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# Radiative behavior of negatively charged excitons in CdTe-based quantum wells: A spectral and temporal analysis

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Using reflectivity and picosecond time-resolved photoluminescence, we have studied the intrinsic optical properties of negatively charged excitons in modulation doped CdTe quantum wells. In emission, we observe simultaneously a low energy exponential tail in the charged exciton spectral line and a linear increase of its radiative lifetime with temperature. In absorption, we find a consistent decrease of the charged exciton oscillator strength with temperature. For low electron concentrations these observations are well reproduced by a model of delocalized and thermalized three-particle complexes. The model takes into account the recoil momentum of the electron during the charged exciton optical transition. It is further found to compare well with lifetime measurements up to high carrier concentrations. Small deviations from the theoretical predictions occur only below 7 K due to localization effects and for the highest carrier concentration of $n_e \sim 2 \times 10^{11}\ \mathrm{cm}^{-2}$.

Since their first identification,[1] negatively charged excitons ($X^-$) have been observed as an important spectral signature of quantum wells (QW's) in which excess electrons are introduced by modulation doping[2–4] or optical excitation.[5] They appear a few meV below the excitonic line ($X$) and their spectral weight increases with electron concentration while that of $X$ decreases. The previously reported studies of their optical properties cover a wide range of investigations. They include specific polarization properties when polarizing the initial electron gas by a magnetic field,[1] the increase of their dissociation energy with the Fermi energy of the initial electron gas in the QW,[6,7] their lineshape[5,8] and their lifetime and dynamics.[9–12] However, intrinsic optical properties of $X^-$ still remain to be established.

Several of the properties found in the above mentioned studies, which are characteristic of $X^-$, can also be attributed to donor bound excitons ($D_0X$).[13,14] $D_0X$ has its spectral line on the low energy side of $X$ and can be seen as an $X^-$ strongly localized by the donor core. There has actually been some controversy in the above cited literature about the distinction between $X^-$ and $D_0X$ as well as to the possible localization of $X^-$, particularly in modulation doped QWs. Indeed, in these structures, on top of interface roughness, the presence of remote ionized donors in the barrier induces electrostatic potential fluctuations. These can localize the electrons and $X^-$, but do not affect much the $X$ which are neutral complexes.[2,15,16]

In this context, we report here on measured photoluminescence (PL) and reflectivity properties of $X^-$ in modulation doped structures which are well described in terms of delocalized and thermalized $X^-$. For our experimental investigations, we have chosen CdTe QWs as the $X^-$ binding energy in these materials is about two times larger than in GaAs based structures. This allows us to study $X^-$ in PL over a wide range of temperatures (2–35 K) before the $X^-$ dissociation becomes important. To obtain a comprehensive picture of $X^-$ PL at low electron concentrations, we have analyzed simultaneously, on the same measurement, the decay times and the lineshapes of $X^-$ following its resonant excitation. We find that the low electron concentration lifetimes and lineshapes are well described by a model composed of delocalized and thermalized ideal three-particle $X^-$ complexes.[8] This model is extended so that it reproduces the change of absorption of $X^-$ as a function of temperature; a property that compares very well with the inverse of the lifetime. Over a wider range of electron concentration $n_e \sim 0.2-2\times10^{11}\ \mathrm{cm}^{-2}$, the measured and predicted $X^-$ lifetime are in good agreement. The main difference between them appears below 7 K due to localization. Localization effects vanish upon raising the temperature.

The sample is a one-side modulation doped CdTe/$Cd_{1-x}Mg_xTe$ heterostructure containing a single 80 Å QW. The remote donor layer of iodine is situated 100 Å from the QW. Its thickness is changed within the same sample in four steps of 0, 2, 5, and 10 monolayers labeled hereafter spot A, B, C, and D.[17] This allows us to tune the concentration of the electron gas in steps by selecting one of the four different spots on the sample. Additionally, on a given spot, the electron concentration can be increased further by illuminating the sample with light of energy higher than the energy gap of the barrier. The mechanism of this effect is based on the competition between the QW and surface states which can both trap carriers and will be discussed elsewhere.[18] The maximum attainable electron concentration is $n_e = 2$

 

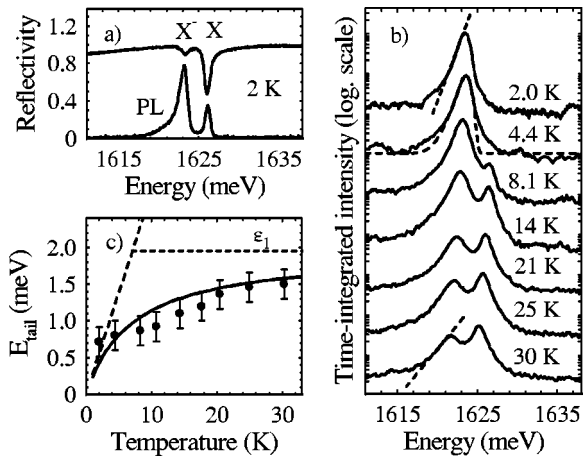


FIG. 1. On spot B, $n_e \leqslant 2\times10^{10}\,\mathrm{cm}^{-2}$: (a) cw PL when exciting nonresonantly at 1.7 eV and normalized reflectivity spectra. (b) Time-integrated spectra at different temperatures when exciting resonantly on $X^-$. The integration time window is about 800 ps starting some 10 ps after the initial laser excitation. The dashed line on the 4 K spectra is an example of our fits when using a Gaussian broadening function. The other dashed lines are guides to the eyes. (c) Fitted values of the decay constant $E_{\mathrm{tail}}$ of the $X^-$ exponential low energy spectral tail as a function of temperature. The full line shows the calculated values of $E_{\mathrm{tail}}$. The horizontal dashed line sets the value of $\epsilon_1$, the other one shows the Boltzmann contribution of $E_{\mathrm{tail}}$.

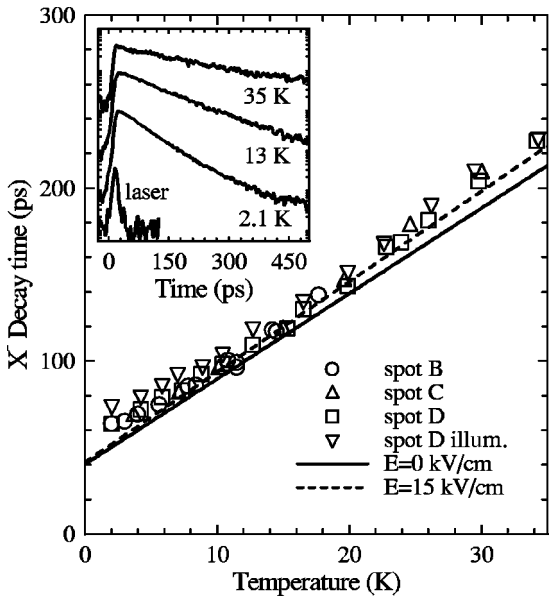


FIG. 2. Inset: Time-resolved spectra for different temperatures for an electron concentration of $n_e \sim 4\times10^{10}\,\mathrm{cm}^{-2}$. Main panel: Decay time of the $X^-$ PL when exciting resonantly on $X^-$ for four different electron concentrations in the QW as a function of temperature. The lines give the predictions of our model for two different electric fields within the sample: 0 and 15 kV/cm.

$\times10^{11}\,\mathrm{cm}^{-2}$ on spot D. All the given electron densities are estimated from the difference in energy between $X^-$ and $X$ in absorption.[6,7] Both lines were unambiguously identified in this sample as they follow the appropriate polarization selection rules in a magnetic field[1] and a transfer of intensity from $X$ to $X^-$ is observed when increasing the electron density.

For our experiments, the sample was either immersed in liquid helium for measurements up to 4 K or suspended in helium vapor for temperatures up to 35 K. High resolution cw PL and reflectivity measurements were detected by a CCD camera. For the time-resolved measurements, resonant excitation of $X^-$ was achieved with a tunable Ti-Sapphire laser with a pulse length of about 2 ps and 80 MHz repetition rate. The excitation density was as low as a few pJ/cm$^2$ per pulse. This yields an $X^-$ density which increases with the electron density from $\sim10^8$ up to $10^9$ cm$^{-2}$. The cross-linearly polarized PL was dispersed by a 0.27 m spectrometer and detected by a synchroscan streak camera. In our experimental arrangement, the temporal and spectral resolutions are better than 7 ps and 0.6 meV. For most of this study we have excited directly in resonance with $X^-$ to allow for a precise measure of the radiative lifetime of $X^-$.[10,19]

For low electron concentrations (spot B), $X$ absorption is dominant as shown on the reflectivity spectra in Fig. 1(a). In the PL spectra, the $X$ line has a narrow linewidth of about 0.7 meV. There is no noticeable shift between the $X$ reflectivity minimum and the corresponding PL peak. This shows that disorder effects are of minor importance for the optical properties. The electron concentration is quite low; we estimate it to be $n_e \leqslant 2\times10^{10}\,\mathrm{cm}^{-2}$. In the PL spectra, the $X$ line is symmetric while the $X^-$ lineshape shows a strong asymmetry on the low energy side. To find the origin of this spectral tail, we have studied its properties as a function of temperature using time-resolved spectroscopy. This allowed us to get, at the same time, the lifetime of $X^-$ and the corresponding lineshapes when exciting resonantly with $X^-$.[20] Indeed, in our configuration the diffused laser light can only influence the first picoseconds of the time-integrated spectra. Its contribution has been eliminated by integrating the PL starting some 10 ps after the laser excitation; the resulting spectra are depicted on a logarithmic scale in Fig. 1(b). By selective excitation on $X^-$, we enhance its optical response and avoid creating $X$ even when the absorption of $X$ is dominant as seen in Fig. 1(a). At low temperatures, $T<8$ K, we are then able to observe both the low and high energy side of the $X^-$ line. $X$ PL only appears at higher temperatures because of the increase of $X^-$ thermal dissociation. The low energy tail of $X^-$ is seen to decay mono-exponentially towards lower energies over one order of magnitude. Its decay constant ($E_{\mathrm{tail}}$) increases with temperature. It was quantified by fitting the $X^-$ lineshape by a convolution of a low energy decaying exponential with a Gaussian. The results of these fits are shown as symbols in Fig. 1(c). Fits were also made using different broadening functions like Lorentzians or Voigts to account, to some extent, for the temperature broadening. Neither reproduce well the entire shape of the $X^-$ spectral line but the extracted values of $E_{\mathrm{tail}}$ depend only weakly on the broadening function used. Less faith should be put in the low temperature values of $E_{\mathrm{tail}}$ as they are very close to that used for the broadening.

On the same measurements, where the importance of the $X^-$ tail increases with temperature, we observe an increase of the decay time of $X^-$ in the time domain. As seen in the inset of Fig. 2, the decay of the PL, following resonant excitation of $X^-$, is mono-exponential over about two orders of magnitude and the rise time is within our experimental resolution. This shows that the $X^-$ population is almost immedi-

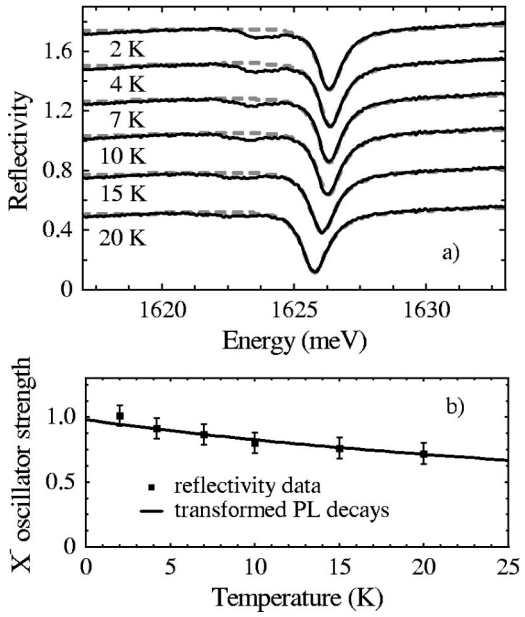


FIG. 3. (a) Normalized reflectivity spectra as a function of temperature for $n_e \sim 2\times10^{10}\,\mathrm{cm}^{-2}$. The dashed lines are fits of the strong $X$ line. (b) Extracted relative oscillator strength of $X^-$ in arbitrary units and comparison with the rescaled inverse radiative lifetimes.

ately thermalized. Only two decay channels then play an important role for the $X^-$ PL decay: the radiative decay of $X^-$ and the dissociation of $X^-$ into $X$ and an electron. Indeed, it has been verified that nonradiative processes are negligible below 30 K as the PL intensity integrated over time and energy remains constant. The probability of dissociation into an exciton and an electron depends on temperature and electron concentration. Here, apart from the lowest electron concentration (spot B), it is quite small over the whole temperature range explored and the PL decay is due to radiative recombination of $X^-$. On Fig. 2, we show the radiative lifetime of $X^-$, which can be extracted from the monoexponential $X^-$ PL decay with a precision that decreases with temperature but is always between 3–10 ps. The lifetime is observed to increase linearly with temperature above 7 K and to be independent of the electron concentration over almost the entire investigated range. A small, reproducible increase of $\sim$10 ps can be seen for the highest electron concentration of $n_e = 2\times10^{11}\,\mathrm{cm}^{-2}$ (spot D illuminated).

The measurements presented above all stop at 30–35 K. The reason for this, when disregarding $X^-$ thermal dissociation, is that less $X^-$ are created at high temperatures when using resonant excitation. This is due to a decrease in $X^-$ absorption with temperature as seen in the reflectivity spectra in Fig. 3(a). To quantify the change of intensity of this reflectivity structure we have fitted the strong $X$ line and subtracted it to the spectra to obtain the reflectivity due to $X^-$ alone. The X reflectivity was best fitted by a complex Lorentzian function[21] and the remaining $X^-$ line by a Gaussian. From this Gaussian area we obtained the relative oscillator strength of $X^-$, which is seen to decrease with temperature in Fig. 3(b).

To understand quantitatively the observed optical properties of $X^-$ in emission and absorption, we compare them with a model of delocalized and thermalized $X^-$. In this model based on $k$-vector conservation, the electron takes away, during the optical transition, the $X^-$ center of mass momentum as the photon momentum is negligibly small. Thus $X^-$ with $k$-vectors larger than zero can also recombine radiatively. This transition is described by the optical matrix element $M(k)$.[8,22] We assume a thermalized $X^-$ distribution and approximate it by a Boltzmann distribution. Both conjectures are justified experimentally: thermalization of $X^-$ is within our experimental resolution (see inset of Fig. 2) and the photocreated $X^-$ densities are low. Neglecting broadening mechanisms, the intensity of the PL line is thus given by[8]

$$I_{X^-}(\hbar\omega) \propto |M(k)|^2 \exp\left(-\frac{\epsilon}{k_B T}\frac{m_e}{M_X}\right)\theta(\epsilon), \qquad (1)$$

in which $\theta$ is the Heaviside step function. The photon energy is given via $\epsilon = E_{X^-}(k=0) - \hbar\omega = \hbar^2 k^2 M_X/(2 m_e M_{X^-})$. The energy-dependent optical matrix element in Eq. (1) can be approximated well by $|M(k)|^2 \approx \exp(-\epsilon/\epsilon_1)$. For our CdTe QW we found a value of $\epsilon_1 = 1.95$ meV from a numerical solution of the three-particle Schrödinger equation.[23] The calculated spectral decay constant $E_{\mathrm{tail}}$ can then be extracted from Eq. (1) and is given by $1/E_{\mathrm{tail}} = (1/k_B T) \times (m_e/M_X) + 1/\epsilon_1$. The values are plotted as a full line in Fig. 1(c) where the model is seen to compare well with the experimental fits. The dashed lines show the two individual components of Eq. (1). The Boltzmann contribution to the lineshape is dominant at low temperatures and increases linearly with temperature as higher $X^-$ $k$-states are increasingly populated. The optical matrix element sets the maximum decay constant of the spectral tail at $\epsilon_1$. This is in clear contrast to Ref. 14, where the low energy tail is claimed to increase continuously with temperature.

The radiative decay time is inversely proportional to the average of the emission probabilities of all populated $k$-states given in Eq. (1). It increases linearly with temperature as the maximum recombination probability is around $k=0$ and the population of these states decreases with temperature. In particular, the analysis can be done analytically and gives[8]

$$\tau_{X^-} = \frac{3 M_X \tau_{0,T}}{4 M_{X^-} E_0}\left(k_B T + \epsilon_1 \frac{m_e}{M_X} + \frac{3}{5}\frac{M_{X^-}}{M_X} E_0\right). \qquad (2)$$

Here we also considered the finite photon momentum (light-cone effect), which gives $E_0 = 0.08$ meV. The absolute value of the lifetime calculations are determined by the material dependent term $\tau_{0,T}$. This term contains the Kane matrix element, which is taken to be 21 eV for CdTe.[24] To get confidence in this value, we have also successfully calculated the positively charged exciton lifetime in a similar $p$-doped sample with the same materials and well width.[25] In Fig. 2 we observe that the calculated radiative lifetimes of $X^-$ are in good agreement with the measurements and deviations are within experimental error bars. For the highest electron concentration, the electric field along the growth axis due to modulation doping of the barrier has been estimated to reach a value of 15 kV/cm. It can contribute to increase the $X^-$ radiative lifetime because of a decreased overlap between the electron and hole confinement wave functions.[26] This effect has been calculated [dashed line in Fig. 2(b)] and is seen to

be very small as our QW is narrow. We conclude that the model reproduces the experiment well up to high electron concentrations and it differs only slightly from the experiment for $n_e = 2 \times 10^{11}$ cm$^{-2}$ Below 7 K, the $X^-$ lifetime deviates from the linear increase tending towards a constant value. This behavior is typical when localization influences the lifetime.[27]

So far we have focused on the optical properties of $X^-$ in emission. We will now link these properties to the absorption of $X^-$. The calculation of the absorption probability is very similar to Eq. (1). The Boltzmann thermal distribution of $X^-$ is replaced by the thermal distribution of the electron which is now the initial state. For low electron concentrations, the electron gas is nondegenerate and its thermal distribution follows a Boltzmann distribution. Thus the absorption probability is obtained by explicitly replacing $m_e$ by $M_{X^-}$. This implies that the main difference between absorption and emission at low electron densities is due to the difference in masses between $X^-$ and electron: $m_e/M_{X^-} \simeq 0.25$. Therefore, we can compare directly the temperature variation of the lifetime, and the absorption when the temperature axis is rescaled by $m_e/M_{X^-}$. The result is shown as a full line in Fig. 3(b), displaying the good agreement between the measured variations of the radiative lifetime and the absorption of $X^-$. This can be seen as another argument of the applicability of our idealized $X^-$ model.

In conclusion, we have obtained experimentally the intrinsic optical properties of $X^-$ in modulation doped CdTe QWs as a function of temperature and electron concentration. We have investigated the $X^-$ PL lineshape, lifetime, and reflectivity carefully. The observations are very well reproduced, at low electron concentrations, by a model of delocalized and thermalized ideal $X^-$. The model also compares well with the radiative lifetime of $X^-$ over a wide range of electron concentrations. All the studied $X^-$ optical properties can be understood by the particular way the three-particle complex couples to light.

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[1] K. Kheng *et al.*, Phys. Rev. Lett. **71**, 1752 (1993).

[2] G. Finkelstein, H. Shtrikman, and I. Bar-Joseph, Phys. Rev. Lett. **74**, 976 (1995).

[3] A. J. Shields *et al.*, Phys. Rev. B **51**, 18 049 (1995).

[4] G. V. Astakhov *et al.*, Phys. Rev. B **60**, 8485 (1999).

[5] A. Manassen *et al.*, Phys. Rev. B **54**, 10 609 (1996).

[6] P. Kossacki *et al.*, Phys. Rev. B **60**, 16 018 (1999).

[7] V. Huard *et al.*, Phys. Rev. Lett. **84**, 187 (2000).

[8] A. Esser, E. Runge, R. Zimmermann, and W. Langbein, Phys. Status Solidi A **178**, 489 (2000); Phys. Rev. B **62**, 8232 (2000).

[9] A. Ron *et al.*, Solid State Commun. **97**, 741 (1996).

[10] G. Finkelstein *et al.*, Phys. Rev. B **58**, 12 637 (1998).

[11] E. Vanelle *et al.*, Phys. Rev. B **62**, 2696 (2000).

[12] R. A. Hogg *et al.*, Physica B **272**, 412 (2000).

[13] A. Kudelski *et al.*, Solid State Commun. **112**, 173 (1999).

[14] O. V. Volkov *et al.*, JETP Lett. **66**, 766 (1997).

[15] G. Eytan *et al.*, Phys. Rev. Lett. **81**, 1666 (1998).

[16] D. Brinkmann *et al.*, Phys. Rev. B **60**, 4474 (1999).

[17] T. Wojtowicz *et al.*, Phys. Rev. B **59**, R10 437 (1999); Appl. Phys. Lett. **73**, 1379 (1998).

[18] M. Kutrowski and P. Kossacki (unpublished).

[19] B. Deveaud *et al.*, Phys. Rev. Lett. **67**, 2355 (1991).

[20] We have also measured high resolution cw PL spectra as a function of temperature. They have confirmed the results on $X^-$ obtained from time-integrated spectra.

[21] E. L. Ivchenko *et al.*, Phys. Rev. B **46**, 7713 (1992).

[22] B. Stébé, E. Feddi, A. Ainane, and F. Dujardin, Phys. Rev. B **58**, 9926 (1998).

[23] CdTe mass parameters used: $m_e = 0.099$ and $m_h = 0.22$.

[24] G. Nimtz, in *Semiconductors*, Vol. 176 of *Landolt-Börnstein*, edited by K.-H. Hellweg and O. Madelung (Springer-Verlag, Berlin, 1982), p. 226.

[25] P. Kossacki *et al.*, J. Cryst. Growth **214/215**, 837 (2000).

[26] A. Esser, E. Runge, R. Zimmermann, and W. Langbein, Phys. Status Solidi B **221**, 281 (2000).

[27] D. S. Citrin, Phys. Rev. B **47**, 3832 (1993).