

The Chromium Impurity in ZnTe: Changes of the Charge State Detected by Optical and EPR Spectroscopy*

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In gasphase-grown p-type ZnTe crystals, the substitutional Cr impurity is detected in the neutral (Cr^{2+}) and both ionized states Cr^{3+} and Cr^+ . While these three oxidation states are now identified by EPR, two of them emerge in the optical spectra as well. Optical irradiation of the samples at low temperatures influences the relative concentrations of these species. By monitoring the respective EPR or optical signals, thresholds for photo-ionization and photo-neutralization processes are derived. In addition to the strong ${}^3\text{E}(\text{D}) \rightarrow {}^3\text{T}_2(\text{D})$ optical absorption of $\text{Cr}^{2+}(\text{d}^4)$, the samples display a luminescence band near 4500 cm^{-1} , structured by Jahn–Teller interaction. For the first time, a no-phonon line at 4989 cm^{-1} is resolved, accompanied by a TA(L) satellite and some local-mode structure. In EPR, the angular dependence of the $\Delta M = \pm 2$ transition characteristic for $\text{Cr}^{2+}(\text{d}^4)$ ions on lattice sites indicates the ${}^3\text{E}(\text{D})$ ground state subject to a static Jahn–Teller effect in the three $\langle 100 \rangle$ directions. Whereas an internal optical transition of $\text{Cr}^{3+}(\text{d}^3)$ could not be identified, in EPR, an isotropic signal at $g = 3.3$ discloses a strongly Jahn–Teller-disturbed ${}^4\text{T}_1(\text{F})$ ground state. On irradiation with band-tail photons, the ionized acceptor state $\text{Cr}^+(\text{d}^5)$ becomes detectable by EPR. Furthermore, an emission with an onset near $10,300 \text{ cm}^{-1}$ is recorded for the first time. Its excitation and optical stimulation spectra are studied in wide spectral ranges; the exponential decay with $\tau \cong 1 \text{ ms}$ supports an assignment to a spin-forbidden transition. The acceptor ionization energy is determined as $10,500 \text{ cm}^{-1}$ (1.3 eV).

1. Introduction

While a considerable literature exists depicting the properties of chromium ions in semiconducting II–VI host materials (cf. review [1]), the infor-

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mation available on Cr ions in ZnTe is scarce. This is so much the more regrettable as ZnTe is receiving an increased attention from the point of view of technological applications, whereas here attention will be focused on basic physical attributes of Cr ions, especially their coupling to lattice vibrations. After Title [2] had demonstrated the occurrence of the $\text{Cr}^+(\text{d}^5)$ configuration in ZnTe, Suto and Aoki [3] studied in some detail the optical generation and quenching of $\text{Cr}^+(3\text{d}^5)$ centres by photo-EPR experiments. After an optical absorption study of $\text{Cr}^{2+}(3\text{d}^4)$ in ZnTe:Cr [4], Vallin and Watkins [5] presented a thorough investigation of the Cr^{2+} EPR in ZnTe. Their results led to an interpretation in terms of a strong static tetragonal Jahn–Teller distortion (point group D_{2d}) related to e-mode coupling. The first report on luminescence of Cr^{2+} ions in ZnTe, together with indications of e-type vibrational interaction, also in the $^5\text{E}(\text{D})$ excited state of Cr^{2+} , was advanced by Kaminska *et al.* [6]. The photoionization of chromium was then studied by combined optical and EPR methods [7].

2. Crystals

ZnTe:Cr crystals were obtained by modified seeded chemical vapour transport (SCVT) with hydrogen as a transport gas. The method of free growth of large II–VI crystals in Ar (PVT) was developed by Markov and Davydov [8] for CdS and later modified for the growth of Zn–VI materials (with VI: S, Se, Te) and their solid solutions in H_2 (SCVT) [9, 10]. The use of additional sources made this technology powerful for homogeneous or controlled inhomogeneous doping of bulk II–VI crystals with high perfection.

The growth conditions for ZnTe:Cr were similar to those for ZnSe:Ti as prepared previously [9]. The crystals were grown at a temperature of 1460 K. Cr doping was carried out from an additional Cr_2Te_3 source placed under the main ZnTe source, both at 1468 K. The growth rate for a specimen with 37 mm diameter was 1.4 mm/day approximately. Cr_2Te_3 was synthesized during two weeks by step-to-step annealing of high-purity Cr (99.9999%) with Te (vacuum-sublimed 99.9999% purity) between 370 and 1350 K. Commercial ZnTe was additionally purified by high-vacuum sublimation.

The untwinned homogeneous ZnTe:Cr crystal has 5 to 7 mm length at 37 mm diameter. On the (111) surfaces, a typical etch-pit density of the order of $4 \times 10^5 \text{ cm}^{-2}$ was measured which diminished to $2.6 \times 10^4 \text{ cm}^{-2}$ on the top surface. Double-crystal X-ray diffractometry of the (111) reflection proved reasonable half-widths (FWHM) of the rocking curves, varying locally between 30 and 50 arc seconds typically, while the best values obtained on top of the crystal were 17 arc seconds.

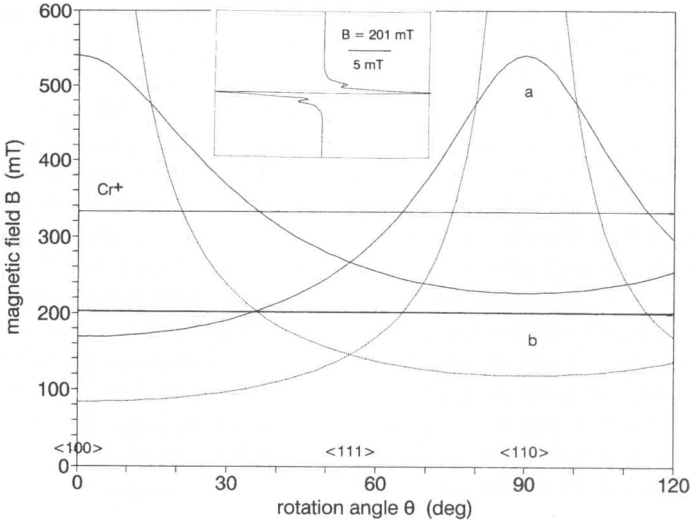


Fig. 1. Angular variation of the EPR signals: (a) $\Delta M = \pm 2$ transitions of $\text{Cr}^{2+}(d^4)$ on lattice sites; the ${}^5E(D)$ ground state undergoes a static Jahn-Teller effect in three $\langle 001 \rangle$ directions. (b) Isotropic $\text{Cr}^{3+}(d^3)$ signal at $g = 3.3$ from a ${}^3T_1(F)$ ground state with strong dynamic Jahn-Teller interaction, see inset.

3. EPR results

EPR spectra of ZnTe:Cr crystals were measured in the temperature range 3 to 77 K using a helium flow cryostat in a homodyne spectrometer working in the X-band (9.5 GHz). Optical excitation in the visible spectral range was provided by a high-pressure Hg lamp. The single-crystal samples were oriented by their cleavage faces (110).

Without optical excitation, a complex anisotropic spectrum is observed at $T \leq 6$ K, identified as Cr^{2+} ($S = 2$). The spectrum can be resolved into three identical, equally intense spectra, each given by

$$\mathcal{H} = \beta g_{\parallel} S_z B_z + \beta g_{\perp} (S_x B_x + S_y B_y) + DS_z^2, \tag{1}$$

but with the z -axis of each along the different cubic axes $\langle 001 \rangle$. Since $|D| \gg h\nu_0$, where ν_0 is the spectrometer frequency, the detectable absorptions are limited to the “forbidden” $\Delta M = 2$ and $\Delta M = 4$ transitions. Only the remaining two doublets of the quintet in the $S = 2$ manifold contribute to resonance spectra so that one may consider the effect of the magnetic field in an effective spin $S' = 1/2$ formalism

$$\mathcal{H} = g'_{\parallel} S_z B_z; \quad g'_{\parallel} = 2 M_s g_{\parallel} \quad \text{and} \quad g'_1 = 0.$$

From the angular dependence (Fig. 1), $g_{\parallel} = 1.97 \pm 0.005$ is determined. The spectra are confirmed by comparative measurements with ZnSe:Cr, where

$g = 1.96 \pm 0.005$ is obtained, and with ZnS:Cr. These present results agree with those of Vallin *et al.* [5] who were able to determine the other parameters of (1) for ZnSe:Cr and ZnTe:Cr using higher spectrometer frequencies and higher magnetic fields. They discussed the anisotropic spectra under the assumption of a static Jahn–Teller effect. The spectra clearly show a pure tetragonal distortion. If the symmetry of a defect with a T_2 ground state [here ${}^5T_2(D)$] is lowered by e-mode coupling from T_d to tetragonal symmetry (D_{2d}), the orbital triplet is split by $\Delta E = 3 E_{JT}$ (where E_{JT} is the Jahn–Teller energy) giving rise to a lowest orbital singlet with $S = 2$, thus leading to the Zeeman Hamiltonian Eq. (1). $Cr^{2+}(A^0)$ is the neutral state in ZnTe (since transition metals normally substitute for cations in II–VI semiconductors), and one may assume the distortions to result from JT coupling rather than from the presence of a compensating defect nearby.

In addition to this well known spectrum, an isotropic Cr spectrum is found only in p-type ZnTe:Cr samples at temperatures of 3.5 K, not requiring optical excitation (Fig. 1). It is described by the simple Hamiltonian

$$\mathcal{H} = g\beta (S_z B_z + S_x B_x + S_y B_y), \quad (2)$$

with $g = 3.301 \pm 0.002$. The small satellites on the wings of the main line ($\Delta B = 0.8$ mT) can be assigned to interaction with ${}^{125}Te$ (7%, $I = 1/2$), implying $|A| = 25 * 10^{-4} \text{ cm}^{-1}$. A spectrum of this kind is clearly indicative of a strong dynamic JT-effect acting on triplet states, such as T_1 and T_2 . Dynamic coupling causes a partial quenching of the matrix elements of orbital operators, for instance in spin-orbit coupling and Zeeman terms, the Ham effect [11]. Presuming the ground state of $Cr^{3+}(3d^3)$ in T_d as ${}^4T_1(F)$, vibronic coupling with e-mode phonons leads to a vibronic T_1 state as well (Fig. 2). If second-order effects arising from the matrix elements of $\lambda \mathbf{L} \cdot \mathbf{S}$ involving excited cubic multiplets are neglected, the spectroscopic splitting factor for the resulting spin-orbit multiplets J (from $|S-1|$ to $|S+1|$) is given by the Landé formula

$$g(J) = [1/2J(J+1)] * [g_l \{J(J+1) + 2 - S(S+1)\} + g_s \{J(J+1) + S(S+1) - 2\}]. \quad (3)$$

Here is $g_l = \alpha g_L$, and $g_s = 2.0023$ is the true spin value, while $\langle \mathbf{L} \rangle = \alpha \mathbf{1}$, the finite orbital momentum of an orbital triplet, which gives $\alpha = -3/2$ for a triplet (T_1) originating from an F term. If the spin-orbit coupling is weak compared with the JT coupling (implying that the spin-orbit coupling is smaller than the vibrational quantum $\hbar\omega$), the coupling of 4T_1 with e-modes leads to triplets of the same nature, i.e. Γ_4 or Γ_5 , where the resulting ground state is the same as the original state Γ_4 . Ham [11] has shown that within the ground triplet the matrix elements of the orbital momentum must be multiplied by a quenching factor

$$\kappa(T_1) = \kappa(T_2) = \exp \{-3 E_{JT}/2 \hbar\omega\}.$$

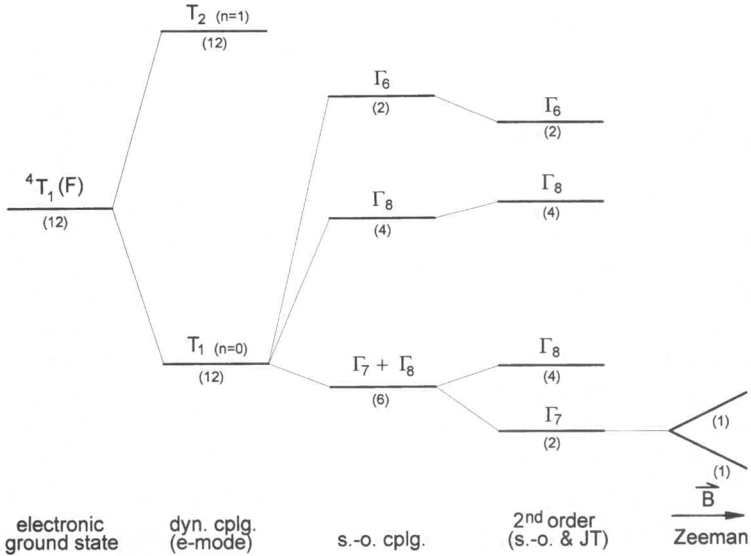


Fig. 2. Splitting scheme for the Cr³⁺ (d³) ion under dynamic JT interaction.

Second order terms of JT effect and spin-orbit coupling then lead to a splitting of multiplets with $J \geq 2$. For very strong JT-coupling, $E_{JT}/\hbar\omega \rightarrow \infty$, the Zeeman energy is to the first order expressed by the operator

$$\mathcal{H}_z = g(J)\beta(\mathbf{J} \cdot \mathbf{B}).$$

In (3), the gyromagnetic factor $g(J)$, $g_l = \alpha g_L$, is replaced by $\kappa_l g_l = \alpha \kappa_l g_L$. For a very strong JT-effect, the orbital Zeeman and spin-orbit energies are completely quenched to the first order. For the state 4T_1 of the ion $\text{Cr}^{3+}(3d^3)$, from Eq. (3) with $S = 3/2$, $J = 1/2$, and $\alpha = -3/2$, for a static field $g(1/2) = (5/3)g_s - (2/3)g_l$ is predicted and $g = 4.33$ is expected, while if $\kappa_l g_l \approx 0$ the value $g = 10/3$ is obtained. As seen above, the measurement of g in ZnTe:Cr yields $g = 3.301$, consistent with Cr^{3+} displaying a strong quenching of the orbital part of the g -factor by a dynamic JT effect.

Similar interpretations have been proposed for $\text{Cr}^{3+}(d^3)$ in GaP [12] and GaAs [13] and $V^{2+}(d^3)$ in ZnTe [14], in these cases with indications of strain-stabilization leading to an orthorhombic symmetry reduction of the cubic vibrational $T_1 - {}^4T_1(F)$ ground state.

The third signal, which is identical with the well known Cr^+ ($g = 1.99$) signal identified first by Title [2] as the ${}^6A_1(S)$ state of the $3d^5$ configuration, is observed in ZnTe:Cr only after optical excitation between 10,500 and 19,400 cm^{-1} , exhibiting a small maximum at 12,000 cm^{-1} and a smaller one at about 18,000 cm^{-1} . The coexistence of Cr^{2+} and Cr^{3+} signals without optical excitation shows that the Fermi level is pinned at the $\text{Cr}^{3+}/\text{Cr}^{2+}$

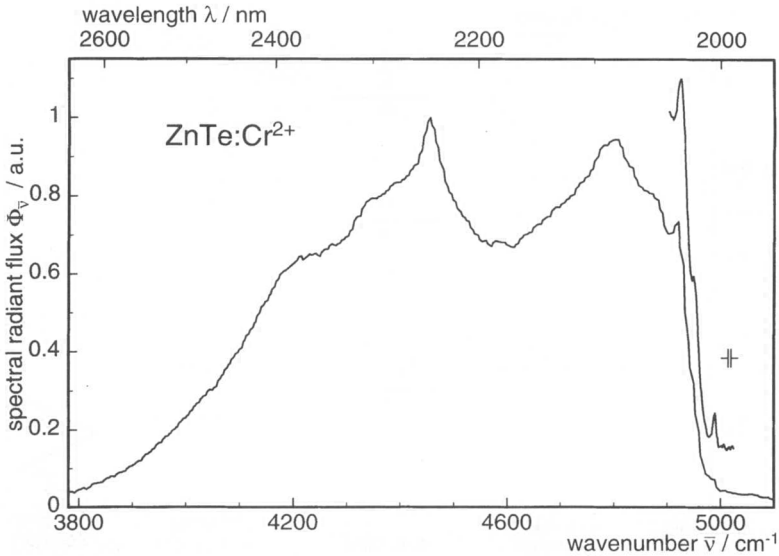


Fig. 3. The ${}^5E(D) \rightarrow {}^5T_2(D)$ photoluminescence of $Cr^{2+}(3d^4)$ in ZnTe (sample no. 7009) at $T = 4.2$ K. Excitation with $18,914\text{ cm}^{-1}$ by Ar ion laser. The NPL and some satellites, such as the TA(L) shoulder at $4,948$ and the local-mode peak at $4,924\text{ cm}^{-1}$ are revealed in a scan with increased resolution, see spectral slit width displayed.

donor level (A^+) of this amphoteric impurity. By irradiation with light, electrons may be excited from the neutral donors (A^0) to the conduction band (excitation maximum at $18,000\text{ cm}^{-1}$) or from the valence band and low-lying acceptor levels, in the range between the bandgap and $12,900\text{ cm}^{-1}$. In the energy range below $10,500\text{ cm}^{-1}$, the Cr^+ signal can be quenched. These results correspond with early measurements by Suto and Aoki [3]. Moreover, the Cr^{2+} signal intensity is lowered by about the same amount as the Cr^+ signal is enhanced by excitation of the $Cr^{2+}/Cr^+(A^0/A^-)$ acceptor in the range near $12,000\text{ cm}^{-1}$. Therefore the acceptor level seems to be situated about $10,500\text{ cm}^{-1}$ above the valence band.

4. Results of optical measurements

Vallin *et al.* [4] reported an ${}^5E(D) \leftarrow {}^5T_2(D)$ absorption of Cr^{2+} in ZnTe peaking at $5,530\text{ cm}^{-1}$ at 2 K with a FWHM of 570 cm^{-1} . On the leading edge, a no-phonon line (NPL) at $4,994\text{ cm}^{-1}$ with 6 cm^{-1} width was resolved. The crystals employed in the present experiments also display the inverse transition in emission, featuring a band around $4,500\text{ cm}^{-1}$ [6]. In addition to the NPL recorded here at $4,989\text{ cm}^{-1}$ (Fig. 3) for the first time, a TA(L) phonon satellite at a distance of 41 cm^{-1} is discerned, while a peak

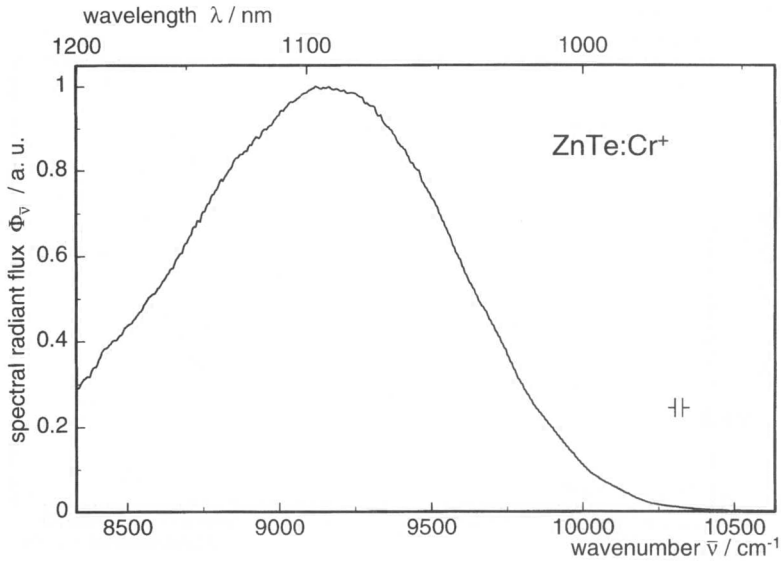


Fig. 4. Emission spectrum of the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ transition of $Cr^{3+}(3d^3)$ in ZnTe (sample no. 7009) at $T = 4.2$ K. Excitation at $18,914$ cm^{-1} by Ar ion laser. Spectral slit width indicated.

shifted by 65 cm^{-1} is evidently due to coupling of a local vibrational mode. The resolution-limited NPL does not display an indication of further splitting, as can be expected from known EPR data [6] and heat-capacity measurements [15] which yield 2.3 and 2.2 cm^{-1} for the parameter D , respectively, which would then imply an optical splitting of $3D$. The range of vibronic transitions is dominated by two broad main maxima with a relative spacing of 350 cm^{-1} . This double structure seems to be characteristic of $Cr^{2+}(3d^4)$ luminescence spectra and has been interpreted by a quadratic Jahn–Teller coupling in the ${}^5E(D)$ excited state of this ion [16]. A radiative ${}^3T_2(F) \rightarrow {}^4T_1(F)$ transition of $Cr^{3+}(3d^3)$ whose presence in these samples has been proved by EPR, should be expected at an NPL energy close to $6,000$ cm^{-1} , as estimated from the known transitions of the isoelectronic vanadium ions. No such emission could be detected, however. On the other hand, there is no reason to believe that the Cr^{3+} levels were degenerate with the valence bands of ZnTe.

The presence of $Cr^{3+}(3d^5)$ was likewise corroborated by photo-EPR experiments. Under similar conditions, an unstructured luminescence band centred near $9,200$ cm^{-1} is observed, viz. excited with photons of comparatively high energy (Fig. 4). It can probably be considered as an analogue to the emission band in ZnSe featuring an NPL structure at $10,702$ cm^{-1} [17] which had been assigned to the ${}^4T_1(G) \rightarrow {}^6A_1(S)$ transition of Cr^{3+} [18]. Its

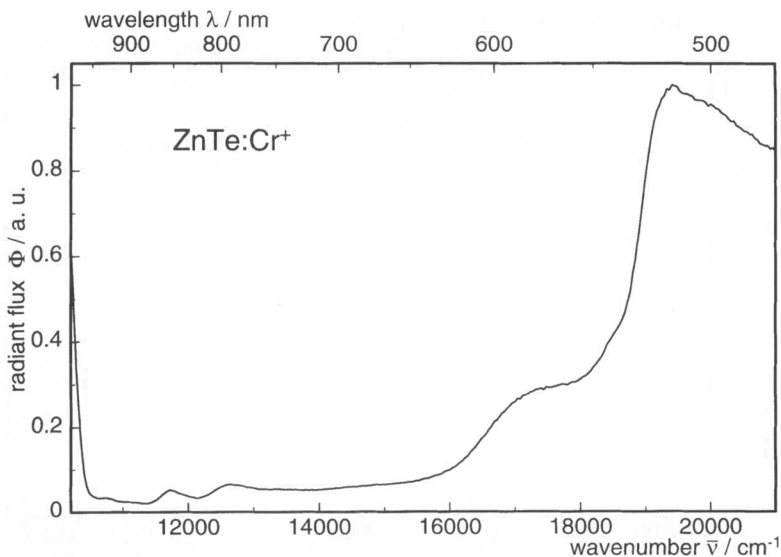


Fig. 5. Excitation spectrum of the Cr^+ photoluminescence shown in Fig. 4 (sample no. 7009) at $T = 4.2$ K. Emission detected in the range from $6,500$ to $10,200$ cm^{-1} . The rise at the low-energy side is an artifact caused by an increasing transmittance of the filter selecting the emission band.

appearance in ZnTe:Cr is anything but natural, since ZnSe:Cr was the only material showing this band up to now. The excitation spectrum (Fig. 5) is dominated by a strong band of charge-transfer type. Thresholds are obvious near $19,000$, $18,000$, and $16,000$ cm^{-1} . Small peaks near $12,600$ and $11,800$ cm^{-1} could point towards internal transitions. In a crude experiment, the decay time constant of this luminescence has here been estimated as 1 ms, a figure which is consistent with the findings at ZnSe:Cr ($\tau \approx 2$ ms) and the corresponding values previously determined for comparable spin-forbidden d^5 internal transitions of Mn^{2+} and Fe^{3+} ions. Based on recent Zeeman data recorded with ZnSe:Cr , the mentioned interpretation of this emission has been modified such that the terminal state is now identified as the Cr^{2+} ground state [19]. The excitation spectrum of our band shows nevertheless a perceptible similarity with the Cr^+ photo-EPR spectrum, indicating a transient occurrence of Cr^+ centres at least.

In a stimulation experiment, the emission (detected in the $6,500$ to $10,200$ cm^{-1} spectral range) was excited by modulated light at $11,765$ cm^{-1} while the influence of an unmodulated auxiliary irradiation was recorded. Whereas above a photon energy of $16,000$ cm^{-1} the photoluminescence is stimulated, beyond $18,200$ and all the more $18,700$ cm^{-1} , the emission is quenched. Evidently the process starting at $16,000$ cm^{-1} is

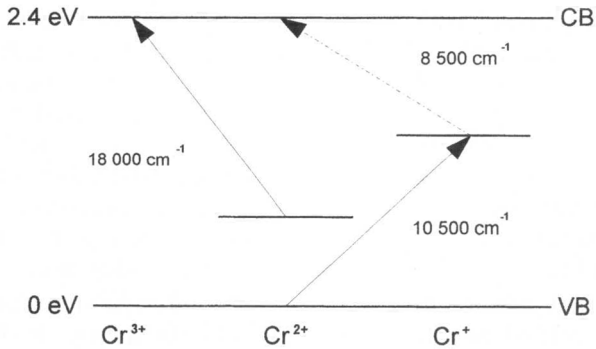
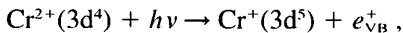


Fig. 6. Model of charge-state conversions depicting the donor- and acceptor-type transitions observed with ZnTe:Cr.

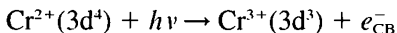
predominantly related with generation of carriers of the sign opposite to that prevailing in the near-gap region. Although the excitation spectrum of Fig. 5 proves the efficiency of near-gap light for an excitation of the emission monitored here, the described quenching action means a lowering of the yield for those internal processes which are effective in the $11,765\text{ cm}^{-1}$ primary excitation.

An interpretation of the described findings becomes feasible by consideration of the photo-EPR results reported here and by recurring to the earlier observations of Suto and Aoki [3] (Fig. 6). Excitation of the Cr^+ resonance evidently requires a minimum energy of $10,500\text{ cm}^{-1}$. Consequently, this threshold is interpreted as the acceptor transition proper, viz. the reaction



while Blazhkiv *et al.* [20] attribute the same energy to the photoneutralization of Cr via the conduction band which in our reasoning would result as $8,000\text{ cm}^{-1}$, the complementary energy difference.

The more prominent structures above $15,000\text{ cm}^{-1}$ evidently comprise a variety of processes. Already Suto and Aoki [3] surmised an interplay of different phenomena here. Particularly they suggested participation of zinc vacancies in addition to Cr-related reactions, a hypothesis later resumed by Godlewski and Kaminska [7]. After detection of the Cr^{3+} ion by EPR in the course of this study, the true donor transition, i.e.



should be expected to emerge. Via subsequent electron capture at Cr^{2+} this reaction would create Cr^+ as well, so that it would induce structure in Fig. 5 and also in the mentioned stimulation spectrum of Cr^+ . Except for the two papers quoted, there are no reports on an identification of Cr donor levels

in ZnTe. An estimate of the position can be made, however, based on the universal reference rule [21–23] for 3d impurity levels in II–VI semiconductors. From a considerable number of such data obtained with Cr-doped materials (ZnS, ZnSe, CdS, and CdSe), the value predicted for ZnTe is $17,700\text{ cm}^{-1}$, referred to the edge of the conduction band. This figure does not only agree with the average of the threshold values derived from the work of Suto and Aoki [3] for the lower-doped specimens, but is also notably consistent with the starting point at one of the reported charge transfer bands in Fig. 5, given as $18,000\text{ cm}^{-1}$ above. In other words, the present results point towards an interpretation of Suto and Aoki's structures in terms of mere Cr-related processes. The threshold rising near $16,000\text{ cm}^{-1}$ in Fig. 5 could indicate a direct transition to a higher excited (quartet) state of Cr^+ . This assignment would evidently conform to the above made conclusion on the sign of the charge carriers liberated between $16,000$ and $18,000\text{ cm}^{-1}$ being different from that of the carriers created beyond $18,000\text{ cm}^{-1}$. Since the processes starting near $18,000\text{ cm}^{-1}$, i.e. slightly below the gap energy, are now identified as donor-type transitions, hole creation seems to be favoured in the adjacent lower-energy range.

5. Discussion

The presented experimental findings testify chromium ions in ZnTe as another example of an amphoteric impurity. Its occurrence as a quasi-neutral substitutional impurity on the cation site as well as the possibility of donor- and acceptor-type changes of its charge state are evidenced by the behaviour under auxiliary irradiation. The properties of Cr^{2+} agree with the established picture of a Jahn-Teller-stabilized ground state, showing a pronounced e-mode coupling. While the ${}^6\text{A}_1(\text{S})$ ground multiplet of the long-known Cr^+ state is not apt to undergo JT interaction, the Cr^{3+} ion provides a new example of a clear Ham effect in a strain-free case.

The derived energy positions of donor- and acceptor levels are in due accordance with the models implying a common level of reference for a particular impurity in different host materials of the same class. The deliberations advanced here are based on the recent proposal [24] of a correction to the published band alignments as suggested by an adaptation of the vanadium levels. The $\text{Cr}^{2+}/\text{Cr}^{3+}$ donor state is determined at $18,000\text{ cm}^{-1}$ below the conduction band minimum, the $\text{Cr}^{2+}/\text{Cr}^+$ acceptor level at $10,500\text{ cm}^{-1}$ above the valence band maximum. These positions of the donor and acceptor levels imply a Hubbard energy of $9,500\text{ cm}^{-1}$ or 1.2 eV approximately.

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