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Excitonic energy transfer to the 3*d* electrons of Mn^{2+} in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$

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We studied the energy transfer between excitons and the 3*d* electrons of Mn^{2+} in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals within a Mn concentration range of $0.2 \leqslant x \leqslant 0.45$ at $T=2$, 5, and 20 K by emission, excitation, and time-resolved photoluminescence measurements. Time-integrated emission spectra show a strong quenching of the L_2-type exciton luminescence together with a strong increase of intensity of the ${}^4T_1(G) \rightarrow {}^6A_1(S)\mathrm{Mn}^{2+}$ luminescence if the Mn concentration is raised from $x=0.32$ to 0.43. Excitation spectra of the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ Mn^{2+} luminescence give evidence of an excitonic energy transfer via free and intrinsically localized excitons to the 3*d* shell of Mn^{2+}. By time-resolved photoluminescence measurements we investigated the lapse of luminescence at discrete energies in the exciton luminescence band using pulsed band-to-band excitation. The luminescence shows a nearly exponential decay. We see a strong decrease of the luminescence decay time when the Mn^{2+} ions act like energy absorbers for the exciton energies. [S0163-1829(97)04911-4]

I. INTRODUCTION

$\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ belongs to the group of semimagnetic semiconductors (SMSC's). They are mostly II-VI compounds doped with 3*d* or 4*f* transition metals with high magnetic moment, embedded in the host crystal on cation sites. Interesting physical properties can be observed in SMSC's, in particular, in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ (e.g., large magneto-optical effects[1–4]), due to a strong s,p-d exchange interaction between band carriers and the Mn^{2+}-3*d* electrons.[5–7] Therefore SMSC's have been subject to many studies in the last 15 years.[8–12]

In $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ the luminescence emission due to the internal transitions within the 3*d* shell of Mn^{2+} can be excited by the direct absorption in the Mn ions or by the absorption of light in the host crystal followed by an energy transfer to the emitting ions. This energy transfer may be realized as an exciton migration process. It is the aim of this paper to present some experimental results on the excitonic energy transfer in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$.

$\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ reflectivity measurements[13,14] of free excitons E_{Ex} reveal that the fundamental band-gap shifts linearly with the Mn concentration x [$E_{\mathrm{Ex}}(x)=1.595+1.592x$ for $0 \leqslant x \leqslant 0.7$ and $T \approx 5$ K.[13] For $x \geqslant 0.37$ an additional strong absorption below the band gap is observed which has been ascribed to Mn^{2+} intraionic transitions.[13,15] Exciting above this threshold a photoluminescence emission band centered near 2 eV is found for temperatures $T<80$ K. This is ascribed to a multiphonon sideband of the intraionic Mn^{2+} transition ${}^4T_1(G) \rightarrow {}^6A_1(S)$.[13] By band-to-band excitation a broad exciton luminescence band can be observed at higher energies.

As it has been reported earlier, the exciton luminescence of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ changes drastically when going from lower to higher Mn concentrations. For $x \leqslant 0.05$ the exciton luminescence is dominated by the recombination of acceptor and donor bound excitons. This exciton luminescence is generally labeled with L_1 (A^0X or D^0X). In the *p*-type semiconductor $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ acceptor bound excitons are dominating. For $x \geqslant 0.05$ an exciton luminescence band is observed which broadens strongly with increasing Mn concentration and shifts to lower energies with respect to the excitonic structure obtained in reflectivity measurements.[16,17] The broadening of the exciton luminescence band is explained, on one hand, by an increasing band-gap fluctuation caused by the local fluctuations of the Mn concentration x in these highly mixed crystals. On the other hand, the influence on the exchange interaction between an exciton and the neighboring Mn^{2+} ions on the exciton states leads to the formation of an excitonic magnetic polaron (EMP) which is typical for the semimagnetic semiconductor $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$.[18–24] Band-gap fluctuations, magnetization fluctuations, and the EMP effect disperse exciton states in the crystal and lead to a broadening of the exciton luminescence band which is usually labeled with L_2. Intrinsic localization of excitons into the potential wells of the band-gap fluctuations and further relaxation by the exchange interaction with neighboring Mn^{2+} ions result in the observed shift of the L_2-type exciton luminescence band to lower energies with respect to the excitonic structure of reflectivity measurements.[25–28]

Time-resolved measurements of the L_2-type exciton luminescence in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ have shown that the decay of emission on the low-energy side of the exciton luminescence band, i.e., for deeply bound exciton states, is longer than the decay of emission on the high-energy side of the exciton luminescence band.[29] The shorter decay of the exciton luminescence on the high-energy side of the exciton luminescence band is explained by a higher probability for these still nonlocalized or weakly bound excitons to scatter and to transfer their energy to nonradiative sites and to relax into deeper bound exciton states by intrinsic localization (self-trapping in potential wells of the band-gap fluctuations) and the EMP effect. Similar effects of intrinsic exciton localization due to band-gap fluctuations have been shown in the mixed nonmagnetic semiconductor $\mathrm{CdS}_{0.53}\mathrm{Se}_{0.47}$.[30]

While the energy of the internal transition ${}^4T_1(G) \rightarrow {}^6A_1(S)$ of Mn^{2+} does not change with increasing x, the energy of excitons, following the change of the band gap, does. There should be a threshold of energy transfer from excitons to the 3*d* shell of Mn^{2+} when x increases. Indeed

TABLE I. Experimental data of the emission, excitation, and SPC measurements.

	Emission	Excitation	SPC measurements
Laser-pulse length	200 ps	5 ps	5 ps/2 ps
Repetition rate	82 MHz	4 MHz	4 MHz/1.8 MHz
Excitation energy	2.54 eV		2.22 eV/2.68 eV
Mean laser power	500 nW	10–30 mW	30 mW/30 mW

this threshold near $x=0.4$ has been observed, above which the emission due to ${}^4T_1(G)\rightarrow{}^6A_1(S)$ appears. This threshold is characterized by a significant change of the decay behavior and intensity of the excitonic luminescence.

II. EXPERIMENT

We investigated the photoluminescence of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ bulk crystals grown by the high-pressure Bridgman method within a Mn concentration range of $0.2\leqslant x\leqslant 0.45$ at $T=2$, 5, and 20 K. For the excitation of luminescence we used a mode-locked Ar-ion laser or a mode-locked synchronously pumped dye laser, respectively, with excitation power densities between 30 kW/cm^2 and 1 MW/cm^2 measured on the sample. The emission was detected by a GaAs photomultiplier and single-photon-counting (SPC) technique[31] was used. The spectral resolution was near 1 meV for both emission and excitation spectra and between 0.1 and 0.4 meV (detection window) in the SPC measurements. The emission spectra were corrected in view of the characteristics of the spectrometer and of the sensitivity of the photomultiplier. The excitation spectra were corrected with respect to the dye laser intensity. Table I shows the experimental data of the emission, excitation, and SPC measurements.

Using a 2-ps laser pulse for our time-resolved measurements the SPC experimental set yielded a transient of 60-ps full width at half maximum (FWHM). In order to improve the time resolution of the SPC measurements we made a fit to the transients of the exciton luminescence. We convoluted the transient of the 2-ps laser pulse, which implies all apparative broadening effects, by one single exponential decay curve [$\exp(-t/\tau)$, τ hypothetical decay time]. We achieved a good agreement between our fit and the experimentally measured transient when detecting on the far high- or on the far low-energy side of the exciton luminescence band. In the center of the exciton luminescence band we found only a poor agreement. This seems to be because at each energy in the L_2-type exciton luminescence band we measure actually the radiative recombination of excitons in different states of energy relaxation. The state distribution of exciton energies in the crystal is mainly due to the spatial inhomogeneity of Mn ions leading to band-gap fluctuations and due to magnetization fluctuations. That is, at each energy we measure a weighted sum of transients due to distinctly intrinsically relaxed (localized) and bound (EMP) excitons. This effect is more pronounced in the center of the exciton luminescence band than on its low- or high-energy side. Therefore, when detecting in the center of the exciton luminescence band we obtained only an average value for τ whereas on the far low- or far high-energy side of the exciton luminescence band we obtained a unique value for τ according to a single exponential decay behavior due to the radiative recombination of still free or deepest bound excitons, respectively. In this way we were able to determine the dominating decay time τ of the exciton luminescence at discrete energies of the exciton luminescence band with an accuracy of about 10 ps.

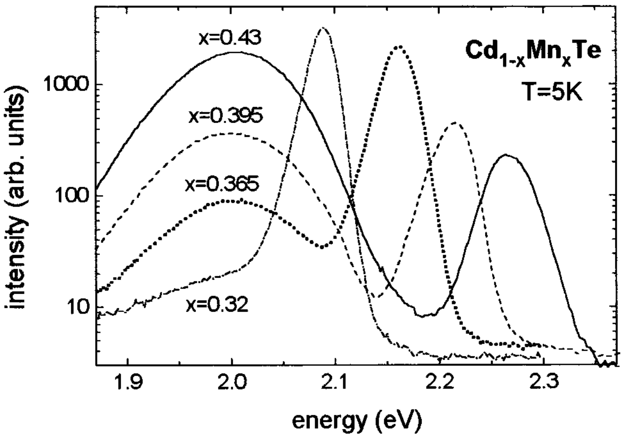

FIG. 1. Emission spectra (in logarithmical scale) of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ for $x=0.32$, $x=0.365$, $x=0.395$, and $x=0.43$ excited at $E=2.54$ eV. Mn^{2+}: ${}^4T_1(G)\rightarrow{}^6A_1(S)$ luminescence band at $E=2.0$ eV, the energy of the exciton luminescence band (L_2-type) varies with Mn concentration x from $E=2.08$ to 2.28 eV.

When registering within the peak maximum of the excitonic emission (L_2 band), the maximum of the excitation spectra of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ with $x\sim 0.4$ is shifted to energies which are 15 meV higher than the luminescence maximum, i.e., the detection energy. We ascribe this excitation maximum of the exciton luminescence to the generation of free excitons. Knowing the free exciton energy $E_{\mathrm{Ex}}(x)=1.595+1.592x$ at 5 K from reflectivity measurements[1] and considering a mean relaxation energy of about 15 meV into the radiative exciton states we are able to determine the local Mn concentration of our crystals with x near to 0.4 by the energetic position of the exciton luminescence maximum with an accuracy of $\Delta x=0.002$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows, in a logarithmical scale, emission spectra of four $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals with a Mn concentration of $x=0.32$, 0.365, 0.395, and 0.43 using band-to-band excitation at 2.54 eV of a constant excitation intensity at 5 K. When going from the Mn concentration $x=0.32$, where still no Mn^{2+} luminescence can be seen, to higher concentrations we observe not only the well-known shift of the exciton luminescence to higher energies but also a very strong de-

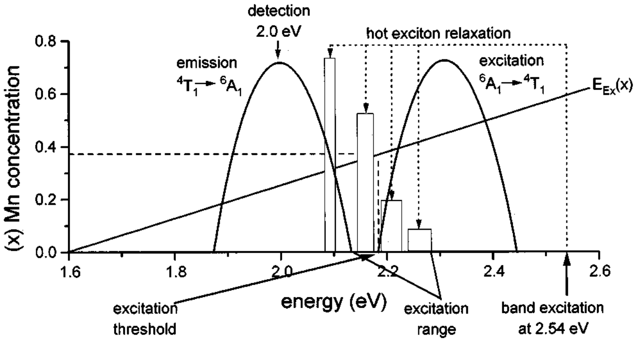

FIG. 2. Model of energy transfer from excitons to the $^4T_1(G)$ excited state of Mn^{2+} ions in $Cd_{1-x}Mn_xTe$. Shown are the free exciton energy as a function of Mn concentration $E_{Ex}(x)=1.592+1.595x$ at $T=5$ K after (Ref. 13), schematically the Mn^{2+} multiphonon sidebands of emission $^4T_1(G)\rightarrow{}^6A_1(S)$ and excitation $^6A_1(S)\rightarrow{}^4T_1(G)$ and, represented by columns, the exciton luminescence bands from Fig. 1.

crease of the exciton luminescence intensity and an equally strong increase of the intensity of the Mn^{2+} luminescence. The FWHM of the exciton luminescence band increases from 25 meV for $x=0.32$ to 46 meV for $x=0.43$ showing the strong dispersion of exciton states due to the band-gap fluctuation and excitonic magnetic polaron relaxation with increasing Mn concentration as mentioned before. For the crystal with $x=0.32$ we can observe on the low-energy side of the exciton luminescence band a very weak luminescence intensity due to weak contributions of A^0X and D^0X bound exciton recombination and not due to Mn luminescence as we want to point out here. This can be deduced by a line-shape analysis of the exciton luminescence in $Cd_{1-x}Mn_xTe$ when raising the Mn concentration above $x=0.05$.[16] For $x>0.1$ a broad and asymmetric exciton luminescence band (L_2-type) is observed. Its asymmetry is due to A^0X and D^0X bound exciton recombination. For higher Mn concentrations, as for instance $x=0.32$, this asymmetry in the line shape of the exciton luminescence is only appreciable in logarithmical presentation of the luminescence intensity.

The change of the luminescence of the $Cd_{1-x}Mn_xTe$ crystals as a function of the Mn concentration and band-to-band excitation, can be explained by a model of energy transfer represented in Fig. 2. Figure 2 shows schematically the Mn^{2+} multiphonon sidebands of the emission $^4T_1(G)\rightarrow{}^6A_1(S)$ and of the excitation $^6A_1(S)\rightarrow{}^4T_1(G)$. The multiphonon sideband of the excitation $^6A_1(S)\rightarrow{}^4T_1(G)$ is drawn mirrorlike to the emission and pinned to the excitation threshold of about 2.18 eV, which is known from the excitation measurements of the Mn^{2+} luminescence (Fig. 3). Figure 2 shows also the free exciton energy as a function of the Mn concentration $E_{Ex}(x)=1.595+1.592x$ at $T=5$ K and the exciton luminescence bands from Fig. 1 represented by the columns.

When exciting at 2.54 eV, which is deep in the conduction band, we create hot excitons which relax intrinsically into radiative exciton states.[25,32,33] For $x=0.32$ we see in Fig. 2 that the exciton luminescence band lies far below the Mn^{2+} excitation threshold and no energy transfer from these exciton states to the Mn^{2+} ions is possible. The fact that no Mn^{2+} luminescence can be observed for $x=0.32$ (Fig. 1) demonstrates that the Mn^{2+} ions cannot be excited directly by the excitation energy of 2.54 eV. Therefore, by band-to-band excitation, the energy transfer to the Mn^{2+} ions has to take place via excitons.

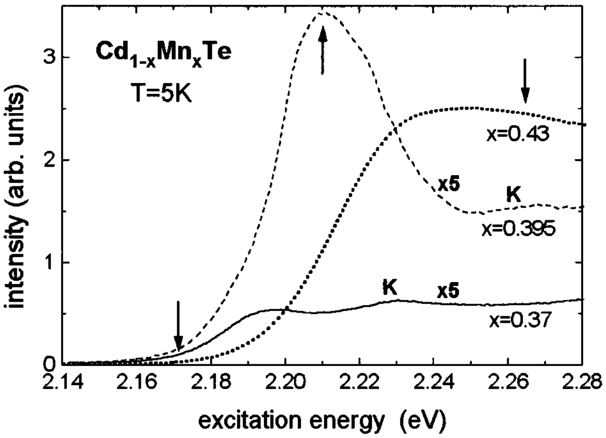

FIG. 3. Excitation spectra of the Mn emission in $Cd_{1-x}Mn_xTe$ for $x=0.37$, $x=0.395$, and $x=0.43$. The arrow indicates the energy of the exciton luminescence band. *K* indicates the band edge.

For $x=0.365$ the high-energy side just overlaps the excitation threshold of the Mn^{2+} luminescence so that only a very small energy transfer is possible. At $x=0.395$ nearly the whole exciton luminescence band overlaps the shoulder of the Mn^{2+} excitation band. This implies that for lower exciton energies a weak, for higher exciton energies a more effective energy transfer to the Mn^{2+} ions is possible. Finally for $x=0.43$ the whole exciton luminescence band lies in the range of strong excitation for the Mn^{2+} luminescence. This means that an effective energy transfer for all excitons is possible.

In the same measure as Mn^{2+} ions are excited by energy transfer from excitons or by reabsorption of photons which are generated by the radiative recombination of excitons the exciton luminescence is weakening. This is the reason for the strong quenching of the exciton luminescence when raising the Mn concentration x in $Cd_{1-x}Mn_xTe$ crystals (Fig. 1).

Figure 3 shows the excitation measurements of the Mn^{2+} luminescence of three crystals at $T=5$ K. In contrast to the crystal with $x=0.43$ we observe for $x=0.37$ and 0.395 still a relatively weak (factor 5) excitation of the Mn^{2+} luminescence. Two other excitation features are observed: (1) a rise of intensity in the exciton region, the arrow indicates the exciton luminescence band; and (2) a weak modulation marked by *K*. For both crystals the modulation *K* is shifted to energies which are approximately 50 meV higher than the exciton luminescence band (arrow) indicating the band edge.[18]

As the model in Fig. 2 shows, we observe for the crystal with $x=0.43$ below the free exciton energies a direct and effective excitation. Going to higher excitation energies the Mn^{2+} luminescence decreases and is quenched. Obviously the emission is restricted to the range of the creation of excitons. For $x=0.37$ the free exciton energy lies just at the excitation threshold of the Mn^{2+} luminescence and therefore the Mn^{2+} luminescence is controlled by the excitation of excitons for all excitation energies. On the other hand, in the case of $x=0.395$, we observe that the exciton luminescence band lies just in the rise of the multiphonon sideband of Mn excitation $^6A_1(S)\rightarrow{}^4T_1(G)$. Besides, in Fig. 3 we can recognize that for this crystal the excitation maximum of the

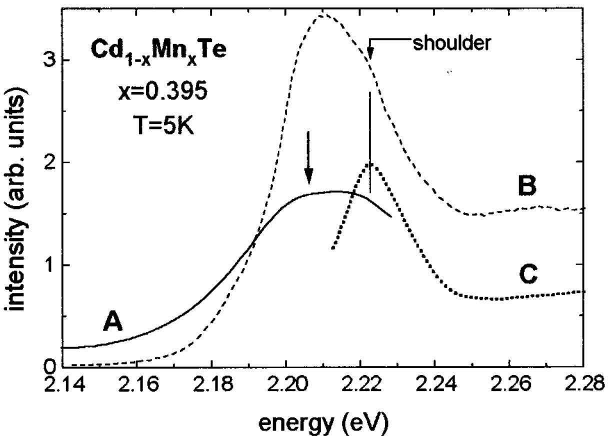

FIG. 4. Excitation spectra of the Mn emission (curve B, dashed line) and of the L_2-type exciton emission (curve C, dotted line). Curve A (solid line) is the emission spectrum of the L_2 exciton luminescence excited at 2.3 eV. The arrow at 2.206 eV indicates the detection energy for curve C.

Mn luminescence coincides in energy with the position of the exciton luminescence band as indicated by the arrow. To simplify further discussion of the excitation behavior for the Cd$_{1-x}$Mn$_x$Te crystal with $x=0.395$, we represent in Fig. 4 its excitation spectrum of the Mn luminescence (B, dashed line) again together with its emission spectrum of the exciton luminescence (A, solid line) and its excitation spectrum of the exciton luminescence (C, dotted line). The detection energy of the excitation spectrum of the exciton luminescence is indicated in Fig. 4 by an arrow. In this figure we can observe for the Cd$_{1-x}$Mn$_x$Te crystal with $x=0.395$ a similar excitation behavior for both the Mn^{2+} luminescence and the exciton luminescence, i.e., the excitation maximum of the exciton luminescence can be seen reproduced as a shoulder on the high-energy wing of the excitation maximum of the Mn luminescence. The latter coincide in energy with the exciton luminescence band. These features indicate clearly an energy transfer via free and bound excitons to the Mn^{2+} ions in the Cd$_{1-x}$Mn$_x$Te crystal with $x=0.395$.

Figure 5 shows the decay times τ of the exciton luminescence of five Cd$_{1-x}$Mn$_x$Te crystals with various x measured at different detection energies in the exciton luminescence band at $T=2$ K. For clarity the curves are shifted so that the peak energies of the exciton luminescence band coincide at 0 meV. Negative values of the energy scale refer to the low-energy wing, positive values to the high-energy wing of the exciton luminescence band.

For all Mn concentrations x in Fig. 5 except for $x=0.45$, we observe a decrease of decay time τ going from the low-energy to the high-energy wing of the exciton luminescence band. This reflects the change from deeply bound exciton states as due to the excitonic magnetic polaron localized in a potential well to less bound exciton states from which excitons are able to diffuse with a higher probability to nonradiative sites. Figure 6 shows the contour lines of 17 SPC measurements at discrete energies in the exciton luminescence band of the Cd$_{0.8}$Mn$_{0.2}$Te crystal using the decay times given by Fig. 5. This diagram is similar to that given by Oka *et al.*[34]

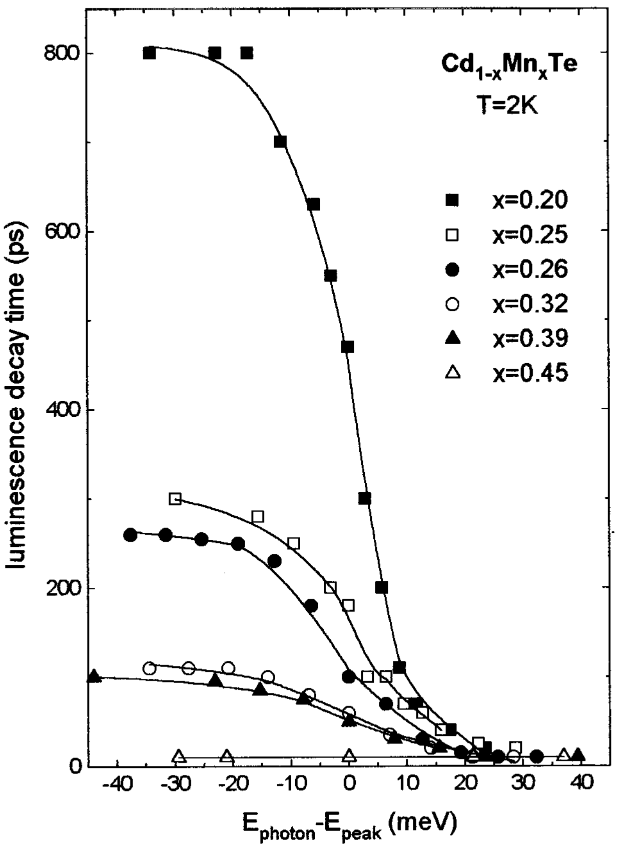

FIG. 5. Exciton decay time τ versus energy of five Cd$_{1-x}$Mn$_x$Te crystals with various x at $T=2$ K. All curves are shifted to coincide in peak energies of the time-integrated luminescence band. Lines are drawn to guide the eye.

As for the influence of temperature upon the decay time of emission, some interesting features are observed. The first observation to be mentioned is the decrease of the decay time when the temperature is raised from $T=5$ to $T=20$ K. The strongest shortening of the decay is observed in the case of the crystal Cd$_{0.74}$Mn$_{0.26}$Te going from $\tau_{max}=250$ to $\tau_{max}=120$ ps. Simultaneously the luminescence intensity decreases to half its initial value, an unusual narrowing from 28 meV FWHM to 22 meV and a shift of 7 meV of the exciton emission band to higher energies is observed. These obser-

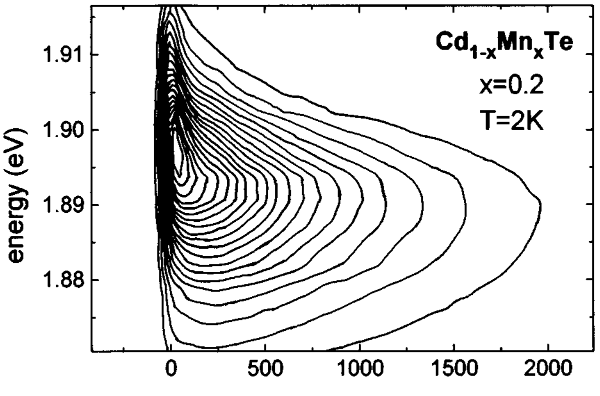

FIG. 6. Contour lines of 17 SPC measurements at discrete energies in the exciton luminescence band of a Cd$_{0.8}$Mn$_{0.2}$Te crystal at $T=2$ K.

vations are not in contradiction to other authors.[4,35–37] We conclude from these features that at $T=20$ K the deepest exciton states are not yet reached, which implies that the diffusion to nonradiative sites is much stronger than at $T=5$ K.

With increasing Mn concentration a strong decrease of the longest decay time of the excitonic emission is observed. The interpretation of the change of the maximum decay time $\tau_{\max}$ can be given considering two Mn concentration ranges: In the first one, from $x=0.20$ to $x=0.32$, $\tau_{\max}$ varies from 800 to 110 ps. As for the crystal with $x=0.39$ having a decay time of $\tau_{\max}=100$ ps no significant change is registered. In the second range, for $x\geqslant0.39$, where the Mn luminescence is already observable, $\tau_{\max}$ drops below 20 ps for $x=0.45$.

In the low-concentration range ($x\leqslant0.32$) the strong decrease of $\tau_{\max}$ from 800 to 110 ps is still unclear. It seems to be the result of an increasing defect density in the crystal when raising the Mn concentration. Consequently, the rate of nonradiative transitions to these defect sites can increase. Recently it has been shown that potential fluctuations increase strongly due to increasing spatial inhomogeneity of Mn ions in the crystal when raising the Mn concentration above $x=0.1$.[26,28] By intrinsic exciton localization in potential wells of band-gap fluctuations and a more pronounced EMP effect due to increasingly more Mn^{2+} ions in the exciton Bohr radius, one would even expect an increase of the longest decay time $\tau_{\max}$ when raising the Mn concentration. Compared to free exciton energies, both exciton localization and EMP formation lead to a higher density of states for excitons at lower energies. These deeper bound excitons should have a lower probability for scattering at nonradiative sites. Obviously the energy relaxation into these deeply bound exciton states is strongly confined which results in the observed decrease of exciton decay times, i.e., the decrease of $\tau_{\max}$ observed in our crystals when raising the Mn concentration. Oka *et al.*[37] measured (as well with the SPC technique) for a $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals with $x=0.18$, also grown by the Bridgman method, a maximum decay time of 1300 ps. This shows in comparison to our crystals with $x\geqslant0.2$ less scattering at nonradiative sites and fits into the trend observed in our crystals of a decreasing decay time with increasing Mn concentration. In contrast to our results Mackh *et al.*[23] observed in molecular-beam epitaxy grown epilayers of $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ ($x\leqslant0.34$) with increasing Mn concentration an increase of decay time. In their case, they determined the decay time from the energy-integrated exciton luminescence band (L_2-type). Here we are not able to resolve this discrepancy but it may indicate that our crystals grown by the Bridgman method seem to be of a lower quality, i.e., with a higher impurity density, than those $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ epilayers studied by Mackh *et al.* Finally, the fact that we observed nearly the same values of $\tau_{\max}$ for $x=0.32$ and 0.39, i.e., 110 and 100 ps, respectively, may indicate a saturation in the balance for the nonradiative energy transfer in our $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals.

In the range of higher concentration (for $x\geqslant0.39$) the excitation range of the Mn^{2+} ions overlap with the exciton energies. In this concentration range the decrease of $\tau_{\max}$ from 100 ps to less than 20 ps may be explained by the opening of an Mn^{2+}-induced recombination channel for the annihilation of excitons. Consequently, we ascribe this drop of $\tau_{\max}$ to less than 20 ps to the onset of energy transfer between excitons and the Mn^{2+} ions in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$. In the case of $x=0.39$ the ${}^4T_1(G)\rightarrow{}^6A_1(S)$ emission of Mn^{2+} can already be observed, but we observe a relatively long decay time ($\tau_{\max}=100$ ps). This can be explained by the fact that only the high-energy side of the exciton luminescence band covers the range of effective excitation of the Mn^{2+} ions (see Fig. 2). The excitons reaching the deep states still recombine radiatively. Finally in the case of $x=0.45$ all exciton energies are overlapping with the range of effective excitation of the Mn^{2+} luminescence. Therefore all exciton states are able to contribute to the energy transfer to the 3*d* shell of Mn^{2+}. This explains the significant drop of $\tau_{\max}$. We would like to point out that this drop of $\tau_{\max}$ to lower than 20 ps gives direct evidence for an energy transfer from the excitons to the Mn^{2+} ions, i.e., that the Mn^{2+} ions do not only reabsorb the energy after a radiative recombination of the excitons. Reabsorption would not change the decay time, but only weaken the intensity of the exciton luminescence. Finally, it should be mentioned that any reliable determination of the rise time and therefore of the kinetic of the excitonic energy transfer is impossible because of the band-gap fluctuation of our mixed crystals.

IV. CONCLUSIONS

The experimental evidence of the energy transfer between excitons and the 3*d* electrons of Mn^{2+} in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals are given by the following.

(1) Exciton luminescence quenching. Strong exciton luminescence quenching is observed when raising the exciton energy with the Mn concentration in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals above the excitation threshold of the Mn^{2+} emission ${}^4T_1(G)\rightarrow{}^6A_1(S)$.

(2) Excitation structures. The excitation structure of the Mn^{2+} luminescence in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals is determined by the excitation of excitons for all excitation energies.

(3) Longest decay time quenching. The change in the longest decay time $\tau_{\max}$ from 100 to less than 20 ps when raising the Mn concentration above $x\approx0.4$ can be explained by the opening of a recombination channel for excitons: the energy transfer between excitons and the Mn^{2+} ions in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ crystals.

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