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Series of "fractional" peaks in multiple paramagnetic resonance Raman scattering by (Cd,Mn)Te quantum wells

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In typical conditions of the observation of multiple paramagnetic Raman resonance in model heterostructures containing manganese ions, we observed a never-reported series of Raman peaks, showing up in a narrow range of applied magnetic fields. These weak "fractional" peaks are located close to the middle between the strong "integer" Mn spin-flip peaks, and they reveal a remarkably weak dependence of the intensity on the peak number, in a pronounced contrast with the "integer" series. We discuss conditions to observe the "fractional" series as well as pathways for further exploration of the effect.

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Diluted magnetic semiconductors (DMSs) have been under study since the late 1970's as a basis for the analysis of spin interactions in semiconductor crystals, especially of those between the band charge carriers (electrons, holes) and the localized spin magnetic moments of magnetic ions. Substitutional manganese is applied as a classical paramagnetic ion in A^2B^6 DMSs. Manganese occupying a cation site behaves as an isovalent impurity with little influence on the electrical properties and no pronounced magnetic (single-ion) anisotropy. Solid solutions including Mn demonstrate strong magneto-optical and galvanomagnetic effects such as the giant spin splitting of energy bands, the magnetopolaron effect, spin-glass behavior, etc. [1–3].

(Cd,Mn)Te/(Cd,Mg)Te quantum wells (QWs), whose highly accurate molecular beam epitaxy (MBE) growth technology has been worked out for the last 25 years, are a model object in the physics of two-dimensional DMS systems. In 1995, a surprising spectroscopic effect named *multiple paramagnetic resonance* (MPR) Raman scattering was discovered in narrow QWs of the (Cd,Mn,Mg)Te family [4]. The effect consisted in the observation of a large number (up to 15) of equidistant Raman repetitions of the cw laser frequency, with energy shifts being integer multiples of the Zeeman splitting of the intrashell $3d^5$ electrons of the Mn ion. The MPR effect is observed with the external magnetic field (B field) parallel to the plane of the QW (Voigt configuration) and at resonance optical excitation inside the QW exciton band. Later on, different aspects of the MPR phenomenon were studied both in Mn-based and non-Mn-based DMS systems [5–10].

A quasiclassical model by Kavokin and Merkulov [11] explained the MPR phenomenon by the strong interaction of a localized exciton with magnetic ions. The essence of the effect was described as follows. In the vicinity of a localized exciton state—initially unpopulated—the B field aligns the manganese spins, as it usually goes in a paramagnet. Then, at some moment, the optical excitation generates a localized heavy-hole exciton, whose "exchange field" acting on the Mn spins is directed along the growth axis, hence, perpendicular to the B field acting on the same Mn spin. Since the accumulated Mn magnetization is not parallel to the resulting total field, it starts a precession which eventually abruptly ends by the radiative recombination of the exciton. In the final Raman state (with the radiantly annihilated exciton), the Mn magnetization finds itself inclined with respect to the direction of the B field, thus the energy of the crystal is enhanced, as compared to the initial state. Therefore, the emitted photon is redshifted, a Raman signal is generated on the Stokes side. The probability distribution over actual exciton lifetimes until the act of recombination, together with a quantum-mechanical projection of the intermediate Raman state (exciton+magnetic ions) onto a multispin system of Zeeman sublevels in the B field, determine the distribution of the Raman response (the observed intensity) over multiple equidistant replicas [11].

In the present Rapid Communication, we report on the observation of a previously unknown series of B-field-dependent Raman lines, in the conditions of the MPR, in a model nanostructure with a DMS QW. The observed series of lines shows up in the gaps between the main MPR peaks in a rather narrow range of B-field values (around 6 T) and seems to manifest a fractional effect: a process of light scattering associated with the spin flip of a half-integer number of $3d^5$ electrons of the manganese. We demonstrate some main peculiarities of the observed series of lines, discuss the appropriateness of the "fractional" interpretation and of alternative interpretations based on the existing experimental data, and discuss steps that ought to be taken toward a further exploration of the effect.

The experiment was conducted with a tunable optical excitation by a dye laser (pyridine 2) in the range of 1.69–1.79 eV, pumped by an argon ion laser. The samples were immersed in pumped liquid helium at temperatures of about 1.5 K. The optical signals were collected in backscattering geometry. A magnetic field up to 7.25 T was applied in the Voigt configuration. The spectra were analyzed with a Dilor triple Raman spectrometer equipped with an Andor CCD detector. The overall spectral resolution ~0.16 meV was limited by the laser linewidth.

Two samples were studied, which contained several separated (001)-oriented (Cd,Mn)Te/(Cd,Mg)Te QWs of various thicknesses; an independent spectroscopic access to every particular QW was provided by different energies of the fundamental excitonic transitions due to the different strengths of

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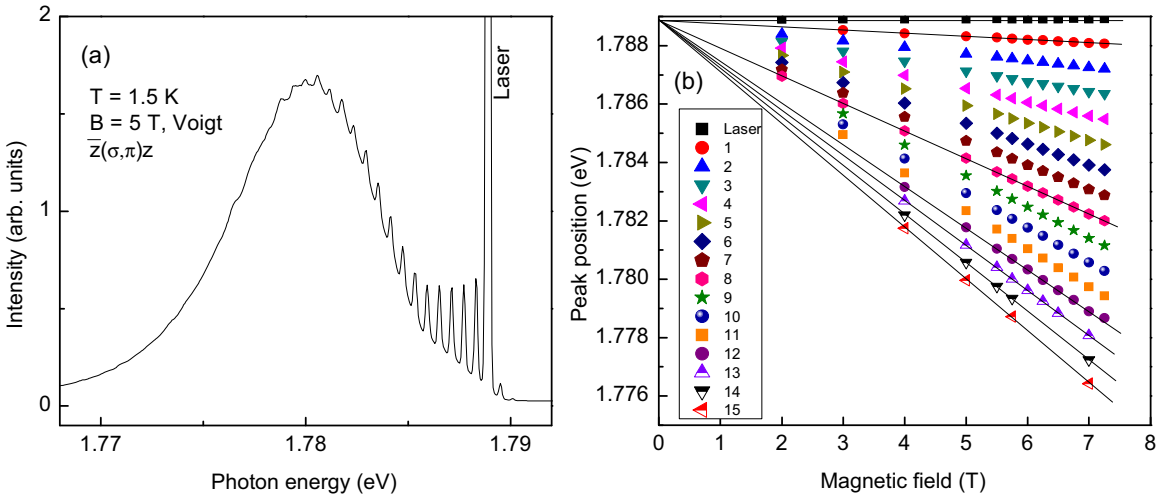

FIG. 1. (a) Representative spectrum of the secondary emission (photoluminescence+MPR) from the 9-ML QW, sample A, at a quasiresonant laser excitation and a B field of 5 T. More than 15 sharp MPR Raman replicas are observed at the Stokes side, to the left from the laser energy. (b) Dependences of positions of the MPR lines on the B-field strength.

the spatial confinement. In particular, both samples contained QWs with thicknesses of 9, 14, and 25 monolayers (ML), comprising about 30, 45, and 80 Å, respectively. The Mg content in the nonmagnetic barrier layers was, as determined by the barrier photoluminescence (PL) position, ∼24% in sample A and ∼22% in sample B. The content of magnetic Mn ions in the QW layers was ∼1.7% (sample A) and ∼2.4% (sample B), as determined by standard means, based on the energy of saturation of the Raman shift of the resonance spin-flip Raman scattering by s-band electrons in wide 25-ML QWs. (The main effect of the present Rapid Communication was observed in narrow 9- and 14-ML QWs.)

Figure 1(a) depicts a typical emission spectrum of a narrow DMS QW in the conditions of the MPR. One can see a spectacular spectroscopic manifestation of the strong coupling between the paramagnetic Mn ions, the QW exciton, and the B field: a series of multiple satellites of the laser frequency which are mainly located below the laser energy, being superimposed on the background of the QW PL. The light scattering by Mn ions shows up when the laser excitation energy hits the range of the QW exciton states [12–14]. In our experiments, up to 15 Stokes-side MPR peaks were clearly observed. These features are fully in line with the MPR results which were reported previously by Stühler *et al.* [4]. The MPR peaks followed at equal intervals in a particular spectrum, the gap between them being linearly dependent on the B field according to the g-factor of the $3d^5$ electron on the inner shell of the Mn ion, $g_{\mathrm{Mn}} = 2.0$. A fan diagram [Fig. 1(b)] shows the energy positions of all MPR peaks against the B-field value, demonstrating a perfect linearity of the peak positions in the applied field. The increasing slope with increasing peak number corresponds to flips of one, two, . . . , 15 $3d^5$ electrons of manganese ions by one photon, leading to the change of the projection of the net magnetic moment by two, four, . . . , 30 Bohr magnetons. In our experiments, the MPR series peaks could be resolved for B fields down to 2 T, and in weaker fields the MPR peaks merged: Their energy separation became smaller than the spectral resolution. All in all, the experimental

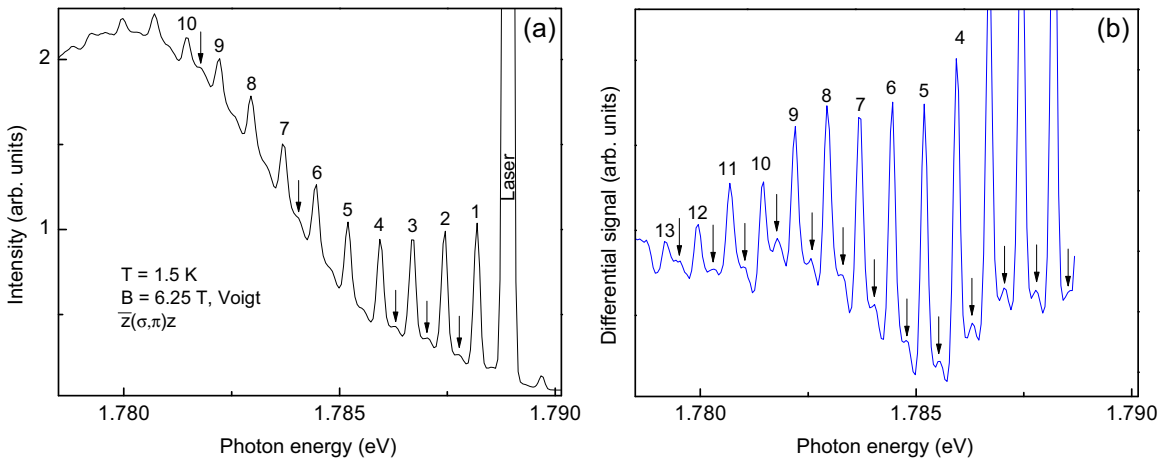

FIG. 2. (a) Spectrum taken at the same conditions as in Fig. 1(a), except for the B-field value, which is now 6.25 T. This spectrum shows a series of additional peaks (marked by arrows) in the gaps between the MPR lines. (b) Differential spectrum produced as the difference between the original spectrum of (a) and a fit of those data by a wide contour simulating the PL.

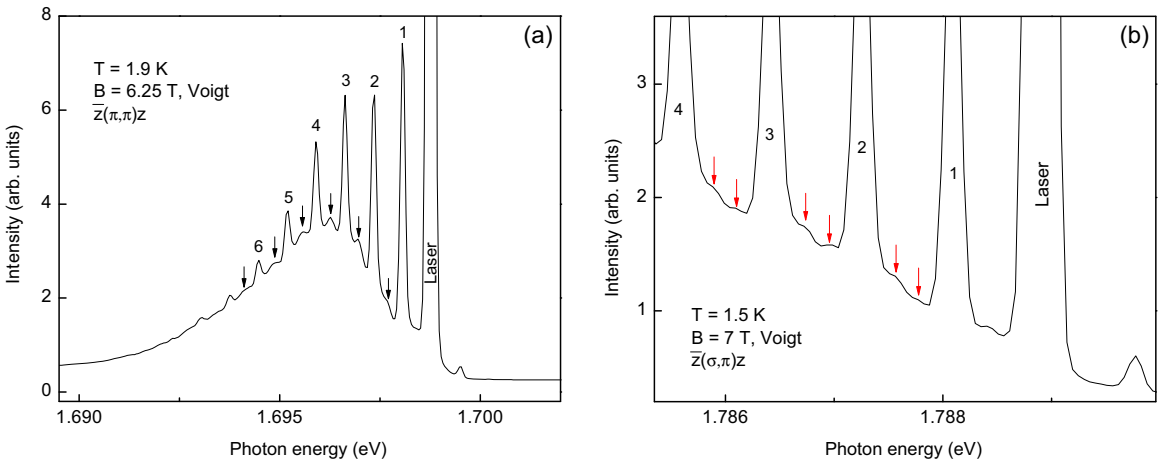

FIG. 3. (a) Spectrum from the 14-ML QW in sample A, taken with the laser excitation deep into the PL band. Some f peaks (marked by arrows) now became quite indisputable without any processing of the signal. (b) Part of the spectrum from the 9-ML QW in sample A, taken at $B = 7$ T. Probably, in the augmenting B field between 6.5 and 7 T, very weak doublet structures appear (denoted by arrows), which may indicate a splitting of the f peaks.

picture, samples, and experimental conditions are very typical for an observation of the MPR effect.

However, we observed, in B fields around 6 T, a modulation of the spectral intensity between the MPR peaks. A closer inspection revealed the onset of a series of weak spectral peaks located in the gaps between the main ("integer") MPR peaks [Fig. 2(a)]. One way of visualizing this long series of peaks more distinctly is as follows: to fit the smooth contour of the PL and to subtract this fit from the experimental spectrum [Fig. 2(b)]. The differential signal shows the intermediate peaks quite indisputably, practically in each gap between neighboring MPR peaks. The other way is to redshift the laser photon energy deeper inside the PL contour. This slightly deteriorates the resonance conditions for the MPR (a lower number of MPR peaks is observed), but this does not apply for the intermediate peaks. Some of them, on top of the PL band, become obvious without any signal processing [Fig. 3(a)].

The additional peaks are roughly centered in the gaps between neighboring MPR peaks and shift more or less linearly with the B-field value. This would imply, at first glance, that they should correspond to inelastic light scattering processes in which a fractional (half-integer) number of manganese electrons flip spins. This is, of course, a paradoxical proposition which needs a realistic alternative. Let us list some facts regarding the series of "fractional" peaks (f peaks), as they showed up in our experiments.

First, the f peaks arose for a rather narrow range of B fields: They manifested themselves essentially for fields between 5.75 and 6.5 T, where a series of more than a dozen f peaks was visible. At stronger fields, the f peaks were weaker and showed up only in some of the gaps between the "integer" MPR peaks. Second, the f peaks were observed for QWs with noticeably different widths, yet with different Mn concentrations—however, the B-field range of the observation of the f series remained unchanged. Seemingly, the QW width and the Mn concentration are not critical parameters of the effect. Third, a change in the incident laser power density by a factor of 5 did not result in any substantial changes in the spectra. This probably speaks against nonlinearity. Fourth, the f series does not demonstrate any pronounced polarization selection rules: The f peaks are equally well observed in both "crossed" [(σ,π) and (π,σ)] and in both "parallel" polarization configurations of the scattering experiment. Thus, they show the same absence of a pronounced polarization behavior which is typical for the "integer" MPR peaks at low temperatures [4,15].

A remarkable feature of the f series is the distribution of the peak intensities over the series. While in the series of the MPR peaks the intensity of overtones monotonously decreases (say, from the first to tenth peak by a factor of 5), in the f series the first ten peaks may demonstrate similar intensities [Fig. 2(b)].

Phenomenologically, the f series can be approached by two different means: (i) as a manifestation of an unknown fractional quantum effect, which would imply a search for an explanation in terms of collective phenomena (quasiparticles); or (ii) in a more trivial way, as a result of an unknown combined process in which the f peaks would be the satellites of the preceding MPR peaks. Let us consider both possibilities in more detail. We ascribe to the f peaks a half-integer indexation in such a way that the f peak located between the laser line and the integer MPR peak No. 1 would get an index 0.5, the f peak between the first and second MPR peaks would get an index 1.5, etc.

In case (i) one should expect that, when describing the B-field dependence of the energy positions of the MPR peaks in units of the slope of peak 1 (i.e., MPR peak 2 has the slope 2, etc.), the f peak indexed 1.5 between MPR1 and MPR2 should move with the B field according to the slope 1.5. Analogously, e.g., for the peaks indexed 7, 7.5, and 8, the relationship of their slopes should show the ratios 7:7.5:8.

In case (ii), the Raman shift of each f peak should be the sum of that of the preceding MPR peak and some field-independent contribution. For instance, the peak 7.5 should move with the B field according to slope 7.

Therefore, the most precise empirical determination of the slopes that describe the B-field motion of the f peaks appears to be an element of critical importance for the understanding of the origin of the effect. Unfortunately, this task is very

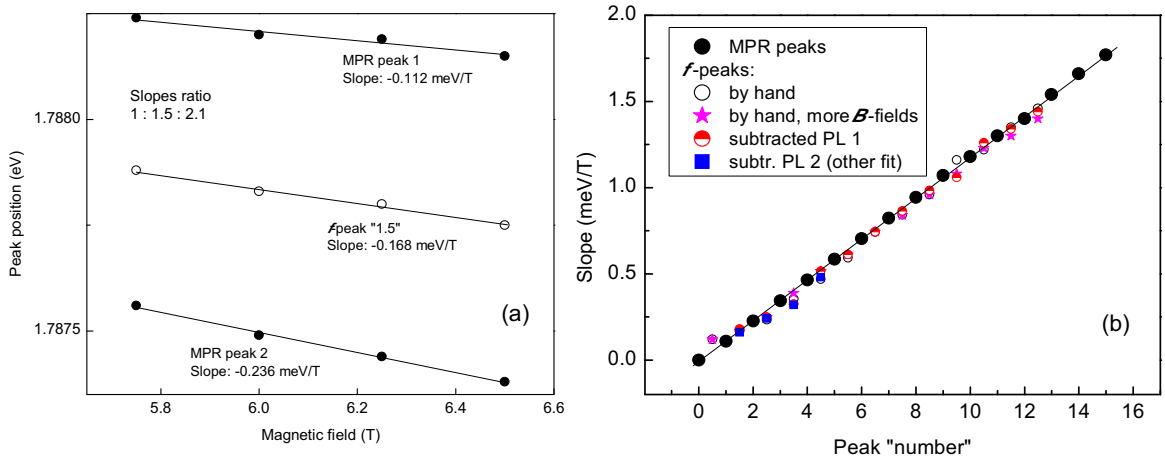

FIG. 4. (a) Linear fits of the B-field dependences of spectral positions of the MPR peaks 1 and 2 (solid circles) and the intermediate f peak (open circles). The slope ratio is close to 1:1.5:2. (b) Sign-reversed slopes of the B-field dependences of positions of the MPR peaks and of the f peaks, taken for different peak indices. The f peaks are indexed by half-integer numbers. Different symbols for f peaks correspond to different methods of determination of the f-peak positions in the original spectra.

demanding for an experimental realization, because it requires a precise determination of the f-peak positions in the spectra. In our experiments, this was hindered by the following: the small intensity of f peaks (up to 20 times lower than that of the next MPR peak); the noticeable observed spectral width of the f peaks (about $1/3$ of the distance between the maxima of the neighboring MPR peaks); the superimposition of the f peaks on the luminescence background with a varying curvature; and the limited dispersion of the spectrometer, which resulted in f-peak widths of as few as 3–4 CCD pixels, leading to odd line shapes.

Moreover, one should note that the f peaks are observed in a rather narrow interval of magnetic fields, which substantially decreases the achievable accuracy of the experimentally determined slopes. For instance, for the peak with index 1.5, for which the expected relative difference in the slopes with the nearest MPR peaks is maximal, the measured slope ratio agrees well with the "fractional" hypothesis (i) [see Fig. 4(a)]. However, in general for the f-series peaks, no such clear agreement is observed: The accuracy of the determined slopes is insufficient, and the scatter of experimental points (including the points extracted from the same data sets by different treatments) is too large [Fig. 4(b)].

In our view, the weak index dependence of the f-peak intensity (against the noticeable index dependence for the MPR peak intensities) is not easy to reconcile with the "satellite" hypothesis (ii). Besides that, the "satellite" process might require a participation of a field-independent energy quantum of about 0.35–0.4 meV. The characteristic energies known for manganese systems (e.g., for the pair of antiferromagnetically coupled nearest-neighbor Mn ions, 2.14 and 1.09 meV [16]) do not match this range. With all that, we have to confess that at the present time we do not have enough grounds to reject hypothesis (ii).

We paid attention to the fact that the zero-field energy of the triplet excitation of the Mn-Mn pair $\Delta_T = 1.09$ meV [16] happens to be close in value to 1.5 times the MPR spin splitting ($g_{\mathrm{Mn}} = 2.0$) at 6.25 T, which is $\Delta_{\mathrm{MPR}} = 0.75$ meV. We attempted to derive half-integer energies from this fact, assuming a participation of the triplet pair state in a hypothetical combined Raman process. However, this attempt fell short with us against the observation of the f peak with index 1.5 and with its clear tendency to redshift as the B field is increased. Indeed, the energy position of peak No. 1.5 is about 1.5 times Δ_{MPR}, which energy can be (approximately) obtained either by a single transition to the pair triplet state $S = 1$, $M = 0$ or by a combined process: one MPR spin-flip plus excitation of a Mn-Mn pair to the triplet state $S = 1$, $M = -1$. However, both the mentioned processes would result in a B-field-independent Raman response, in pronounced contrast with observations. On the other hand, the transition that might give a replica with a necessary B-field behavior (to the triplet state $S = 1$, $M = +1$) can only produce peak positions starting from $\sim$2.5, by no means 1.5.

One should note that, in principle, participation of a particle with g-factor unity may somehow add to the conventional MPR, producing half-integer Raman shifts. Indeed, the tetrahedral ^{55}Mn center in CdTe has been recently shown to reveal a g-factor $g_{\mathrm{Mn}} = 1$ via the interaction of the d-shell spin moment with the nuclear spin [17]. However, this was observed at few-mT B fields in a spin-noise experiment. Contrary to that, in our few-T range of B fields which exceed the hyperfine field (few mT [18] to few tenths mT [17]) by three to four orders of magnitude, the d-electron spin and the nuclear spin should be quite decoupled, resulting in the usual g-factor $g_{\mathrm{Mn}} = 2$ (not to mention that the involvement of $g_{\mathrm{Mn}} = 1$ does not explain features such as the B-field-range selectivity of f peaks and the strange intensity distribution in the series).

We finish this Rapid Communication with a somewhat indistinct but quite intriguing observation. A comparison of the spectra taken at different B fields gives the impression that at about 7 T, a crossover occurs in the system of f peaks. Namely, as the B field goes up, each f peak fades in its original centered position between the "integer" peaks, and instead a doublet of very weak structures appears on both sides of this center [Fig. 3(b)]. But the latter observation is at the very edge of capabilities of our present experimental setup, so it needs to be readdressed with a better spectral resolution, as discussed below.

In conclusion, for typical conditions of the observation of multiple paramagnetic Raman resonance in model heterostructures with DMS quantum wells, we observed a never-reported series of Raman peaks showing up in a narrow range of applied magnetic fields. These weak f peaks are located close to the middle between the strong MPR peaks, they move linearly in the magnetic field value, and they reveal a remarkably weak dependence of the intensity on the peak index number. We discussed conditions to observe the f series, described two possible approaches to the interpretation, and the conclusion was that we do not have grounds for having a preference for either approach. Meanwhile, one of the interpretations is especially exciting, as it implies a manifestation of a fractional quantum effect. We should note that the specific microscopic origin of the observed effect is quite vague, which is unexpected for such a well-studied model object.

Towards the experimental progress in the exploration of the f series, the following steps appear to be necessary. First, while we are confident in the high quality of our samples, a reproduction of the main effect on samples of a different technological origin makes sense. Second, it is essential to increase the accuracy of determination of the positions of the f peaks. To this end, a narrow-band tunable cw laser should be used for optical excitation, e.g., a ring-cavity Ti:sapphire laser. And, simultaneously, the dispersion of the spectroscopic unit should be at a level of the best Raman spectrographs. In aggregate, these two measures will probably decrease the observed linewidths of the f peaks and ultimately increase the accuracy of the key experiment with the determination of slopes of the B-field dependences.

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[1] *Diluted Magnetic Semiconductors*, edited by J. K. Furdyna and J. Kossut, Semiconductors and Semimetals (Academic Press, New York, 1988), Vol. 25.

[2] *Introduction to the Physics of Diluted Magnetic Semiconductors*, edited by J. Gaj and J. Kossut (Springer, Berlin, 2010).

[3] G. Mackh, W. Ossau, D. R. Yakovlev, A. Waag, G. Landwehr, R. Hellmann, and E. O. Göbel, Phys. Rev. B **49**, 10248 (1994).

[4] J. Stühler, G. Schaack, M. Dahl, A. Waag, G. Landwehr, K. V. Kavokin, and I. A. Merkulov, Phys. Rev. Lett. **74**, 2567 (1995).

[5] C. Kehl, G. V. Astakhov, K. V. Kavokin, Yu. G. Kusrayev, W. Ossau, G. Karczewski, T. Wojtowicz, and J. Geurts, Phys. Rev. B **80**, 241203(R) (2009).

[6] L. C. Smith, J. J. Davies, D. Wolverson, M. Lentze, J. Geurts, T. Wojtowicz, and G. Karczewski, Phys. Rev. B **77**, 115341 (2008).

[7] M. J. Seong, H. Alawadhi, I. Miotkowski, A. K. Ramdas, and S. Miotkowska, Phys. Rev. B **63**, 125208 (2001).

[8] X. Lu, S. Tsoi, I. Miotkowski, S. Rodriguez, A. K. Ramdas, and H. Alawadhi, Phys. Rev. B **75**, 155206 (2007).

[9] A. V. Koudinov, Yu. G. Kusrayev, D. Wolverson, L. C. Smith, J. J. Davies, G. Karczewski, and T. Wojtowicz, Phys. Rev. B **79**, 241310(R) (2009).

[10] M. Byszewski, D. Plantier, M. L. Sadowski, M. Potemski, A. Sachrajda, Z. Wilamowski, and G. Karczewski, Physica E **22**, 652 (2004).

[11] K. V. Kavokin and I. A. Merkulov, Phys. Rev. B **55**, R7371(R) (1997).

[12] J. Stühler, M. Hirsch, G. Schaack, and A. Waag, Phys. Rev. B **49**, 7345 (1994).

[13] A. V. Koudinov, Yu. G. Kusrayev, B. P. Zakharchenya, D. Wolverson, J. J. Davies, T. Wojtowicz, G. Karczewski, and J. Kossut, Phys. Rev. B **67**, 115304 (2003).

[14] A. V. Koudinov, N. S. Averkiev, Yu. G. Kusrayev, B. R. Namozov, B. P. Zakharchenya, D. Wolverson, J. J. Davies, T. Wojtowicz, G. Karczewski, and J. Kossut, Phys. Rev. B **74**, 195338 (2006).

[15] J. Stühler, G. Schaack, M. Dahl, A. Waag, G. Landwehr, K. V. Kavokin, and I. A. Merkulov, J. Cryst. Growth **159**, 1001 (1996).

[16] J. Stühler, G. Schaack, M. Dahl, A. Waag, G. Landwehr, K. V. Kavokin and I. A. Merkulov, J. Raman Spectrosc. **27**, 281 (1996).

[17] S. Cronenberger, D. Scalbert, D. Ferrand, H. Boukari, and J. Cibert, Nat. Commun. **6**, 8121 (2015).

[18] M. L. Sadowski, M. Byszewski, M. Potemski, A. Sachrajda, and G. Karczewski, Appl. Phys. Lett. **82**, 3719 (2003).