Multiple Mn^{2+}-Spin-Flip Raman Scattering at High Fields via Magnetic Polaron States in Semimagnetic Quantum Wells

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We observed up to 15 paramagnetic resonance Raman lines due to collective multiple spin flips within the Zeeman split Mn^{2+} ground state $^6S_{5/2}$ in a quantum well structure with semimagnetic $Cd_{0.98}Mn_{0.02}Te$ wells and nonmagnetic $Cd_{0.76}Mn_{0.24}Te$ barriers with external magnetic fields $B_{ext} \leq 7.5$ T. This effect appears near resonance with the heavy-hole transitions of narrow quantum wells in the Voigt backscattering geometry and can be explained by a precession of the total spin of all Mn^{2+} ions in the sum of external and exchange field ($\vec{B}_{ext} \perp \vec{B}_{exch}$), the latter produced by the heavy hole.

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In dilute magnetic II-VI semiconductors (DMS), e.g., in $Cd_{1-x}Mn_xTe$ ($x \leq 0.2$), the large exchange interaction between the extended charge carriers and the localized electrons [$3d^5(^6S_{5/2})$ in Mn^{2+}] manifests itself in the giant Zeeman splitting of the s-p hybridized valence and conduction band-edge states with a g factor near 100 and in the formation of magnetic polarons (MP) [1]. The MP consists of a fluctuating magnetization cloud of the Mn^{2+} spins associated with a localized charge carrier. A ferromagnetic spin correlation within the orbit of the carrier is produced [2]. The MP is usually studied at low or zero external field. In the following we present experimental insight into the formation process of a similar phenomenon, a magnonlike collective precession motion of the Mn^{2+} spins in an effective magnetic field which is a superposition of the external field B_{ext} along the quantum well interfaces ($\| x$) and the exchange field B_{exch} oriented normal ($\| z$) to the interfaces.

We observe in the Raman spectrum a large number ($n > 5$) of simultaneous spin flips $\Delta m = 1$ of Mn^{2+} ions. Because of the Zeeman ground-state sextet of a single Mn^{2+} ion, this clearly has to be a simultaneous transition of many ions. We interpret these findings in short as follows: In the homogeneous external magnetic field in the Voigt geometry ($\vec{B}_{ext} \| x$) the Mn^{2+} moments are oriented along $\vec{B}_{ext}$. After a localized exciton has been created; i.e., $\vec{B}_{exch} \| z$ has been switched on, the effective field $\vec{B}_{eff} = \vec{B}_{ext} + \vec{B}_{exch}$ has changed its direction and the I_x component of the total angular momentum $\vec{I}$ of the Mn^{2+} ions in the interaction volume is no longer conserved. The quantum energy of the light emitted in the recombination process of the exciton is reduced with respect to the incoming laser energy by the amount spent to reorient the ensemble of Mn^{2+} ions, which is an integer number n of energy steps of a single spin flip.

In the case of bulk $Cd_{1-x}Mn_xTe$ or MBE (molecular beam epitaxy) grown epilayers of $Cd_{1-x}Mn_xTe$ with low x, where effects of large Mn clusters are negligible, magnetic excitations have been observed previously by means of Raman spectroscopy, which are caused by spin flips of electrons in the conduction band [3] and by spin flips $\Delta m_S = 1$ and $\Delta m_S = 2$ of a single Mn^{2+} within the Zeeman levels of the ^6S ground state. These are the paramagnetic resonance (PR) signals, which linearly shift with B, $g_{Landé} = 2$. The limitation $\Delta m_S = 1, 2$ transitions in the Raman spectra is a consequence of the angular momentum conservation of the system radiation—Mn^{2+} spin. The 2PR Raman line is in general very weak compared to the 1PR line [4]. Investigations of the PR Raman scattering cross section for $Cd_{1-x}Mn_xTe$ epilayers showed that free excitons are involved as intermediate states in the Raman process [5]. A weak $\Delta m_S = 1$ spin flip has also been observed as a combination with the LO phonons in (CdMn)Te [4,5].

We have studied a multiple quantum well (MQW) structure grown in the [001] direction (z) and consisting of semimagnetic wells of $Cd_{0.98}Mn_{0.02}Te$ and nonmagnetic barriers of $Cd_{0.76}Mn_{0.24}Te$ with gap energies in the bulk of about 1.64 and 2.03 eV, respectively. The sample comprises four single quantum wells of 18, 45, 60, and 100 Å widths, which are separated by 500 Å barriers. We have also used a 75 × (75 Å/75 Å) barrier/well MQW sample (wells: $Cd_{0.985}Mn_{0.015}Te$, barriers: $Cd_{0.62}Mn_{0.38}Te$). The samples were studied near $T = 1.8$ K in a split coil magnet ($B \leq 7.5$ T) either in the Voigt ($B_{ext} \| x$) or Faraday ($B_{ext} \| z$) backscattering geometry. The light is π polarized for $\vec{E} \| \vec{B}_{ext}$ and σ polarized for $\vec{E} \perp \vec{B}_{ext}$ (Voigt). For $\vec{B}_{ext} \| z$ circularly polarized light was applied (σ^+ and σ^-) and analyzed. A dye laser was used as a tunable light source with power densities ≤ 0.1 W cm^{-2}. The spectrometer was equipped with a charge-coupled-device multichannel detection system.

Figure 1 shows several near-resonance Raman spectra for various magnetic fields in the Voigt geometry $-z(\sigma, \sigma)z$ for the 18 Å well. Up to $n = 15$ PR Stokes lines can be seen at $B = 7.0$ T, n is decreas-

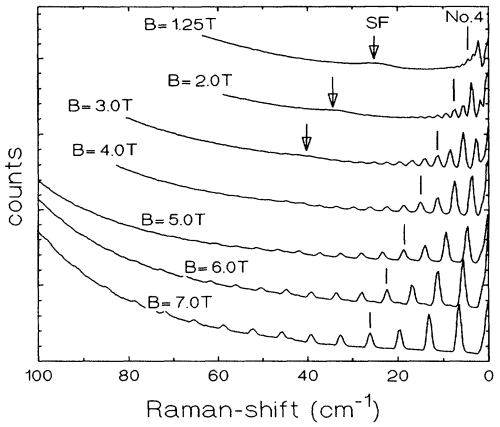

FIG. 1. Raman spectra $-z(\sigma,\sigma)z$ of a single quantum well (18 Å) of $Cd_{0.76}Mn_{0.24}Te/Cd_{0.98}Mn_{0.02}Te$ for various magnetic fields $B \parallel [110]$ (Voigt geometry) taken close to resonance with the heavy-hole (HH) dipole transition. The PR lines No. 4 have been marked as a guide. For $B_{ext} \leq 3.0$ T the lines No. 1 are partially suppressed by the band pass function of the spectrometer. The increasing background is caused by the luminescence of the 18 Å well. SF represents electronic spin flip.

ing at smaller fields. The shift E_n is linear in B and follows $E_n = ng\mu_B B_{ext}$, $g = 1.997$, $n \in \mathbb{N}$ (ESR value: $g = 2.010$) [6]. This is completely different from all previous observations in bulk material or epilayers [4,5] and also from observations in Faraday geometry, where only the well-known two resonances $\Delta m = \pm 1, \pm 2$ can be seen together with some pair transitions [see Fig. 2 (in which Ref. [8] is cited)]. Up to 19 PR lines have

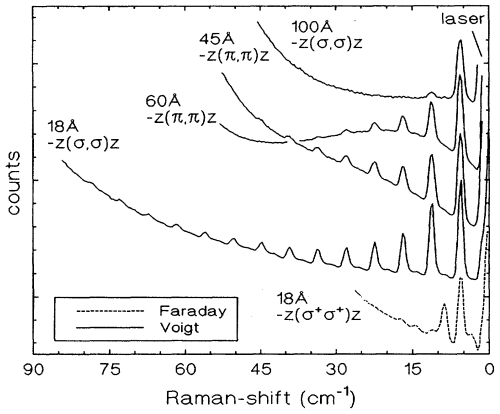

FIG. 2. Comparison of PR Raman spectra for Voigt (18, 45, 60, and 100 Å well widths) and Faraday geometry (18 Å well width) at $B_{ext} = 6.0$ T. All spectra were taken under comparable conditions of resonance. For the Voigt geometry those spectra are plotted which display the largest number n of lines for each quantum well. The strong line in Faraday geometry at 8.85 cm^{-1} and the weak lines at 14.4 and 3.3 cm^{-1} are $S = 0 \rightarrow S = 1, m = 0, \pm 1$ transitions of the antiferromagnetically-coupled nearest neighbor (nn) Mn^{2+} pairs with energy shifts $\Delta E = -2J_{nn} + m\mu_B B$, $J_{nn} = -6.4$ K, which compares favorably well with previous results ($J_{nn} = -6.3$ K) from Raman and high-field magnetization measurements [8].

been found in the 75 × (75 Å/75 Å) MQW sample. The LO phonon companions also demonstrate a large n sequence under favorable resonance conditions. A PR sequence with $n \leq 5$ has been observed previously [7] in a [111] $Cd_{0.89}Mn_{0.11}Te/Cd_{0.50}Mn_{0.50}Te$ superlattice [135 × (59 Å/59 Å)], but was interpreted as due to excitations in antiferromagnetically coupled Mn^{2+} pairs.

In Fig. 2 the dependence of the multiple-PR Raman scattering on the well widths is shown by spectra taken under comparable conditions of resonance near the heavy-hole (HH) dipole transition of each well. The number of observable PR lines n_{max} is clearly decreasing with increasing well width from 15 lines at 18 Å, to 8 lines at 45 Å, and 6 at 60 Å. At 100 Å the spectrum is in principle bulklike ($n = 2$). n_{max} also decreases with increasing x.

The resonance behavior of the PR Raman cross section identifies the intermediate states involved in the scattering process: As Fig. 3 clearly indicates, these are localized excitons, whose recombination energy, displayed by the PL signal, coincides with the resonance maximum. Free excitons, which have been identified as intermediate states in the usual PR Raman process in the Voigt geometry [5], can be excluded because of the energy difference between the photoluminescence excitation (PLE) maximum and the Raman resonance. This resonance behavior is also displayed by the number n_{max} of observable PR Raman lines.

At low temperatures ($T = 1.8$ K) there are no intensity differences discernible between parallel (σ,σ) and crossed polarizations (σ,π) of incident and scattered light, i.e., no selection rules are effective. However, with increasing T the intensity relations between consecutive peaks change and the number of observable peaks reduces with a stronger intensity decrease in the (σ,π) spectra. At intermediate temperatures ($15 \lesssim T \lesssim 35$ K) the odd-numbered PR lines are more intense in crossed polariza-

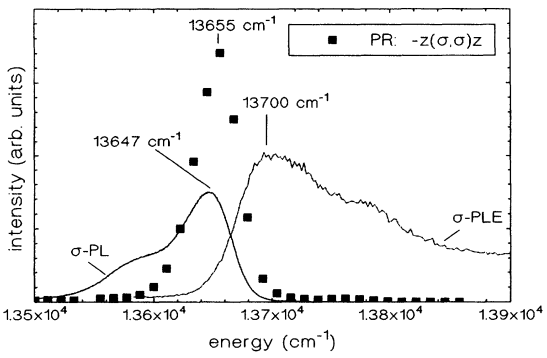

FIG. 3. Raman resonance (full squares) of the ($n = 1$) PR line (well width 45 Å) as a function of the quantum energy of the incident light at $B_{ext} = 6.0$ T. We have also plotted the photoluminescence (PL) under σ polarization of the luminescence light and the σ photoluminescence excitation (PLE) (σ polarization of the exciting light) obtained from this well under the same conditions.

tion than the even numbered, the opposite behavior is observed for parallel polarization. Near $T = 70$ K the multi-PR lines have disappeared and the Raman spectra are bulklike at all well widths with polarization properties as reported earlier [5].

We consider the multiple-PR process to result from the creation of a localized exciton formed by an electron hole pair belonging to the lowest subbands of spatial quantization. In these states the spins of the HHs are aligned normal to the quantum well plane ($J_z = \pm 3/2$) because of the strong spin-orbit interaction in the valence band and the large HH-LH splitting in narrow quantum wells [9]. For the sample considered here the HH levels with opposite values of J_z are degenerate in the Voigt geometry. In this case linearly polarized light will create a HH in a state, which is a coherent superposition of the states with $J_z = \pm 3/2$.

The exciton and the magnetic Mn^{2+} ions are coupled by the strong exchange interaction described by the usual scalar Hamiltonian: $\hat{H}_{\text{exch}} = \frac{1}{3}\beta\vec{S}_i \cdot \vec{J}|\Psi_{\text{HH}}(\vec{R}_i)|^2$, where $\vec{S}_i$ is the spin of the Mn^{2+} ion i at $\vec{R}_i$ and β is the hole-magnetic ion exchange integral [10]. A distinctive feature of this interaction is its anisotropy resulting from the absence of HH spin components in the well plane ($J_x = J_y = 0$). In the Voigt geometry, the hole with a fixed value of J_z can cause transitions among states with different projections I_x of the total spin $\vec{I}$ of the Mn^{2+} ions (inside the hole orbit) on $\vec{B}_{\text{ext}} \parallel x$.

This can be visualized by an exchange field along z $\vec{B}_{\text{exch}}(\vec{R}_i) = (\beta 3 g \mu_B)\vec{J}|\Psi_{\text{HH}}(\vec{R}_i)|^2$ produced by the HH, which acts on the magnetic ions. The multiple PR Raman scattering strongly depends on $\vec{B}_{\text{exch}}(\vec{R}_i)$ and therefore on $\Psi_{\text{HH}}(\vec{R}_i)$ of the exciton localized due to alloy or well width fluctuations or lattice defects and is for that reason very sensitive to variation of the well width.

The multiple PR process can then be described as the result of a precession motion of the manganese spins in the total field $\vec{B}_{\text{eff}} = \vec{B}_{\text{ext}} + \vec{B}_{\text{exch}}$. When the exciton recombines, the projection of $\vec{I}$ on $\vec{B}_{\text{ext}}$ differs from the initial value (compare inset of Fig. 4) [11].

The following formal model quantifies this. The total energy of the system (exciton + magnetic ions) consists of two parts: the regular component E_n of the system in a stationary state and the random part E due to the exciton localization in a fluctuating potential. The random component E is considered to be distributed in a wide range (strong inhomogeneous broadening) and therefore, close to the energy of the incident laser light $\hbar\omega_i$, the distribution function $\rho(E)$ is approximately constant.

The Raman scattering intensity I_S can then be written in the following way:

$$I_S \propto \int dE\,\rho(E)\left|\sum_n \frac{\langle f|V^+|n\rangle\langle n|V|i\rangle}{\hbar\omega_i - E_n - E - i\frac{\Gamma}{2}}\right|^2 \propto \int_0^\infty dt\, e^{-t/\tau}\left|\langle f|V^+|e^{-i(\hat{H}t/\hbar)}|V|i\rangle\right|^2, \quad (1)$$

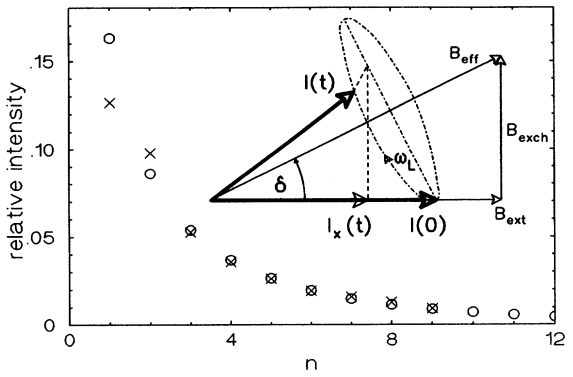

FIG. 4. Relative intensities of the PR Raman peaks n for the 18 Å well; ×: experiment; ∘: calculation using Eq. (4), $\tau = 0.3$ ps, $B_{\text{ext}} = 6.0$ T, $T = 1.7$ K, $x = 0.02$. The inset displays the precession motion of the total spin $\vec{I}$ of all magnetic ions in $\vec{B}_{\text{eff}} = \vec{B}_{\text{ext}} + \vec{B}_{\text{exch}}$ with ω_L. When the exciton recombines, the projection of $\vec{I}(t)$ on $\vec{B}_{\text{ext}}$, e.g., $I_x(t)$, is different from the initial value $\vec{I}(0)$.

where $|i\rangle$, $|f\rangle$, and $|n\rangle$ denote initial, final, and intermediate states of the system, the operators V and V^+ describe absorption and emission of a photon, and Γ describes the homogeneous broadening of the intermediate states caused by the finite lifetime τ of the exciton in these states ($\tau = \hbar/\Gamma$). The intermediate state evolves under the Hamiltonian $\hat{H}$,

$$\hat{H} = \sum_i g_{\text{Mn}}\mu_B\vec{S}_i \cdot \vec{B}_{\text{ext}} + \frac{1}{3}\beta\vec{S}_i \cdot \vec{J}|\Psi(\vec{R}_i)|^2. \quad (2)$$

Eigenstates of $\hat{H}$, which allow a correlation of magnetic ion spins and charge carriers, are the magnetic polaron states for the system under study.

As in absence of the exciton $\vec{S}_i$ has a fixed projection onto $\vec{B}_{\text{ext}}$, the time dependence of the wave functions of the ions can be expressed by operators

$$d^{S_i}_{m''m}(\delta)e^{-im''\omega_L t}d^{S_i}_{m'm''}(-\delta), \quad (3)$$

where $d^{S_i}_{kl}(\alpha)$ are matrices of finite rotations for a spin S around the y axis. δ is the angle between $\vec{B}_{\text{eff}}$ and $\vec{B}_{\text{ext}}$, ω_L is the Larmor frequency in $\vec{B}_{\text{eff}}$. It is easily seen that Eq. (1) is completely consistent with the above mentioned model of a spin precession in an effective field.

From Eq. (3) and $d^S_{kl}(\alpha) = (-1)^{k-l}d^S_{kl}(-\alpha)$ polarization rules can be determined: even (odd) numbered peaks should be observable for parallel (crossed) polarization of incident and scattered light. Physically this results from the coherence between $\pm 3/2$ HH states. Similar polarization properties have been observed for Raman cascades of Fe^{2+} transitions in $Cd_{1-x}Fe_xSe$ [12]. Another manifestation of this coherence are "spin beats" observed in time-resolved Faraday spectroscopy [13]. As mentioned above, these polarization properties could not be observed

for low temperatures but for elevated temperatures. This may be due to an additional reduction of symmetry at low temperatures. Possible mechanisms are still in discussion.

From Eqs. (1) and (3) relations among the intensities of the PR peaks can now be derived. For complete alignment of the Mn^{2+} spins along $\vec{B}_{ext}$ (strong B_{ext}, low temperatures), we achieve for the intensity of peak n

$$P_n(\tau) = \frac{1}{\tau}\int_0^\infty dt\, e^{-t/\tau}\frac{N(t)^n}{n!}e^{-N(t)}, \qquad (4)$$

where $N(t) = \int_V dV\, n'_{Mn} S \sin^2\delta(1 - \cos(\omega_L t))$ is the average change of total spin of the magnetic ions interacting with the exciton, n'_{Mn} being the density of Mn^{2+} ions.

We have evaluated Eq. (4) for various τ values and compared the results with our experimental data on the relative Raman intensities of the spin-flip lines. We have chosen an exciton center of mass localization radius $(a_0)_{x,y} = 30$ Å for the in-plane directions [14] and a cosine function for the z dependence in the following [the well width and $(a_0)_{x,y}$ determine $|\Psi_{HH}(\vec{R}_i)|^2$ and therefore $\vec{B}_{exch}(\vec{R}_i)$]. This plot is shown in Fig. 4 for the 18 Å well, which demonstrates a satisfying agreement between results for $B_{ext} = 6$ T and the calculated data assuming $\tau = 0.3$ ps.

A reduction of τ with decreasing B_{ext} is observed: τ decays from 0.3 ps at $B_{ext} = 6$ T to $\tau = 0.22$ ps at $B_{ext} = 4$ T (18 Å). These τ values are in good agreement with subpicosecond dephasing times derived from transient four-wave-mixing experiments in comparable MQW samples ($x = 0.015 - 0.04$) at $B_{ext} = 0$ [15]. It should be mentioned that τ is smaller by several orders of magnitude than any time constant in the process of MP formation at zero field; i.e., the formation time τ_f, the spin-spin relaxation time τ_{ss} in (Cd,Mn)Te [16], and the photoluminescence decay time τ_{PL} (≈200 ps) of the localized excitons in these samples.

In a series of MQW samples with increasing x in the well ($x = 0.015$, 0.022, 0.040, and 0.078) a strong reduction of τ and a broadening of the single PR line was observed. This indicates that τ is dependent on x. This is consistent with a decrease of the dephasing time with increasing x which was obtained by Cundiff *et al.* [15] for the same samples at $B_{ext} = 0$.

In conclusion, we have observed a new collective spin excitation in a DMS with low Mn concentration, associated with a fast relaxing intermediate state. It is interpreted in terms of a MP effect not only because of the time evolution under the MP Hamiltonian [Eq. (2)], but also because the total spin $\vec{I}$ of the Mn ions inside the hole orbit is changed during the scattering process. The phenomenon described here offers the challenge of studying various effects of a "confined" exchange field in a DMS. It bears some resemblance to the Hanle effect well known in atomic physics, which is its analog in single-atom elastic resonance scattering.

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[1] J. K. Furdyna, J. Appl. Phys. **64**, R29-R64 (1988).
[2] P. A. Wolff, in *Semiconductors and Semimetals,* edited by J. K. Furdyna and J. Kossut (Academic Press, Boston, 1988), Vol. 25, p. 413.
[3] M. Hirsch, R. Meyer, G. Schaack, and A. Waag, Phys. Rev. B **48**, 5217 (1993).
[4] A. Petrou, D. L. Peterson, S. Venugopalan, R. R. Galazka, A. K. Ramdas, and S. Rodriguez, Phys. Rev. B **27**, 3471 (1983).
[5] J. Stühler, M. Hirsch, G. Schaack, and A. Waag, Phys. Rev. B **49**, 7345 (1994).
[6] J. Lambe and C. Kikuchi, Phys. Rev. **119**, 1256 (1960).
[7] E.-K. Suh, D. U. Bartholomew, A. K. Ramdas, S. Rodriguez, S. Venugopalan, L. A. Kolodziejski, and R. L. Gunshor, Phys. Rev. B **36**, 4316 (1987).
[8] B. E. Larson, K. C. Haas, and R. L. Aggarwal, Phys. Rev. B **33**, 1789 (1986).
[9] R. W. Martin, R. J. Nicholas, G. J. Rees, S. K. Haywood, N. J. Mason, and P. J. Walker, Phys. Rev. B **42**, 9237 (1990).
[10] J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).
[11] This simple picture, neglecting precession of the hole, is valid under the assumption of negligible light-hole–heavy-hole mixing (HH-LH splitting = 320 cm^{-1} for the 18 Å well; no Zeeman splitting of the HH states in the Voigt geometry is observable).
[12] D. Scalbert, J. A. Gaj, A. Mauger, J. Cernogora, C. Benoitála Guillaume, and A. Mycielski, J. Cryst. Growth **101**, 940 (1990).
[13] J. J. Baumberg, D. D. Awschalom, N. Samarth, H. Luo, and J. K. Furdyna, Phys. Rev. Lett. **72**, 717 (1994).
[14] C. E. T. Gonçalves da Silva, Phys. Rev. B **33**, 2923 (1986).
[15] S. T. Cundiff, R. Hellmann, M. Koch, E. O. Göbel, D. R. Yakovlev, A. Waag, and G. Landwehr, in Proceedings of the International Workshops on II-VI and Semimagnetic Semiconductors, Linz, 1994, edited by J. B. Mullin and H. Heinrich (Trans. Tech. Publ. Ltd, to be published).
[16] T. Dietl, P. Peyla, W. Grieshaber, and Y. Merle d'Aubigné, in Proceedings of the International Conference on Magnetism, 1994 [J. Magn. Magn. Mater. (to be published)], and references therein.