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Coherent Raman spectroscopy of spin transitions in semimagnetic $Pb_{1-x}Mn_xTe$

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Using four-photon mixing of the radiation of two CO_2 lasers, high-precision measurements of spin-flip transitions of electrons and holes in $Pb_{1-x}Mn_xTe$ were performed. The experimental results clearly show that the spin-flip transition energy tends to zero for vanishing magnetic fields, thus yielding an upper limit for the binding energy of a free magnetic polaron as low as 0.5 meV in $Pb_{1-x}Mn_xTe$ ($x \leq 0.01$). Fits to the experimentally observed temperature dependence of the g factors of electrons and holes demonstrate the necessity of an interpretation beyond the mean-field approach.

Dilute magnetic semiconductors (DMS's) have attracted continued interest and intensive experimental and theoretical examination.[1] The presence of the exchange interaction between the free carriers and paramagnetic ions results in a number of dramatic effects, among them, extremely large and temperature-dependent g factors of electrons and holes. These effects were studied extensively in Mn-based II-VI DMS's. In cubic IV-VI DMS's, which exhibit a direct minimum gap at the L point of the Brillouin zone, antiferromagnetic interaction between Mn ions is relatively small.[2] However, the exchange interaction between the free carriers and the localized spins is still not well understood, apart from the fact that a number of observations indicate that the mean-field approach in which the mobile carrier experiences an averaged effective field of the spins is insufficient. Karczewski and von Ortenberg[3] even observed a zero-field splitting of the energy gap in $Pb_{1-x}Mn_xS$ from laser emission experiments and Pascher *et al.*[4] performed interband magneto-optical experiments in PbMnTe which resulted in the fact that there is an additional contribution to the spin splitting of the Landau states which is independent of the applied field between about 1 and 7 T. The experimental data, extrapolated to a zero magnetic field resulted also in a nonvanishing spin splitting of the valence-band states in $Pb_{1-x}Mn_xTe$.

In order to obtain a detailed understanding of these properties a precise measurement of the g factors of electrons and holes and their magnetic field and temperature dependence is necessary.

In this paper we report on a direct determination of components of the g tensor of electrons and holes in the many valley DMS $Pb_{1-x}Mn_xTe$ using a coherent anti-Stokes Raman scattering (CARS) experiment in the *mid infrared* region.

Two CO_2 laser beams (pulse power of 5 kW; 100 ns pulse duration) with frequencies ω_1 and ω_2, $(\omega_1-\omega_2)=\Delta\omega$ are superimposed in the semiconductor sample. Because of the nonlinear susceptibility, radiation with frequencies $\omega_1 \pm n\Delta\omega$ is produced by four-photon mixing.[5]

In the CARS experiment, radiation with the frequency $\omega_1+\Delta\omega$ is observed. Its intensity is resonantly increased if $\Delta\omega$ corresponds to the transition energy of a Raman allowed transition. Using a magnetic field orientation $\mathbf{B}\perp\mathbf{k}$ ($\mathbf{k}$ denoting the propagation direction of radiation), i.e., Voigt configuration, the spin-flip resonance $\hbar\omega_S = g\mu_B B$ is the strongest one. The set up for the experiments is described in Ref. 6. Because of the high peak powers of the two laser beams, in p- or n-type samples minority carriers are photoexcited across the energy gap and their respective g factors can be determined together with those of majority carriers.

This method is not only the most exact one for the determination of g factors and thus spin-split energies, but can also be used at magnetic fields as low as 0.05 T, which is particularly important for the answer to the question of whether or not a finite spin splitting of band states exists in PbMnTe at zero field.

The $Pb_{1-x}Mn_xTe$ samples ($x \leq 0.02$, n or p type) were grown epitaxially on cleaved (111) BaF_2 substrates.[7] For a magnetic field orientation $\mathbf{B}\parallel[\bar{1}10]$, two valleys in the conduction and valence band are oriented with an angle $\Phi=90°$ between their main axes and the applied field and the other two valleys by $\Phi=35.26°$. Figure 1 shows experimental recordings of the CARS intensity (at $\omega_1+\Delta\omega$) versus magnetic field for a fixed $\Delta\omega$ for p-type $Pb_{1-x}Mn_xTe$ ($x=0.006$) at two temperatures: 1.8 and 12 K. The four distinct resonances observed are all spin-flip transitions within the $n=0$ Landau states of holes (ⓑ, $\Phi=90°$; ⓓ, $\Phi=35.26°$) and electrons, photoexcited by two-photon absorption (ⓐ, $\Phi=90°$; ⓒ, $\Phi=35.26°$). Whereas the spin-flip resonances associated with holes shift their resonance positions strongly with temperature, the corresponding ones for the electrons are nearly independent of T. The weak resonance labeled ⓒ is barely observable since it is hidden below the strong hole spin-flip

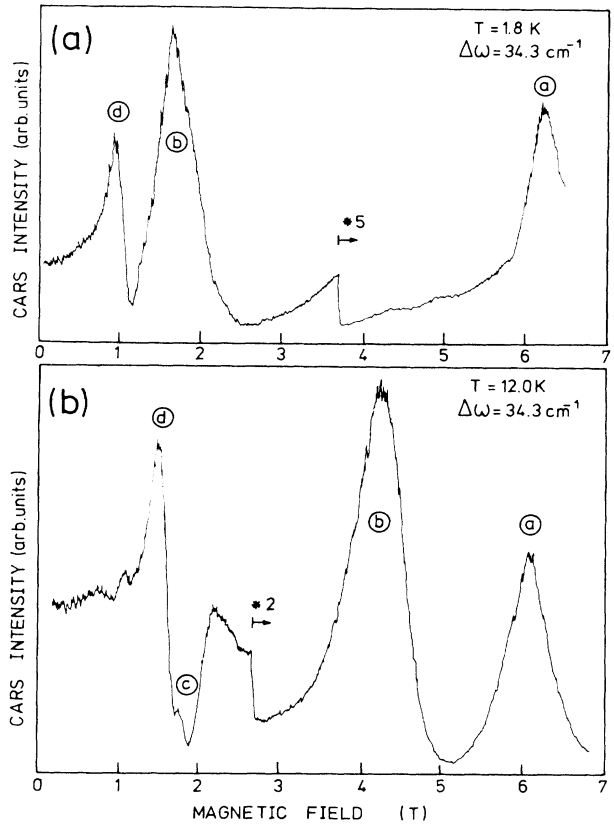

FIG. 1. CARS intensity at frequency $\omega_1+\Delta\omega$ vs magnetic field for p-type $Pb_{1-x}Mn_xTe$. (a) $T=1.8$ K, (b) $Te=12.0$ K. Intensity peaks labeled ⓐ are due to spin-flip transitions of photoexcited electrons for the $\Phi=90°$ valleys, ⓑ for holes ($\Phi=90°$), ⓒ for photoexcited electrons ($\Phi=35,26°$), and ⓓ for holes ($\Phi=35,26°$).

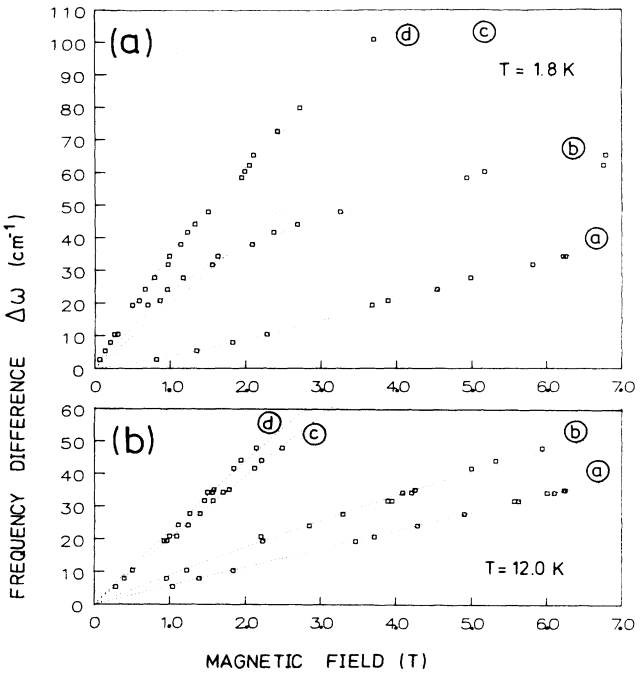

FIG. 2. Frequency difference for spin transitions as a function of magnetic field for p-type PbMnTe; (a) $T=1.8K$, (b) $T=12$ K. □, experimental results for electrons and holes in the bands as indicated. Dotted line indicates calculated spin-flip transition frequencies.

transition ⓑ.

These data are taken for a larger number of different combinations of CO_2 laser frequencies with about 40 different values of $\Delta\omega$, and in Fig. 2 the resonance positions ⓐ–ⓓ are shown as a function of the applied field for p-type $Pb_{1-x}Mn_xTe$ ($x=0.006$) for 1.8 and 12 K. A similar plot with results obtained on n-type $Pb_{1-x}Mn_xTe$ with a larger Mn content, and thus a larger energy gap, is shown in Fig. 3. The hole spin-flip resonances show a pronounced dependence on a magnetic field, especially at low fields in a region which was so far unaccessible. Also, the temperature dependence is quite dramatic, as seen in Fig. 2. The most important result is the fact that all transitions start at $\hbar\omega=0$ for $B\rightarrow 0$, i.e., they do not exhibit a zero magnetic field spin splitting. The g factors for $\mathbf{B}\|[110]$ are plotted in Fig. 4 for all valleys and the two temperatures. A close inspection reveals that the conduction-band states are affected also by the exchange interaction but to a much lesser extent than the valence-band states.

It is important to note that the lattice temperature of the $Pb_{1-x}Mn_xTe$ samples is not increased remarkably above the helium bath temperature due to heating by pulsed laser radiation. An attenuation of the laser power by about a factor of 10 does not affect the position of the observed spin-flip transitions. However, an increase of the lattice temperature by 1 K already shows drastic shifts of the effective g factors, especially in the low-temperature regime.

The g factor of electrons of the $\Phi=90°$ valleys increases with increasing field, which is opposite to the dependence as anticipated from the band nonparabolicity. The inset of Fig. 4 shows the temperature dependence of the hole g factor for the 90° valleys between 1.8 and 22 K.

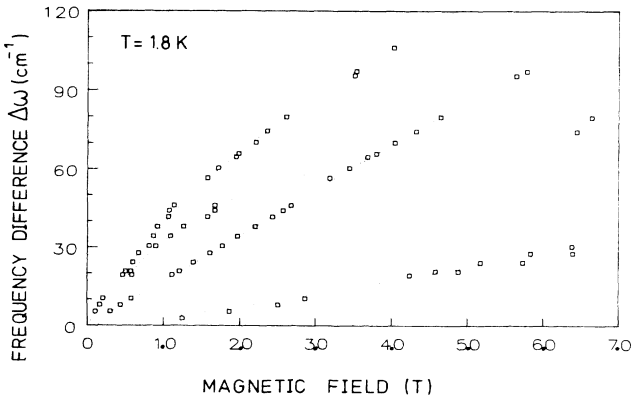

FIG. 3. Same as Fig. 2 but for n-type $Pb_{1-x}Mn_xTe$ at $T=1.8$ K.

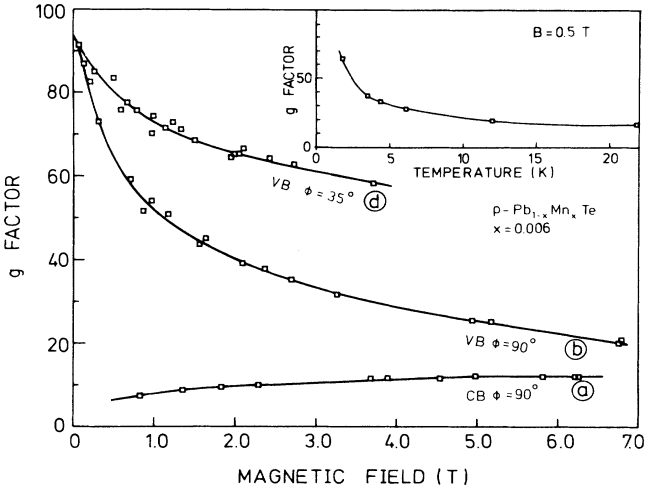

FIG. 4. g factors as a function of magnetic field for the $\Phi=90°$ and $\Phi=35,26°$ valleys at $T=1.8$ K. Inset: hole g factor ($\Phi=90°$) at $B=0.5$ T vs temperature.

Thus we are led to the conclusion that in the magnetic field range around and below 1 T, $Pb_{1-x}Mn_xTe$ indeed exhibits electronic properties which are strongly affected by the spin-spin exchange interaction. In order to get an estimate on the relevant exchange integrals, we apply the mean-field approach, appropriate for this many-valley semiconductor.

For the calculation of the observed $0^- \rightarrow 0^+$ transitions in the conduction and valence band, the $\mathbf{k}\cdot\mathbf{p}$ model according to Mitchell and Wallis[8] is used and an exchange matrix according to Eq. (1) is added to the (4×4) $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian:[9]

$$\tfrac{1}{2}xS_0B_{5/2}(5\mu_BB/k_B(T+T_0))\begin{pmatrix} a & c & 0 & 0 \\ c & -a & 0 & 0 \\ 0 & 0 & +b & d \\ 0 & 0 & d & -b \end{pmatrix}, \quad (1)$$

where $B_{5/2}(\,)$ is a modified Brillouin function; S_0 and T_0 are taken from fits of experimental magnetization data on PbMnTe by Anderson and Gorska.[2] The elements in the matrix are given by[4]

$$\begin{aligned} a &= A\cos\Phi\cos\gamma + a_1\sin\Phi\sin\gamma\ , \\ c &= -A\cos\Phi\sin\gamma + a_1\sin\Phi\cos\gamma\ , \\ b &= B\cos\Phi\cos\gamma - b_1\sin\Phi\sin\gamma\ , \\ d &= -B\cos\Phi\sin\gamma - b_1\sin\Phi\cos\gamma\ , \end{aligned} \quad (2)$$

$$\begin{aligned} A &= a_1 - a_2 = \alpha\cos^2\Theta^+ - \delta\sin^2\Theta^+\ , \\ B &= b_1 - b_2 = \beta_\parallel\sin^2\Theta - \beta_\perp\cos^2\Theta^-\ . \end{aligned} \quad (3)$$

$\Theta^\pm$ are spin-orbit mixing parameters, given in Ref. 10, which are used here for $Pb_{1-x}Mn_xTe$ as well because of the rather small Mn content. The four exchange integrals are given by

$$\begin{aligned} &\alpha=(R\,|\,Y\,|\,R)/\Omega,\ \delta=(S_\pm\,|\,Y\,|\,S_\pm\,|)/\Omega\ , \\ &\beta_\parallel=(X_\pm\,|\,Y\,|\,X_\pm)/\Omega,\ \beta_\perp=(Z\,|\,Y\,|\,Z)/\Omega\ . \end{aligned} \quad (4)$$

The symmetry properties of $X_\pm$, Z, R, and S are defined in Refs. 4 and 9. J is the exchange coupling constant and γ is defined by

$$\cos\gamma=\left[(\cos^2\phi)\frac{P_\perp^2}{P_\parallel^2}\Big/\left[\cos^2\phi\frac{P_\perp^2}{P_\parallel^2}+\sin^2\phi\right]\right]^{1/2}\ . \quad (5)$$

The off-diagonal terms c and d in Eq. (1) cause a strong mixing of Landau states with different spin and Landau quantum numbers. Therefore the energies of the $0^+,0^-$ Landau states are calculated by using an extended scheme, a (12×12) Hamiltonian with three (4×4) blocks along the main diagonal in the notation of Adler, Hewes, and Senturia.[11] The elements a, $-a$, b, and $-b$ are added. The elements c, which couple Landau states with equal Landau and different spin quantum number in the valence band occur then as (5,2) and (9,6) elements of the (12×12) Hamiltonian. The elements d are added at the (7,4) and (11,8) positions.

The two band parameters like the energy gap E_g and the momentum matrix elements $2P_\perp^2/m_0$, $P_\perp/P_\parallel$ are taken from Refs. 4 and 12, i.e., from a fit to interband magneto-optical data. With increasing Mn content $P_\perp$ decreases and the anisotropy ratio increases. The far-band parameters are taken from Ref. 4 and the exchange-induced coefficients A, a_1, B, and b_1 are determined by a least-squares fit to the experimentally observed $0^- \rightarrow 0^+$ transitions of the two kinds of valleys in the conduction and valence band. The resulting calculated transition energies are shown in Figs. 2 and 3 and in Table I the resulting band parameters are summarized. The exchange parameters have different signs for the two bands, those for the valence band are more accurate. $|A|$ decreases with increasing temperature. The large absolute value for δ is most probably an artifact caused by the small value for $\sin\Theta^+$ (as taken from Ref. 10) since a small change of the spin-orbit mixing parameter Θ^+ drastically affects the value of δ.

In this paper only the four exchange parameters are used as fit parameters. The other two band parameters (e.g., $P_\parallel$, $P_\perp$, E_g) are taken from fits to the experimental results of interband magneto-optical transitions in $Pb_{1-x}Mn_xTe$ in $\mathbf{B}\parallel[111]$ and $\mathbf{B}\parallel[110]$ configurations (cf. Ref. 4). However, the far-band parameters are taken to be identical to those of PbTe, an assumption which is justified because of the small Mn contents of our samples ($x\leq 0.01$).

The PbTe ($x=0$) band parameters in the many-parameter fit are well established and yield a perfect agreement with experimentally observed g factors and magneto-optical interband transitions.[6]

However, the results of the fit demonstrate a drastic temperature dependence of A. Such a dramatic variation of exchange parameters indicates the breakdown of the mean-field approach. The exchange-induced contribution to the g factors does not reflect the temperature depen-

TABLE I. Fitting parameters.

Sample characteristics	Temp. (K)	E_g (meV)	$\frac{2P_\perp^2}{m_0}$ (eV)	$\frac{P_\perp}{P_\parallel}$	A (meV)	a_1 (meV)	B (meV)	b_1 (meV)	α (meV)	δ (meV)	$\beta_\parallel$ (meV)	$\beta_\perp$ (meV)
n type, $x=0.01$	1.8	221.9	5.51	3.74	−182	-292 ± 15	-50 ± 50	26.5 ± 5	-305 ± 15	−2643	109.0	79
p type, $x=0.006$	1.8	209.8	5.77	3.52	−222	-292 ± 15	· · ·	55 ± 5	-305 ± 15	−1706	226 ± 20	· · ·
p type, $x=0.006$	4.4	210.5	5.77	3.52	−124	-292 ± 15	-50 ± 50	55 ± 5	-305 ± 15	−4037	226 ± 20	139
p type, $x=0.006$	12	211.8	5.77	3.52	−51	-292 ± 15	-50 ± 50	55 ± 5	-305 ± 15	−5791	226 ± 20	139

dence of the macroscopic magnetization.[13] This result, as well as the numerical values of the spin splittings at high magnetic fields, is in agreement with our previous conclusions drawn from the magneto-optical interband absorption measurements.[4,12]

To summarize, we have shown that at very low magnetic fields $Pb_{1-x}Mn_xTe$ exhibits dramatic changes of the g factor of electrons and holes due to the exchange interaction of the mobile carriers and the localized spins. There is *no finite-energy difference* between spin-split states in the valence band for vanishing magnetic fields with an experimental uncertainty of <0.5 meV. Therefore, the free magnetic polaron[13,14] energy is also less than 0.5 meV.

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