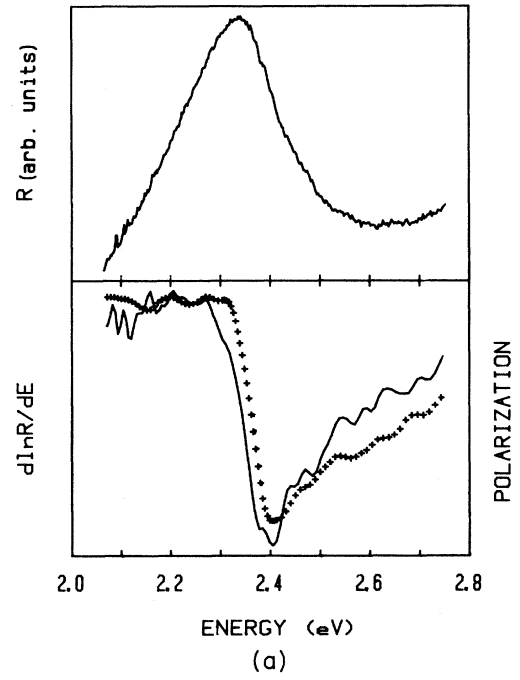


FIG. 1. Experimental setup for modulation magnetoreflectivity measurements: SC, source; *L*, lenses; *F*, filter; *D*, depolarizer; PR, reflecting prism; *S*, sample; *C*, superconducting coil; CH, chopper; *P*, polarizer; PM, photoelastic modulator; *M*, monochromator.

NEW RESULTS

For $Zn_{1-x}Mn_xTe$, polarization modulation measurements were performed for two alloy compositions: $x=0.02$ and 0.17. The experiments were carried out at



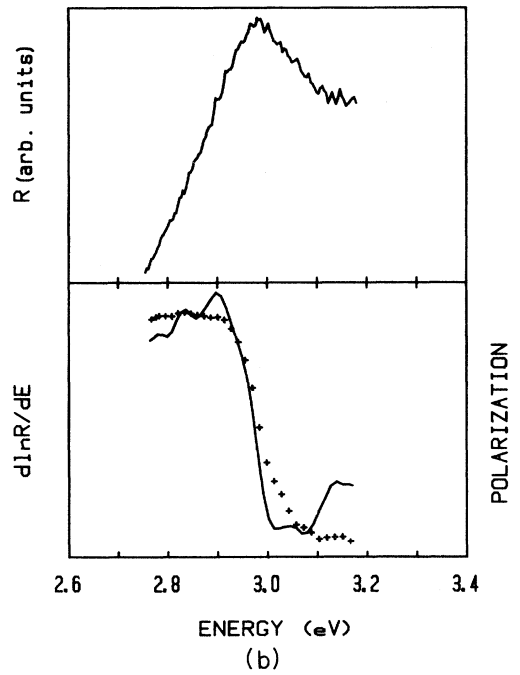


FIG. 2. Reflectivity spectra for $Hg_{1-x}Mn_xTe$ at 4.5 K and 5.5 T for (a) E_1 and (b) $E_1+\Delta_1$ transitions. Below, the measured polarization spectra (crosses) are compared to the logarithmic derivative of the reflectivity spectra (solid line).

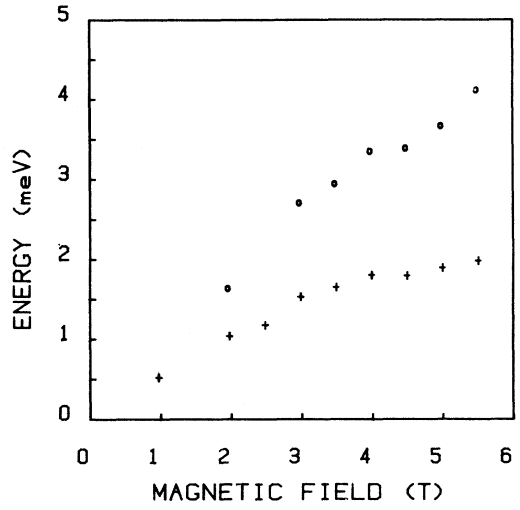


FIG. 3. Splitting of the E_1 reflectivity feature in $Zn_{1-x}Mn_xTe$ at 4.5 K vs magnetic field [$x=0.02$ (crosses) and 0.17 (circles)].

4.5 K, with magnetic field ranging from 0.5 to 5.5 T. The spectra were similar to those for $Cd_{1-x}Mn_xTe$ measured in Ref. 5. Splittings at the L point, determined with the help of Eq. (1), are shown in Fig. 3.

Figure 4 shows a standard reflectivity spectrum obtained for $Zn_{1-x}Mn_xTe$ with $x=0.02$ in the Faraday configuration. Four well-known components are visible (two in each circular polarization). The splitting ΔE_Γ between the two strong components (marked by arrows in

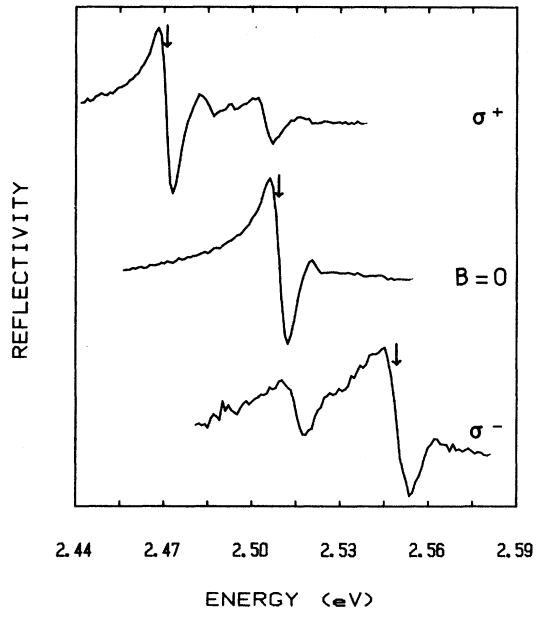


FIG. 4. Reflectivity spectra for $Zn_{0.83}Mn_{0.17}Te$ in the Faraday configuration at $B=0$ and at $B=5.5$ T, for σ^+ and σ^- polarizations.

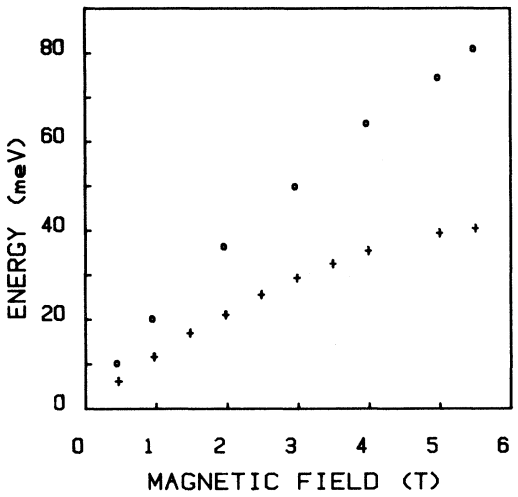


FIG. 5. Splittings of the two strong components of the exciton reflectivity structure at the Γ point in $Zn_{1-x}Mn_xTe$ at 4.5 K vs magnetic field [$x=0.02$ (crosses) and 0.17 (circles)].

Fig. 4) is plotted versus magnetic field in Fig. 5. As indicated in the experimental section, the measurements at the Γ point were done on the same samples and in the same experimental conditions as those at the L point.

For $Hg_{1-x}Mn_xTe$, an alloy of zero or small energy gap, optical measurements have been done only at the L point, for two alloy composition values, $x=0.05$ and 0.20, at 4.5 K. The results are shown in Fig. 2 both for the E_1 and the $E_1+\Delta_1$ transitions. The observed form of the polarization spectra allowed us to determine the Zeeman splittings ΔE_L for both transitions. These are plotted versus magnetic field in Fig. 6.

Besides the optical experiments, magnetization measurements were performed at 4.2 K in the magnetic field range corresponding to the optical experiments for both alloys studied in this work. Magnetization data are shown in Fig. 7. A small difference between the tempera-

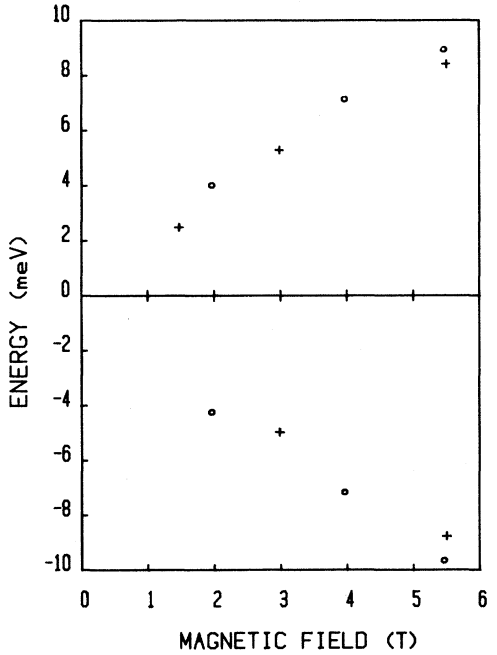


FIG. 6. Splitting of the E_1 (positive values) and $E_1+\Delta_1$ (negative values) reflectivity features in $Hg_{1-x}Mn_xTe$ at 4.5 K vs magnetic field [$x=0.05$ (crosses) and 0.20 (circles)].

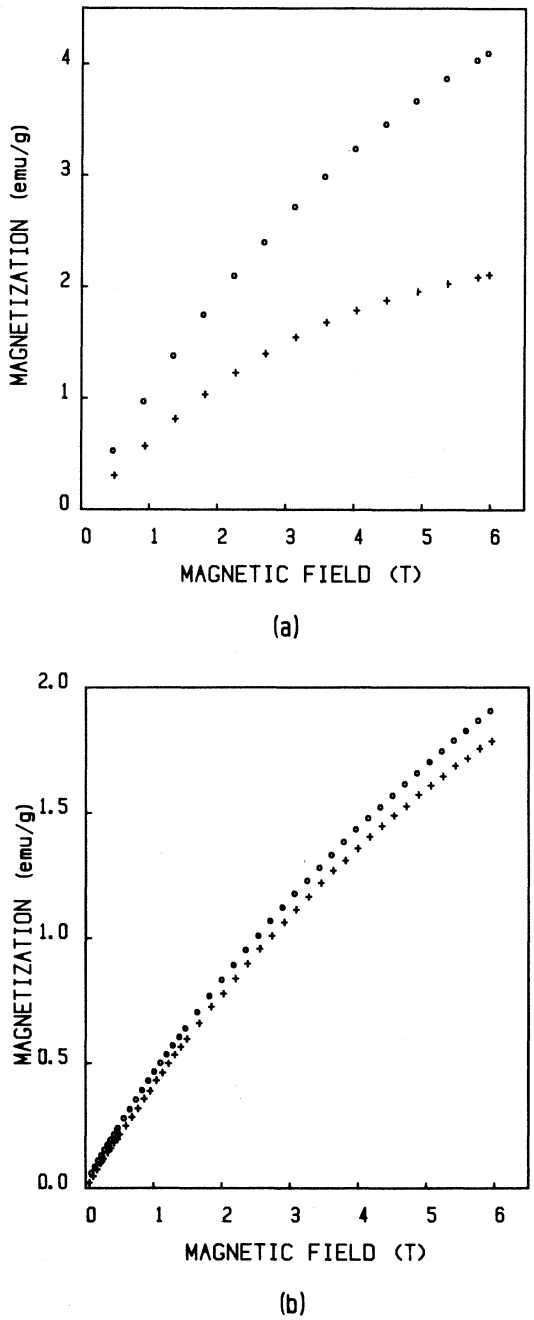


FIG. 7. Magnetization vs magnetic field at 4.2 K: (a) $Zn_{1-x}Mn_xTe$, $x=0.02$ (crosses) and 0.17 (circles); (b) $Hg_{1-x}Mn_xTe$, $x=0.05$ (crosses) and 0.20 (circles).

tures of the optical (4.5 K) and the magnetical (4.2 K) measurements has been neglected in the following sections.

DISCUSSION

The results obtained for $Zn_{1-x}Mn_xTe$ resemble those known for $Cd_{1-x}Mn_xTe$. In Fig. 8 the splitting ΔE_L of the E_1 transition is compared to ΔE_Γ, measured at the Γ point. Similarly as in $Cd_{1-x}Mn_xTe$, a proportionality coefficient between the two splittings $\Delta E_L/\Delta E_\Gamma = \frac{1}{20}$ is much smaller than that calculated in Ref. 3 using a tight-binding model.

The observed results confirm for yet another alloy ($Zn_{1-x}Mn_xTe$, in addition to $Cd_{1-x}Mn_xTe$) a significant difference between the experimental values of Zeeman splittings at the L point of the Brillouin zone, and calculations based on wave-vector-independent exchange integrals α and β. That difference (a factor of 4 for $Cd_{1-x}Mn_xTe$, and a factor of 5 for $Zn_{1-x}Mn_xTe$) cannot, in our opinion, be explained only by the approximations of the tight-binding model alone.

A natural way to explain these data is to assume that the exchange integrals are significantly reduced at the L point compared to the Γ point. This idea is qualitatively supported by the results of Refs. 7 and 8, which explain the variation of the energy gap in $Cd_{1-x}Mn_xTe$ (Ref. 7) and $Zn_{1-x}Mn_xTe$ (Ref. 8) by the influence of magnetic fluctuations. By fitting the experimental values of the energy gap the authors of Refs. 7 and 8 find that the ion-carrier exchange interaction for the valence band decreases with the wave vector. An estimate of the cut-off wave-vector value, representing that decrease, is found to be 6.6×10^7 cm^{-1} in $Cd_{1-x}Mn_xTe$ and 9.6×10^7 cm^{-1} in $Zn_{1-x}Mn_xTe$.

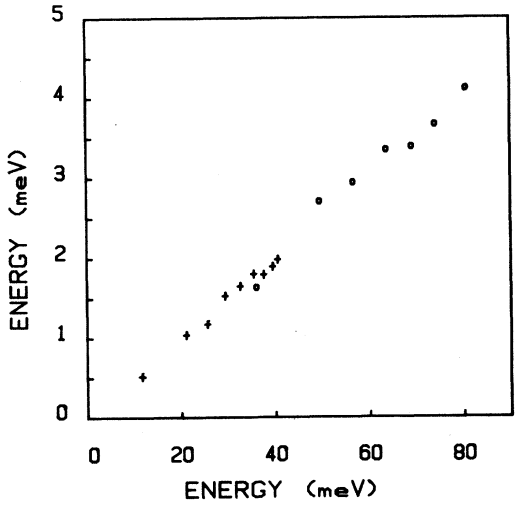


FIG. 8. Splitting of the E_1 reflectivity structure in $Zn_{1-x}Mn_xTe$ at 4.5 K vs that of the two strong components of the exciton reflectivity structure at the Γ point in $Zn_{1-x}Mn_xTe$ at 4.5 K [$x=0.02$ (crosses) and 0.17 (circles)].

Since in our experiments it has not been possible to separate the influence of the valence band from that of the conduction band, a quantitative comparison of both results (i.e., energy gap variation versus Zeeman splittings at the L point) cannot be done at the present stage. However a qualitative agreement between the two is quite clear. There is a need for a precise theory allowing a quantitative analysis of both effects.

In $Hg_{1-x}Mn_xTe$ the situation is very much different. The splitting pattern of energy bands in a narrow band semimagnetic semiconductor results from a combination of Landau quantization and exchange effects, and does not resemble that of large gap materials. Furthermore, the available data on ion-carrier exchange parameters of $Hg_{1-x}Mn_xTe$ show considerable inconsistencies between different authors (more than a factor of 2[9]). Therefore, in order to compare the splitting values for the two alloys studied in this work, we choose to plot ΔE_L as a function of magnetization expressed in terms of $x\langle S_z\rangle$. This has been done in Fig. 9 (where ΔE_L for $Cd_{1-x}Mn_xTe$ has also been shown for completeness). The values for $Hg_{1-x}Mn_xTe$ are much higher than for both $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xTe$. We would not like, however, to comment on the physical meaning of that difference without a better knowledge of the exchange parameter values.

Our magnetoreflectivity measurements on $Hg_{1-x}Mn_xTe$ allowed us also to determine the splittings of the structure $E_1+\Delta_1$ transition for the first time in any semimagnetic semiconductor. We obtain a striking regu-

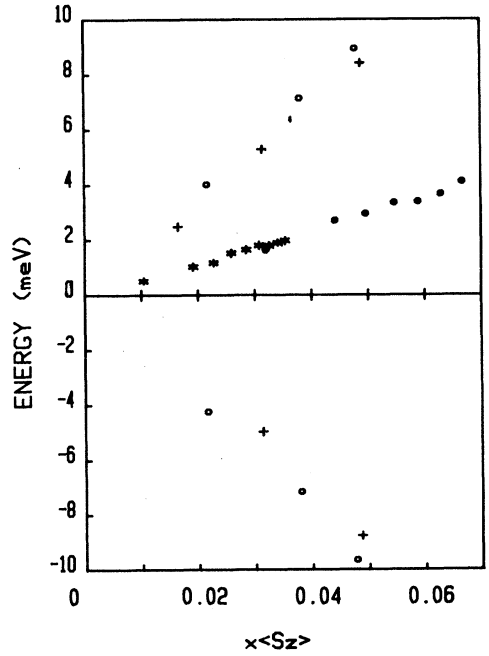


FIG. 9. Splitting of the E_1 (positive values) and $E_1+\Delta_1$ (negative values) reflectivity structures in $Hg_{1-x}Mn_xTe$ [$x=0.05$ (crosses) and 0.20 (empty circles)], $Zn_{1-x}Mn_xTe$ (solid circles), and $Cd_{1-x}Mn_xTe$ (asterisks) plotted vs magnetization (expressed in $g\mu_B$ per unit cell).

larity: the values of the splittings for both reflectivity features (E_1 and $E_1+\Delta_1$, respectively) are approximately equal in magnitude, and are opposite in sign (Fig. 6). This feature, predicted by Ginter *et al.*,[3] reflects the fact that in order to obtain a nonequivalence between σ^+ and σ^- polarizations, a coupling of the orbital movement of the electrons to their spin is necessary, since light interacts predominantly with orbital degrees of freedom of the electron. This prediction is more general than the simple tight-binding approximation used in Ref. 3, and is expected to be a universal feature in semimagnetic semiconductors. The results of the present paper give strong support to this expectation.

ACKNOWLEDGMENTS

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