High-resolution Resonance Spin-flip Raman Spectroscopy of Pairs of Manganese Ions in CdTe

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We report the observation of tens of minor lines of the combinational spin-flip Raman scattering in a CdTe:Mn quantum well by means of the high-resolution optical spectroscopy. Classification of this manifold leads to four characteristic values of energy, that correspond to four different types of pair clusters of Mn ions: the nearest, second, third etc. neighbors. All the four energies show up in a single experiment with a very high precision, providing experimental grounds for a deeper understanding of the d-d exchange interactions in a diluted magnetic semiconductor and demonstrating the capacity of the employed method. Notably, the major nearest-neighbor exchange constant \( J₁ = 5.22 \pm 0.05 \text{ K} \) was found to be smaller than its established value (6.1 K). Other detected characteristic energies are as follows: \( J₂(3) = 1.51 \text{ K} \), \( J₃(1) = 1.16 \text{ K} \), \( J₄(4) = 0.70 \text{ K} \).

Diluted magnetic semiconductors (DMSs) exhibit a pronounced response to external magnetic fields and a variety of other spin-related phenomena.¹,² While materials belonging to this family retain practical prospects of several kinds, they are especially important as a testing area for magnetic interactions in crystals. (Cd,Mn)Te pseudobinary solid solutions are model representatives of the family and perhaps the best-studied wide-gap DMSs. At any composition, they crystallize in a zinc blende lattice and show random occupation of the cation sites by substitutional Mn\(^{2+}\) ions.³ Each Mn ion bears a local spin magnetic moment (due to the internal 3d\(^5\) electrons) which, in addition, possesses small

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crystal-field anisotropy. So the local Mn spins are easily involved in various kinds of interactions, e.g., with the s- and p-band charge carriers or with each other.

In very dilute compositions (low manganese concentration \( x \leq 0.1\% \)), the vast majority of Mn substitutional ions sit well away from each other, leading, at a local scale, to a single-spin behavior and, in aggregate, to veritable paramagnetic properties. However, as \( x \) increases, inter-manganese short-range interactions become important very soon, because a rapidly increasing fraction of Mn spins find themselves close to another Mn spin.\(^4\) These interactions, due to their antiferromagnetic origin, impair the mean magnetic susceptibility and modify the magnetic-saturation behavior by the formation of a net of interacting spins.\(^5\) Thus the Mn-to-Mn interactions are of major importance for the physics of the DMSs.

Because the Mn ions occupy regular cation sites of the matrix crystal, their neighborhood can be described in terms of discrete configurations, or types. The nearest-neighbor (NN) configuration is characterized by the largest value of the Mn-to-Mn exchange constant, which was quantified by several techniques. Early estimates were based on the Curie-Weiss temperature.\(^4,6\) More reliable values follow from neutron-scattering data\(^7\) and, especially, the magnetization-steps (MST) method,\(^8\) in which the total magnetization of a sample in an increasing external magnetic field experiences a step-up every time the field becomes strong enough to increase the total spin of an antiferromagnetically coupled pair of Mn ions by another unity. While different approaches more or less agree in the value of the NN exchange constant \( J_1 \), the next-nearest-neighbor (NNN) interactions are studied not so reliably.\(^7,9,10,11,12,13\) The reason is that the mentioned methods are not really selective in respect with the “sort of pairing” of Mn ions (i.e., the question whether the two involved Mn ions see each other in the first coordination sphere (NN locations), or the second, etc). As a result, the signals are usually dominated by contributions from single Mn’s with an addition from the NN pairs. Existing estimates of the NNN exchange constants \( J_2, J_3, \) etc. are based on marginal discrepancies between the measured and calculated MST curves.
In the present Letter, we report a selective approach to this problem. We demonstrate that high-resolution resonant spin-flip Raman spectroscopy can yield, for a model object like a (Cd,Mn)Te quantum well, separate signatures from the different types of close pairs of neighboring Mn’s. We obtained up to 4 different characteristic energies in one measurement and with a remarkable precision of ±0.01 meV. The effect inspires optimism as a basis for a prospective method of characterization applicable also to other Mn-based as well as non-Mn-based DMS materials.

The samples for the present study were conventional MBE-grown nanostructures of a common design (as described, e.g., in Ref [14]). They are all grown on GaAs substrates followed by a several (3 – 4) micron thick CdTe buffer. In essence, they included narrow (3 or 4.5 nm) isolated (Cd,Mn)Te quantum wells (QWs) with symmetric non-magnetic barriers of (Cd,Mg)Te containing ~20% of Mg. The Mn concentrations inside the QW layers were different but did not exceed few percent. We chose for demonstration the experimental results obtained using the sample A described earlier (1.7% of Mn).14

We performed an experimental multiple Mn$^{2+}$ paramagnetic resonance Raman study using the original configuration, as described in Ref.[15]. Namely, the external magnetic field was parallel to the plain of the QWs while the light emission was collected in the backscattering geometry. However, the resolution of the experiment was beyond standard: owing to the use of a narrow-band laser (Coherent MBR-110) and a triple grating spectrometer in the additive mode, we achieved an overall spectral resolution of about 25 μeV, which is, e.g., ~ 6 times smaller than in Ref.[14]. We discovered that such instrumental improvement immensely enriches the spectral picture and the informative value of the effect.

Figure 1 shows a spectral map of the radiation from the QW in the coordinate frame ‘energy – magnetic field’, where the emission intensity is encoded by the points’ color. The incident laser energy (1762.6 meV for Fig.1) is somewhat above the exciton luminescence band (maximum ~ 1755 meV, FWHM ~ 5 meV, visible as a blurry ocher yellow area). The sharp brown stripes depict replicas of the resonance Rayleigh (the
horizontal stripe) and spin-flip Raman (inclined stripes) scattering of the laser light. Note that all replicas are greatly enhanced in the vicinity of the exciton state, meaning that the mechanisms behind the scattering processes have a direct relationship to the QW exciton.\textsuperscript{16,17,18} In Fig.1, the \(i\)-th inclined track (counting from the Rayleigh line) corresponds to the light scattering process in which the scattered photon leaves behind \(i\) flipped spins of \(3d^5\) electrons of the Mn ions. The inclination of the tracks with regard to the magnetic field axis represents the magnetic-field dependence of the change of the scattered photon energy. This directly reflects the energy corresponding to the spin flip in the external magnetic field.\textsuperscript{19}

Figure 1. Spectral map of the radiation from the 9ML (3 nm) QW for \(B\)-fields up to 7 T, \(T=1.5\) K, the laser excitation energy (1762.6 meV) hits the high-energy side of the QW exciton band (blurry ocher yellow area). The thick horizontal bar corresponds to the elastic light scattering, the sharp inclined stripes below (above) that – to Stokes (anti-Stokes) multiple inelastic light scattering by paramagnetic spins of single Mn ions. A tracery of weak tracks between the major lines represents the subject of the present study.

The fan-like system of stripes in Fig.1 makes the typical picture of the multiple Raman paramagnetic resonance, alike observed many times in similar systems.\textsuperscript{20,21,22,23,24,25} Almost 20 stripes below the laser energy correspond to Stokes processes (those in which
the energy of the crystal is increased), a dozen of stripes above the laser – to the anti-Stokes processes.

However, in marked contrast to the previous studies, the high-resolution experiment reveals umpteen minor tracks which do not belong to the main fan. These tracks are visible in some areas of the map and disappear in other areas; some of them make scissor-like structures, some appear as twinned lines through a long path, or manifest themselves as close satellites of the strong lines of the main fan (Fig.2 (a)). While some elements clearly made repeating patterns, they did not secure an immediate perception of the entire picture. Ultimately, we found a scheme to classify the variety of minor tracks by affiliating them to several additional fan-like features. Each of the fans roots at a unique point in energy (above or below the laser) at zero magnetic field, and each one includes a significant number of stripes (Fig.2 (b) – (d)). Each root energy represents the spin-flip-induced energy difference of a spin system in its zero-field extrapolation, i.e., after correction for the Zeeman term. Therefore it is attributed to the exchange interaction.
Figure 2. Resonance Raman scattering in a (Cd,Mn)Te QW: a detailed presentation of some regions of the experimental intensity maps (similar to Fig.1). Panel (a) illustrates typical repeating patterns of the tracery: 1 – “scissors”, 2 – twinned tracks, 3 – satellite weak lines. Panels (b) to (d) depict the fitting of the key elements of the observed tracery by the specific fan-like structures. Thick dotted line in every panel marks the exact position of the peak of the excitation laser.

Let us introduce a notation for specific fan-making stripes. Let the stripe \((E, n)\) be characterized by the energy \(E\) of the fan root (i.e., at \(B = 0\)) and by an integer \(n\) indicating the slope toward the \(B\)-field axis. With this notation, the major fan in Fig.1 will be designated as \((0 \text{ meV}, n)\) and will include the Rayleigh line \((0 \text{ meV}, 0)\), the first Stokes Raman line \((0 \text{ meV}, +1)\) and, e.g., the fourth anti-Stokes Raman component \((0 \text{ meV}, -4)\).

Inspection of minor tracks shows that many of them belong either to the fan \((+0.9 \text{ meV}, n)\) or to its anti-Stokes partner \((-0.9 \text{ meV}, n)\), see Fig. 2 (b). The experimental tracks \((+0.9 \text{ meV}, n)\) are particularly well-seen; for instance, they form upper elements of the “scissors” at high fields. The tracks \((-0.9 \text{ meV}, n)\) are less pronounced, even when their total Raman shifts are about those of the corresponding \((+0.9 \text{ meV}, m)\) tracks. This can be ascribed to the fact that the processes \((-0.9 \text{ meV}, n)\) probably include absorption of a 0.9-meV excitation within the crystal; that is, the resulting Raman processes are not fully energy-dispelling but require an available portion of energy, missing at helium temperatures.

Other very pronounced elements of the observed tracery belong to the fans \((-0.26 \text{ meV}, n)\) and \((-0.20 \text{ meV}, n)\). The former of them make the lower elements of the “scissors”, while in combination, they form the long twinned track in the “scissors handle” (see Fig.2 (c)). Strange enough, the Stokes partners of the above fans are barely visible. One can just notice tracks \((+0.26 \text{ meV}, n)\) with \(n = 0, \pm 1\), while the track \((+0.20 \text{ meV}, -1)\) is only visible above the Rayleigh line. Tracks \((-0.26 \text{ meV}, 0)\) and \((-0.20 \text{ meV}, 0)\) are not visible, for some reason.
Finally, the remaining tracks can be attributed to the fan (+0.12 meV, \( n \)) and its anti-Stokes partner (-0.12 meV, \( n \)). They appear as close satellites on either side of the intense (0 meV, \( n \)) lines (see Fig 2 (d)). For both the Stokes and anti-Stokes fans, only lines with positive numbers were detectable.

Thereby, the experimental tracks of the spin-flip positons point for vanishing B-field to four well-defined values of energy in the sub-meV range which are characteristic for the system under study. The only candidates in sight to provide such energies are pairs of coupled Mn ions.\(^{26,27,28,29}\) Different types of local coordination (nearest, second, third, etc. neighbors) can justify unique energies: the latter are measures of the magnetic interactions in the corresponding pairs. In order to compare our values with the data of previous authors, let us assume each observed energy equal to a doubled exchange constant (of the corresponding sort), and we will obey the tradition of expressing their values in Kelvins (1 K \( \approx 0.086 \) meV). In such a way, we report \( J_\text{(1)} = 5.22 \) K, \( J_\text{(2)} = 1.51 \) K, \( J_\text{(3)} = 1.16 \) K, \( J_\text{(4)} = 0.70 \) K. (Here, as usual, parenthesized indices are used to designate exchange constants which are ranged only by their descending value, not by the increasing distance between the ions constituting the pair.)

Basically, this agrees with the previous knowledge regarding various DMSs and, in particular, (Cd,Mn)Te.\(^{30}\) At the same time, even for the most important NN constant, the measured \( J_1 = J_\text{(1)} = 5.22 \) K differs some 15\% from the widely accepted value \( J_1 = 6.1 \) K.\(^{31,32,33}\) It is unlikely that possible strain of the QW material could have caused such a big discrepancy.\(^{34}\) Seemingly, the true value of \( J_1 \) in (Cd,Mn)Te is smaller than it was believed before. However, all previous work was conducted on relaxed bulk material. The relevant length scales for d-d exchange are much smaller than our quantum well widths, so an impact of quantum confinement effects on \( J_1 \) is rather unlikely. The role of residual strain is less clear and calls for a systematic study.
Both the values $J_{(2)}$ and $J_{(3)}$ hit the interval of expectations (1-2 K) for the NNN constants;\textsuperscript{9-11,30} the same refers to $J_{(4)}$. Excellent precision (about ±0.05 K) is an obvious advantage of the Raman method. But the latter does not allow for an easy attribution of the observed exchange constants to the specific types of pair clusters. We suggest a combined study, in which the Raman-obtained values would be a prerequisite (as a precisely known set including a detailed investigation of their strain dependence); then different attributions of $J_{(2)}, J_{(3)}, J_{(4)}$ to $J_2, J_3, J_4$ would represent models for the simulation of the MST curves (in the spirit of Refs.[9,12,13]); finally, one of the resulting MST curves would be preferred by comparison with the experimental MST data. This is, however, beyond the framework of the present study.

In summary, by the application of the high-resolution resonance multiple Mn\textsuperscript{2+} spin-flip Raman spectroscopy we observed umpteen never-reported Raman lines in the spectra of the model DMS QWs in the conditions of the Raman paramagnetic resonance. Magnetic-field dependence of the positions of the lines revealed four different characteristic energies of the system. We attribute these energies to pair clusters of Mn\textsuperscript{2+} ions whose spins are coupled by an exchange interaction. Thus we report four exchange constants of the pair interaction in a CdTe:Mn quantum well with a remarkable experimental precision; interestingly, for the best-studied NN exchange constant, a 15% discrepancy with the previous results was found. Overall, the straightforward interpretation of the experimental Raman tracks looks satisfactory; a little cloud on the horizon is the unclearly low intensity of the (+0.26 meV, $n$) and (+0.20 meV, $n$) fans with respect to their anti-Stokes partners.

The present study solves the previous puzzle of the “fractional peaks” which was reported in Ref.[14]. Obviously, the “half-integer” positions of the minor Raman lines in Ref.[14] originated from the coincidental crossing of (+0.9 meV, $n$) and (-0.26 meV, $n + 3$) tracks right between the (0 meV, $n + 1$) and (0 meV, $n + 2$) stripes of the major fan (at the field $B \approx 6$ T). In addition to that, the “half-integer” slopes between the stripes ($n +$
and \( n + 2 \) were imitated by an average of the slopes \( n \) and \( n + 3 \) of the unresolved minor peaks.

We note that the experimental technique reported here can become a prototype for the accurate quantitative investigation of the exchange interactions between the neighboring spins in various crystals. The Raman paramagnetic resonance effect was already reported for several semiconductor systems (i.a., not only with substituting Mn).\(^{35,36}\) Essential elements for the method would be: a narrow QW showing an exciton resonance, an appropriate concentration of magnetic ions, a magnetic field and a high-resolution Raman-scattering experiment.

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Worth noting, we observed no minor tracks in similar samples with lower Mn concentrations $x \approx 0.1\%$, while the major fan with many stripes was visible quite clear. This is in agreement with a lower occurrence of isolated pairs, as compared to isolated single ions, in very dilute DMSs (R.E. Behringer. J. Chem. Phys. 29, 537 (1958)).