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Identification of near-infrared Cr²⁺ luminescence in ZnSe

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Abstract. A Cr-related near-infrared photoluminescence (PL) band in ZnSe with a main no-phonon line at 10 702.2 cm⁻¹ is investigated. Zeeman splitting indicates a tetragonally distorted ground state. The experimental data agree well with calculations using a spin Hamiltonian with parameters obtained from the ⁵T₂(D) ground state of ZnSe:Cr²⁺(d⁴). This contradicts a former assignment of the PL band to a ⁴T₁(G) → ⁶A₁(S) emission of ZnSe : Cr⁺(d⁵). Crystal field calculations demonstrate that the observed no-phonon lines and the corresponding luminescence band can reasonably be interpreted in terms of a ³T₁(H) → ⁵T₂(D) transition within the d⁴ configuration of Cr²⁺. Furthermore, the influence of unmodulated supplementary irradiation on transmission and PL excitation spectra is discussed.

1. Introduction

In II–VI semiconductors chromium is known to be substitutionally incorporated as Cr²⁺ at a cation site, thus attaining a 3d⁴ configuration (see e.g. [1–3]). The ionized acceptor state Cr⁺(3d⁵) can be induced by an optical charge-transfer process lifting an electron from the valence band to the isoelectronic Cr²⁺ [4–7]. Both charge states of the Cr acceptor in ZnSe have been detected using electron paramagnetic resonance (EPR).

In this paper, the Cr-related near-infrared (NIR) photoluminescence (PL) band of ZnSe centred near $\bar{\nu} = 10\,300\text{ cm}^{-1}$ ($\lambda = 0.98\ \mu\text{m}$) [8] is investigated. This PL band has previously been ascribed to the ⁴T₁(G) → ⁶A₁(S) transition of Cr⁺ [9, 10]. This attribution was essentially based on comparison with the intensively studied ion Mn²⁺(d⁵). In the Mn²⁺ centre in II–VI and III–V semiconductors, the four spin components of the excited ⁴T₁(G) level are merged by a strong Jahn–Teller effect into a state of $\Gamma_6 + \Gamma_8$ symmetry and a lower $\Gamma_7 + \Gamma_8$ state, separated by approximately 10 cm⁻¹ [11]. The ⁶A₁(S) ground state exhibits a splitting of the order of 0.002 cm⁻¹ [12] into two levels of Γ_7 and Γ_8 symmetry, too small to be resolved in optical spectra. The ⁴T₁(G) → ⁶A₁(S) luminescent transition is both spin and symmetry forbidden, resulting in comparatively long lifetimes of the ⁴T₁(G) state, viz. in the millisecond range.

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The NIR Cr-related emission band has been ascribed to the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ transition of ZnSe:Cr^+ [9,10] for the following reasons. First, the no-phonon line (NPL) and a thermalized satellite indicate an excited state with a splitting of about 14 cm^{-1} which is similar to that of $\text{Mn}^{2+}(d^5)$ emissions in various II–VI and III–V compounds. Second, the decay time of the luminescence ($\tau = 1.8\text{ ms}$ [9]) is comparable with that of the Mn^{2+} emission in different host crystals. Third, the excitation (PLE) spectrum corresponds to the charge-transfer band of $\text{Cr}^{2+} \rightarrow \text{Cr}^+$ transitions known from photo-EPR experiments [13,14], as indicated by a coinciding threshold value (about 16900 cm^{-1}) and maximum (around 19000 cm^{-1}). Fourth, an optically detected magnetic resonance (ODMR) attributed to Cr^+ was found [10] possessing the same spectral excitation characteristics as the PLE spectrum.

Zeeman-effect measurements of this luminescence were supposed to provide the final proof for identification of the radiative centre as Cr^+ . Magneto-optical spectra, however, contradict this simple analogy. The present investigations rather point to a Cr^{2+} centre with an NIR emission which can be interpreted in terms of a ${}^3T_1(H) \rightarrow {}^5T_2(D)$ transition within the d^4 configuration.

2. Experimental details

Some of the crystals investigated were grown by a halogen transport method in sealed quartz ampoules using iodine as transport agent. Doping was achieved during growth by adding elemental chromium in nominal concentrations between 10 and 3000 ppm. More efficient luminescence was observed with samples grown by a seeded chemical vapour transport (SCVT) method in hydrogen ambient [15]. Doping with Cr was in this case performed during growth ($T = 1440\text{ K}$) from an additional Cr_2Se_3 source arranged under the main ZnSe crystal. It resulted in concentrations estimated to be approximately 100 ppm.

The optical spectra were recorded at low temperatures with samples mounted in He immersion cryostats. For Zeeman experiments, a 5 T split-coil magnet was used. Emission spectra were excited by an Ar^+ laser while the PL was recorded by a photomultiplier tube with an S1 cathode. In the PL excitation and sensitization experiments, the excitation was provided by an Xe arc lamp and the emission was detected by Ge and PbS detectors. In the transmission measurements a W filament lamp served as the light source.

3. Photoluminescence

3.1. Zero-field no-phonon spectra

In earlier investigations of the NIR ZnSe:Cr luminescence [8,9], only one NPL along with an accompanying thermalized line were observed. With the crystals now available, it was possible to detect further no-phonon structures (figure 1). The main NPL appears at 10702.2 cm^{-1} . The small shoulder at 10703.2 cm^{-1} does not depend on the temperature. In addition to the already known thermalized line at 10716.8 cm^{-1} , a further weak emission line at 10709.7 cm^{-1} is identified, whose strength does not depend on the temperature. The Zeeman spectra presented in the next section show the close relation of this line to the main emission line.

The radiant flux of the luminescence has been proved to be proportional to the excitation density over at least five orders of magnitude. This result evidences a one-step excitation mechanism for the emission.

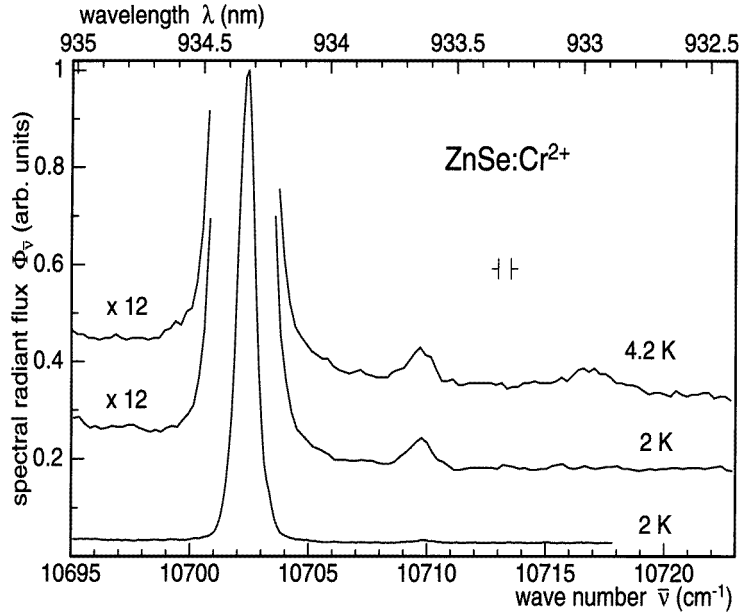


Figure 1. The no-phonon range of the NIR PL of $\text{ZnSe}:\text{Cr}^{2+}$. The temperature dependence features beside the known thermalized line (10716.8 cm^{-1}) a lower-energy peak at 10709.7 cm^{-1} , which is independent of T . (Excitation with 19435 cm^{-1} , Cr doping of about 100 ppm.)

3.2. Zeeman effect

The splitting behaviour of the PL lines under the influence of a magnetic field is an appropriate means to decide whether the NIR PL results from the ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ transition of Cr^{2+} or not. The ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ Zeeman spectra of the substitutional d^5 ions Mn^{2+} in ZnS [16] and Fe^{3+} in ZnS [17], ZnO [18] and GaN [19] are very similar. They show a characteristic pattern of six equidistant peaks with monotonically increasing intensities towards higher energies. The splitting, which is isotropic with $g \approx 2$, reflects the magnetic behaviour of the ${}^6\text{A}_1(\text{S})$ ground state.

In contrast, the Zeeman effect of the NIR PL of Cr in ZnSe results in a completely different splitting. More than six lines appear in the spectra; these are neither equidistant nor monotonically increasing in intensity (figure 2). Furthermore, a strong anisotropy is observed. The spectra shown in figure 2 recorded with $\mathbf{B} \parallel \langle 110 \rangle$ differ significantly from the spectra in figure 3 recorded with $\mathbf{B} \parallel \langle 111 \rangle$. An increase of the sample temperature from 2 to 4.2 K does not change the spectra. Since no thermalization is discernible, it must be concluded that the whole splitting pattern originates from properties of the ground state. No polarization of the Zeeman spectra was observed for any of the principal axes.

The dependences of the peak energies of the low-energy Zeeman components (figure 4) point to the energy of 10699.6 cm^{-1} as the origin of the Zeeman components. For $B = 0 \text{ T}$, this transition is obviously forbidden. With increasing magnetic field, however, it becomes noticeably allowed. In both geometries the overall splitting is nearly linear in the low-field range. Above 3 T, the evolution of the Zeeman components indicates term interactions. Up to 5 T, the centre of gravity of all lines shifts only slightly and almost linearly to lower

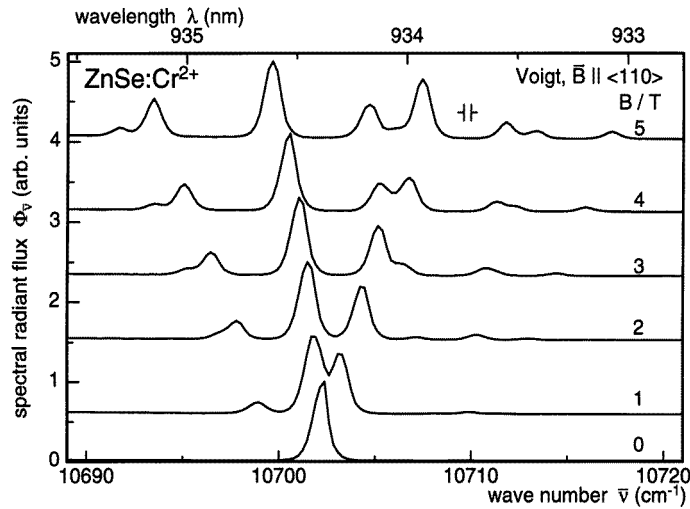


Figure 2. The influence of a magnetic field on the NPLs of the NIR emission of ZnSe:Cr²⁺. Measurement is with $B \parallel \langle 110 \rangle$ in the Voigt configuration. (Excitation with 19435 cm^{-1} , $T = 2 \text{ K}$, Cr doping of about 100 ppm.)

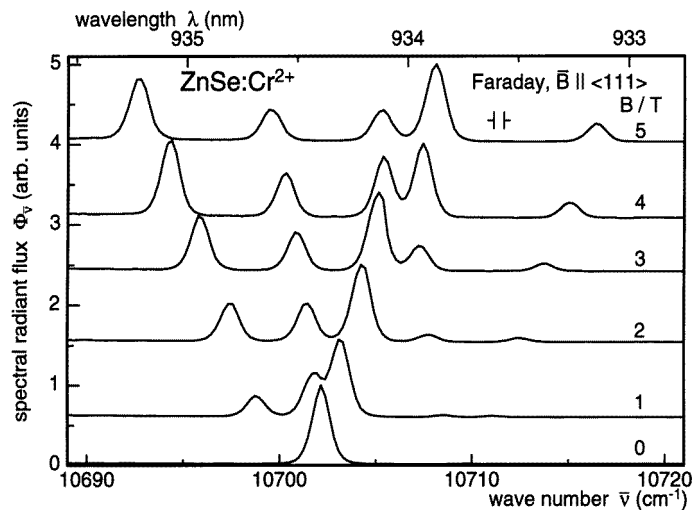


Figure 3. The Zeeman effect of the NIR PL of ZnSe:Cr²⁺ for a magnetic field along $\langle 111 \rangle$ in the Faraday configuration. (Excitation with 19435 cm^{-1} , $T = 2 \text{ K}$, Cr concentration of about 100 ppm.)

energy by 1.5 cm^{-1} . No evidence for a quadratic component of the shift was found.

To examine the anisotropic feature of the luminescence centre, the sample was rotated in the Voigt configuration at $B = 5 \text{ T}$ within the $\{110\}$ plane so that all three principal axes were covered (figure 5). The peak positions were monitored as a function of the angle of rotation (figure 6). For $B \parallel \langle 112 \rangle$ (this orientation is equivalent to rotation angles 90° and 160° in figure 6), ten magnetically split lines can be resolved. The Zeeman splitting has a maximum

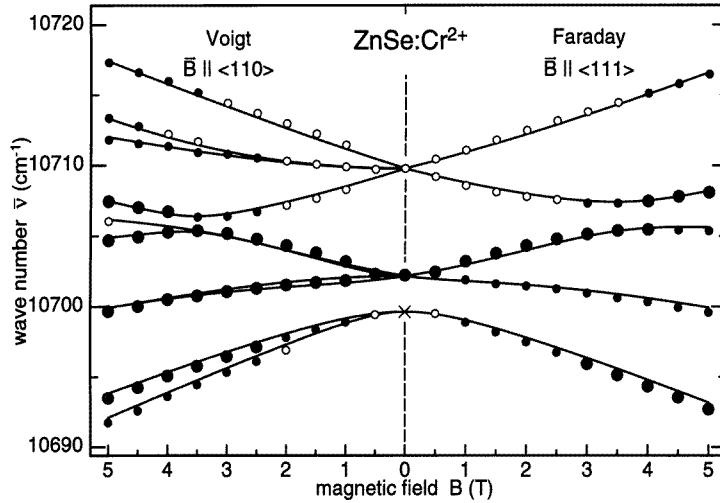


Figure 4. The energy shift of the lines of the NIR PL of $\text{ZnSe}:\text{Cr}^{2+}$ with increasing magnetic field. The data for $B \parallel \langle 110 \rangle$ in the Voigt configuration are shown on the left-hand side, those for $B \parallel \langle 111 \rangle$ in the Faraday configuration on the right-hand side. Experimental data (filled circles for stronger, open circles for weaker peaks) are compared with the results of calculations (solid lines) using the spin Hamiltonian of equation (1). The data point at 10699.6 cm^{-1} and zero field (cross) was obtained by extrapolation.

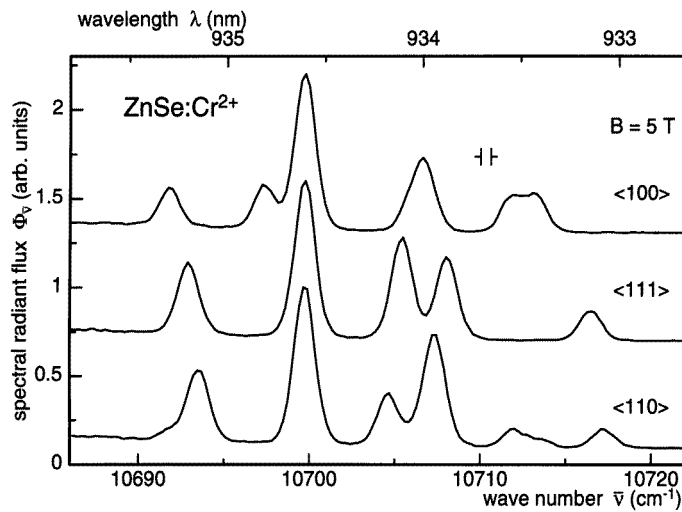


Figure 5. The Zeeman effect of the NIR Cr^{2+} emission in ZnSe at $B = 5 \text{ T}$ along the three principal axes. $B \parallel \langle 110 \rangle$ in the Voigt configuration. (Excitation with 19435 cm^{-1} , $T = 2 \text{ K}$, Cr concentration around 100 ppm.)

along $\langle 100 \rangle$. Parallel to $\langle 111 \rangle$, the splitting reaches a minimum, and the degeneracy becomes maximal. These results indicate that the Cr centre has tetragonal symmetry, i.e. the cubic crystalline field is distorted along a $\langle 100 \rangle$ direction. For an orientation of the magnetic field parallel to the $\langle 111 \rangle$ axis, all three cubic $\langle 100 \rangle$ directions are equivalent. Therefore, the

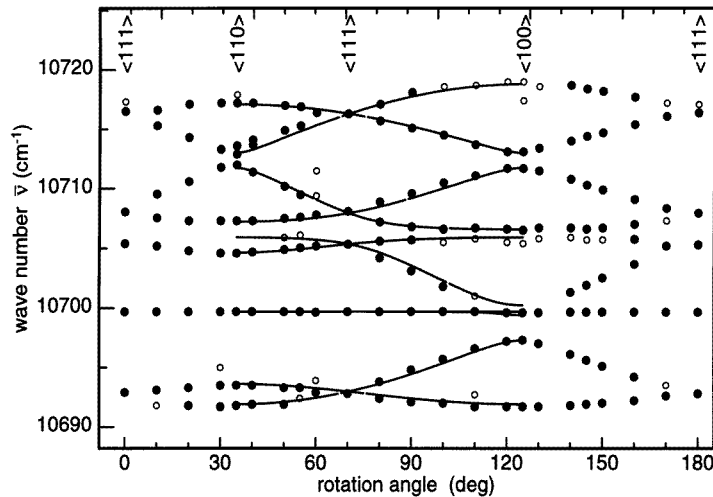


Figure 6. The angular dependence of the Zeeman splitting of the magnetic subcomponents due to the NIR PL of ZnSe:Cr²⁺. The sample was rotated in the {110} plane with $B = 5$ T applied in the Voigt configuration. Stronger peaks are indicated by filled circles, weaker lines are symbolized with open circles. The solid lines represent the results of the calculations employing the spin Hamiltonian (1). (Excitation with 19435 cm^{-1} , $T = 2\text{ K}$, 100 ppm Cr.)

Zeeman levels are threefold degenerate, resulting in a five-level scheme.

The magneto-optical spectra thus reveal the anisotropic properties of the impurity ion ground state.

3.3. Calculation of the Zeeman spectra

The results of the Zeeman experiments raise doubts about Cr⁺(d⁵) being the origin of the studied PL because 3d⁵ ions (Cr⁺, Mn²⁺, Fe³⁺) have hitherto been known to possess a ⁶A₁(S) ground state, keeping the cubic site symmetry. Furthermore, EPR investigations of the same crystals as used in the optical experiments verify the tetragonal Cr²⁺ centre, confirming the parameters given by Vallin and Watkins [2]. Under optical stimulation, Cr²⁺ is partially converted into the charged Cr⁺ state. The EPR of the photo-stimulated Cr⁺ reveals the cubic symmetry by its nearly isotropic spectrum in accordance with the data given in the literature [5]. All previous studies indicate a close relationship between incorporation of Cr ions and occurrence of the 10700 cm^{-1} emission. Therefore, Cr²⁺(d⁴), whose presence in the samples is proved by EPR under the same conditions, is a conceivable candidate for being the luminescent state of the Cr impurity.

To check this assumption, the effect of a magnetic field on the ground state ⁵T₂(D) is calculated using the data determined by analysing EPR spectra of ZnSe:Cr²⁺ [2]. In ZnSe:Cr²⁺, a Jahn–Teller effect causes a tetragonal distortion of the cubic crystal field along a <100> axis and thus a further splitting of the ⁵T₂ state. The five lowest states of ⁵T₂ can be described by the spin Hamiltonian with $S = 2$ (see e.g. [2]):

$$\begin{aligned}
 H = & g_{\parallel} \mu_B B_z S_z + g_{\perp} \mu_B (B_x S_x + B_y S_y) + D \left(S_z^2 - \frac{1}{3} S(S+1) \right) + \frac{1}{6} a (S_x^4 + S_y^4 + S_z^4) \\
 & + \frac{1}{180} F \left(35 S_z^4 + (25 - 30 S(S+1)) S_z^2 \right) \quad (1)
 \end{aligned}$$

where the z axis of the coordinate system coincides with the cubic [001] axis, the x and y axes being parallel to [100] and [010], respectively. There are three magnetically inequivalent sites. The spin Hamiltonian (1) consists of the Zeeman and a fine-structure term. By using the values $g_{\parallel} = 1.961$, $g_{\perp} = 1.98$, $D = -2.48 \text{ cm}^{-1}$ and $a = \pm 0.024 \text{ cm}^{-1}$ (F is assumed to be zero) given by the EPR results [2], this Hamiltonian (1) yields the solid lines drawn in figures 4 and 6. Keeping in mind that no fit to the optical spectra was performed, the excellent match of the experimental and calculated data is striking. From the possibility of accounting for the Zeeman data exclusively with ground-state properties it can be deduced that the excited state of the luminescent transition is isotropic and shows only a very small magnetic shift of its centre of gravity.

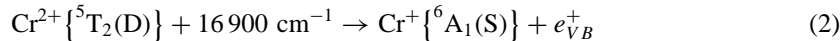
An attempt to calculate the Zeeman properties in terms of a ${}^6A_1(S)$ ground state of Cr⁺ was not successful under assumptions which are reasonable for a 3d ion in ZnSe. There are essential contradictions concerning the symmetry, the number of Zeeman levels, and the expected value of the zero-field splitting.

The perfect description of the Zeeman behaviour of the NIR ZnSe:Cr PL with the data derived from the EPR spectra of ZnSe:Cr²⁺ proves a common origin, viz. Cr²⁺ impurity ions. Having thus shown that the PL under study results from transitions within the Cr²⁺ centre, further optical properties of these crystals will now be examined in the light of these results.

4. Charge-transfer spectra

4.1. Photoluminescence excitation (PLE)

The PLE spectra of the NIR luminescence at issue [9] and of the ${}^5E(D) \rightarrow {}^5T_2(D)$ emission [8, 20] of ZnSe:Cr²⁺ are dominated by intense bands centred near $18\,800 \text{ cm}^{-1}$ and starting at approximately $16\,900 \text{ cm}^{-1}$. In PLE spectra, broad bands just below the band gap are usually caused by charge-transfer reactions. From the comparison with photo-EPR experiments [13, 14], the main PLE band in both spectra can be connected to the acceptor process



where e_{VB}^+ denotes a hole in the valence band.

The radiative transitions within Cr²⁺ are obviously much more efficiently pumped by an intermediate creation of a transient Cr⁺ state (reaction (2)) than by internal Cr²⁺ transitions. This feature distinguishes Cr²⁺ from the isoelectronic V⁺ in ZnSe [21] or ZnTe [22] where the internal absorptions are as efficient as band-related processes. From absorption experiments with ZnSe:Cr [1], the absorption due to process (2) is known to be very efficient. After creation of Cr⁺, the ions can either stay in the 1+ charge state or release an electron to the conduction band, resulting in an excited state [Cr²⁺]*. Even if only a small fraction of the Cr⁺ ions undergoes the latter reaction, the emissions are strongly enhanced due to the high number of Cr⁺ centres created according to process (2).

Figure 7 displays the low-energy part of the PLE spectrum of the ZnSe:Cr²⁺ NIR emission. The observed peaks are approximately three orders of magnitude weaker than the above-discussed charge-transfer band and have, therefore, not been detected previously [8, 9, 20]. To check whether these bands reflect internal absorptions within the Cr²⁺ configuration, the electronic states were calculated using a Tanabe–Sugano scheme [23]. The crystal-field splitting parameter $\Delta = 10Dq$ can be derived from the ${}^5E(D) \leftrightarrow {}^5T_2(D)$ transition and was set to 4800 cm^{-1} [8]. The energies of the absorptions from the ${}^5T_2(D)$

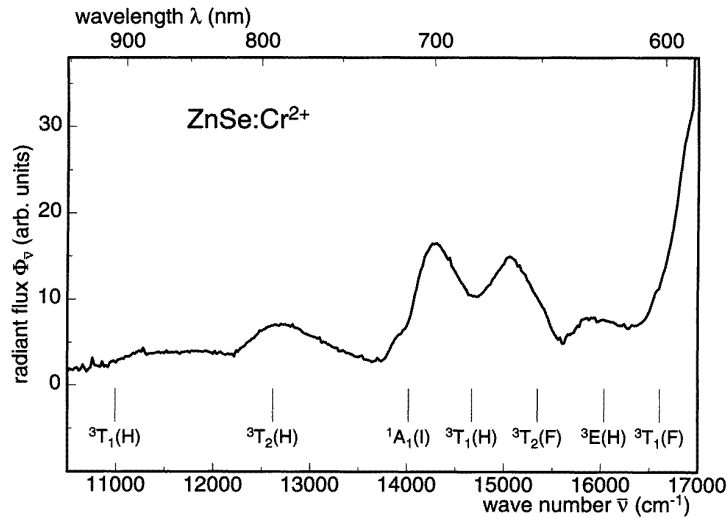


Figure 7. The lower-energy part of the PLE spectrum of the NIR luminescence of ZnSe:Cr²⁺ monitored between 8000 and 10000 cm⁻¹. The Cr²⁺ → Cr⁺ charge-transfer process (2) causes the increase for wavenumbers above 16 900 cm⁻¹. The electronic states of the Cr²⁺ ions which were calculated using a Tanabe–Sugano scheme are shown below the spectrum. ($T = 4.2$ K, 100 ppm Cr.)

ground state to the excited states $^3T_1(H)a$, $^3T_2(H)$, and $^3T_1(H)b$ were taken as 11 200 (following the mirror rule of emission), 12 800, and 14 300 cm⁻¹, respectively, and were used for the calculations. The resulting energy levels are shown below the spectrum of figure 7. Their positions are close to the observed PLE peaks. The best fit was attained with the parameters $B = 460$ cm⁻¹ and $C = 3040$ cm⁻¹. These values differ slightly from those earlier obtained ($B = 510$ cm⁻¹, $C = 3053$ cm⁻¹ [20]) deploying PLE data of the $^5E(D) \rightarrow ^5T_2(D)$ transition of ZnSe:Cr²⁺. The ratio $C/B = 6.6$ found in the current investigation is somewhat higher than in [20] (6.0) and for most 3d impurity ions (usually around 4.5). Numerical estimations of the relative intensities of the PLE bands on the basis of the squared $^5E(D)$ fraction $\langle \Psi_{5E} | \Psi_{5E} \rangle^2$ of the resulting spin–orbit eigenfunctions $|\Psi\rangle$ yield similar intensities as detected in the spectrum of figure 7. (Transitions between the ground state $^5T_2(D)$ and the excited state $^5E(D)$ are the only transitions within the d^4 configuration that are allowed by symmetry and spin selection rules.)

Based on Tanabe–Sugano calculations, the observed PLE peaks can be ascribed to $^5T_2(D) \rightarrow$ triplet transitions. This identification is free of contradictions, but not free of doubts due to the incomplete agreement between the numerical and experimental results. Having in mind the semi-empirical character of energy-level calculations in the Tanabe–Sugano scheme, which is a relatively restricted approach using only a few parameters, the level of agreement is nevertheless quite satisfying.

4.2. Spectra under additional irradiation

The influence of additional unmodulated irradiation on the radiant flux of an optical transition is displayed in sensitization spectra. They provide an effective way to detect charge-transfer processes. If ZnSe:Cr is excited with low-energy light of $\bar{\nu} < 16 900$ cm⁻¹, the NIR

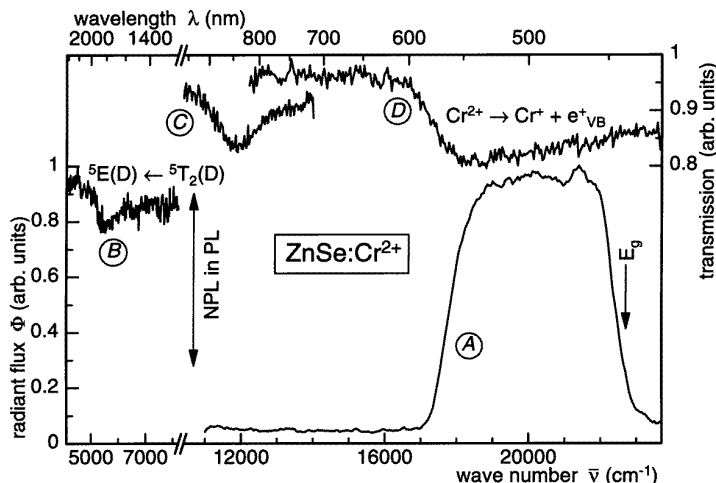


Figure 8. Charge-transfer processes related to the NIR PL of $\text{ZnSe}:\text{Cr}^{2+}$. The sensitization spectrum A displays the increased PL intensity due to the $\text{Cr}^{2+} \rightarrow \text{Cr}^+$ reaction (2) whereas the dip in the sensitization spectrum B results from the ${}^5\text{E}(\text{D}) \leftarrow {}^5\text{T}_2(\text{D})$ absorption of Cr^{2+} (modulated excitation with $12\,870\text{ cm}^{-1}$, detected range $7\,400\text{--}10\,400\text{ cm}^{-1}$). Graph C shows the optically pumped absorption (pumping with unmodulated light of $18\,450\text{ cm}^{-1}$). The sensitization spectrum of the transmission (D) reveals the charge-transfer process (2); detected at $11\,806\text{ cm}^{-1}$ in the maximum of the absorption, the additional light is unmodulated. The nominal Cr doping concentrations are 260 ppm (A, B) and 3300 ppm (C, D). $T = 4.2\text{ K}$ for all spectra.

emission only appears when the unmodulated pumping energy exceeds the charge-transfer threshold of reaction (2) so that Cr^+ ions are created (see curve A of figure 8). Therefore, the high-energy band of the sensitization spectrum coincides with the main band of the PLE spectrum. The decline of the NIR luminescence intensity at the low-energy side near 5500 cm^{-1} (spectrum B of figure 8) results from excitation of Cr^{2+} ions due to their ${}^5\text{E}(\text{D}) \leftarrow {}^5\text{T}_2(\text{D})$ absorption [1]. This competing process leaves fewer ions available for the production of Cr^+ so that only a smaller number of Cr^{2+} ions can be excited.

No absorption band inverse to the NIR Cr emission could be found. This is consistent with the very low oscillator strength of the luminescent transition which can be concluded from the long lifetime of the excited state (1.8 ms [9]).

Under intensive additional irradiation including the charge-transfer process (2), however, an absorption can be detected which is probably inverse to the NIR PL (graph C of figure 8). This photoinduced transition decays exponentially with a time constant of approximately 320 s , which is comparable with the decay time observed in photo-EPR experiments of $\text{ZnSe}:\text{Cr}^+$ [13]. The absorption is only detectable after creation of a sufficiently high concentration of Cr^+ centres.

In the sensitization spectrum D in figure 8, the changes of the maximum absorption of spectrum C are measured as a function of the energy of an additional unmodulated illumination. This spectrum displays the band due to the $\text{Cr}^{2+} \rightarrow \text{Cr}^+$ charge-transfer reaction (2) as a descent. It can be concluded that the transmission decreases (i.e. the absorption grows) with increasing number of Cr^+ ions in their ground state.

In both transmission spectra, the presumed generation of Cr^+ centres leads to an increased absorption. This fact is hard to understand if the NIR emission is assigned to an

internal Cr^{2+} emission. One explanation might be that the pumped absorption (band C of figure 8) is related to an internal Cr^+ transition without correlation to the NIR PL.

5. Discussion

The Cr-related luminescence in ZnSe at $10\,300\text{ cm}^{-1}$ had formerly been ascribed to the ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ transition of $\text{Cr}^+(\text{d}^5)$ because all available data fitted into that explanation scheme. The presented magneto-optical study, however, dismisses this assumption. The ground state is perfectly described by a spin Hamiltonian with the parameters obtained from the ${}^5\text{T}_2(\text{D})$ state of $\text{Cr}^{2+}(\text{d}^4)$. Therefore, the NIR PL is connected to a transition within the 3d^4 configuration. Tanabe–Sugano calculations accounting for the energies of the bands in the PLE spectrum suggest ${}^3\text{T}_1(\text{H})$ as the initial state of the NIR emission.

Excitation of the NIR luminescence is evidently almost impossible via internal transitions of Cr^{2+} , but strong by generation of Cr^+ centres and their subsequent recombination producing $[\text{Cr}^{2+}]^*$. This behaviour is in some respects similar to that of $\text{Fe}^{2+}(\text{d}^6)$ in ZnS. After photoionization transitions $\text{Fe}^{2+} + h\nu \rightarrow \text{Fe}^{3+} + e_{\text{CB}}^-$, the recombination $\text{Fe}^{3+} + e_{\text{CB}}^-$ results in a strong enhancement of the ${}^5\text{T}_2(\text{D}) \rightarrow {}^5\text{E}(\text{D})$ emission of ZnS:Fe²⁺ [24].

The ${}^5\text{T}_2(\text{D})$ ground state of ZnSe:Cr²⁺ is split as a result of spin–orbit and Jahn–Teller interactions leading to $\Gamma_1 + \Gamma_2$, Γ_5 , and Γ_4 as the lowest states, in the order of increasing energy (cf [1]). The spectra of the NPLs of the NIR emission reveal the second lowest state (Γ_5) as the final state of the dominant NPL. The initial state of the NIR luminescence ${}^3\text{T}_1(\text{H})$ is split due to the spin–orbit interaction into Γ_1 , Γ_4 , Γ_3 , and Γ_5 . The occurrence of only one strong NPL can be explained under the assumption of Γ_1 as the initial state of the luminescent transition. Otherwise, more than one NPL would be allowed according to the symmetry selection rules. The thermalization behaviour of the NPL points to only two excited levels. The merging of the originally four levels may be caused by a Jahn–Teller effect in analogy to the properties of the ${}^4\text{T}_1(\text{G})$ state of Mn^{2+} [11] or the ${}^3\text{T}_1(\text{H})$ state of Fe^{2+} [25].

Given the linear dependence of the emission intensity on the excitation density, the NIR PL was supposed to be excited via a one-step process. If the excitation requires two charge-transfer reactions, one would instead expect a nonlinear relationship between optical input and output. Owing to the very large time constant of the reverse process of (2), however, the ${}^6\text{A}_1(\text{S})$ ground state of Cr^+ appears to be metastable. Under the pre-condition of excitation with photons exceeding the threshold energy corresponding to (2), there are always $\text{Cr}^+\{{}^6\text{A}_1(\text{S})\}$ ions, which can recombine yielding $[\text{Cr}^{2+}]^*$. Therefore, the overall excitation process appears as a one-photon reaction leading to the proportionality between emission and excitation density.

Very long decay times as reported for the NIR PL (1.8 ms [9]) have up to now only been observed for the spin- and symmetry-forbidden ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ emission of 3d^5 ions in different host lattices (e.g. 0.24 ms for ZnSe:Mn²⁺ [9], 1.8 ms for ZnS:Mn²⁺ [26], 25.2 ms for ZnO:Fe³⁺ [18]). The decay constant of the ${}^3\text{T}_1(\text{H}) \rightarrow {}^5\text{E}(\text{D})$ emission of Fe^{2+} in ZnSe (0.35 ms [27]), a transition similar to ${}^3\text{T}_1(\text{H}) \rightarrow {}^5\text{T}_2(\text{D})$ of ZnSe:Cr²⁺, is however at least comparable with the time constant for Cr^{2+} .

The ODMR results [10] that connect the NIR PL and the simultaneous presence of Cr^+ centres do not present decisive evidence against an assignment of the emission to the ${}^3\text{T}_1(\text{H}) \rightarrow {}^5\text{T}_2(\text{D})$ transition of Cr^{2+} . First, it is known from earlier ODMR investigations of Mn^{2+} centres in ZnSe [28] that the direct identification of centres taking part in the recombination process is not in each case unambiguous. Resonances due to the $\text{Mn}^{2+}(3\text{d}^5)$

ground state were observed not only in the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ emission band of Mn²⁺ but also in two donor–acceptor recombination bands. Therefore, in the present case it could be possible that the Cr⁺ resonance is monitored in the Cr²⁺-related emission band. Second, an ODMR signal with $g \approx 2$ which has a poor signal-to-noise ratio is not very specific and may have its origin in several other free electron-like defect states.

To conclude, the presented study provides striking evidence for an assignment of the Cr-related NIR luminescence band in ZnSe centred near 10 300 cm⁻¹ to an internal transition of the Cr²⁺(d⁴) ion. Zeeman spectra of the corresponding NPLs are described by the ground state properties of Cr²⁺ known from EPR investigations. Crystal field calculations suggest an assignment of the emission to the ${}^3T_1(H) \rightarrow {}^5T_2(D)$ transition.

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References

- [1] Vallin J T, Slack G A, Roberts S and Hughes A E 1970 *Phys. Rev. B* **2** 4313
- [2] Vallin J T and Watkins G D 1974 *Phys. Rev. B* **9** 2051
- [3] Baranowski J M 1986 in *Deep Centers in Semiconductors* ed S T Pantelides S T (New York: Gordon and Breach) p 691
- [4] Title R S 1963 *Phys. Rev.* **131** 623
- [5] Title R S 1964 *Phys. Rev.* **133** A1613
- [6] Dieleman J, Title R S and Smith W V 1962 *Phys. Lett.* **1** 334
- [7] Ludwig G W and Lorenz M R 1963 *Phys. Rev.* **131** 601
- [8] Grebe G, Roussos G and Schulz H-J 1976 *J. Lumin.* **12/13** 701
- [9] Pradella H and Pohl U W 1987 *Phys. Status Solidi b* **141** K143
- [10] Pradella H 1995 *Optische und mikrowellenspektroskopische Untersuchungen des Cr⁺-Zentrums in ZnSe* (Berlin: Köster)
- [11] Koidl P 1976 *Phys. Status Solidi b* **74** 477
- [12] Schneider J, Sircar S R and Räuber A 1963 *Phys. Rev.* **140** 202; *Z. Naturf.* a **18** 980
- [13] Röppischer H, Elssner W and Böttner H 1975 *Phys. Status Solidi a* **27** 375
- [14] Godlewski M and Kaminska M 1980 *J. Phys. C: Solid State Phys.* **13** 6537
- [15] Klimakow A, Dziesiaty J, Korostelin J, Lehr M U, Peka P and Schulz H-J 1994 *Adv. Mater. Opt. Electron.* **3** 253
- [16] Pohl U W and Gumlich H-E 1989 *Phys. Rev. B* **40** 1194
- [17] Hoffmann A, Heitz R and Broser I 1990 *Phys. Rev. B* **41** 5806
- [18] Heitz R, Hoffmann A and Broser I 1992 *Phys. Rev. B* **45** 8977
- [19] Heitz R, Thurian P, Loa I, Eckey L, Hoffmann A, Broser I, Pressel K, Meyer B K and Mokhov E N 1995 *Appl. Phys. Lett.* **67** 2822
- [20] Grebe G, Roussos G and Schulz H-J 1976 *J. Phys. C: Solid State Phys.* **9** 4511
- [21] Goetz G, Pohl U W, Schulz H-J and Thiede M 1994 *J. Lumin.* **60/61** 16
- [22] Peka P, Lehr M U, Schulz H-J, Pohl U W, Kreissl J and Irmscher K 1996 *Phys. Rev. B* **53** 1907
- [23] Sugano S, Tanabe Y and Kamimura H 1970 *Multiplets of Transition-Metal Ions in Crystals* (New York: Academic)
- [24] Godlewski M and Skowronski M 1985 *Phys. Rev. B* **32** 4007
- [25] Skowronski M and Liro Z 1981 *J. Lumin.* **24/25** 253
- [26] Busse W, Gumlich H-E, Geoffroy A and Parrot R 1979 *Phys. Status Solidi b* **93** 591
- [27] Litzenburger B, Pohl U W, Poschenrieder M and Gumlich H-E 1995 *Mater. Sci. Forum* **182–184** 695
- [28] Kluge J and Donecker J 1984 *Phys. Status Solidi a* **81** 675