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## Luminescence of tungsten impurities in ZnSe

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**Abstract.** A new near-infrared luminescence band due to internal transitions of tungsten in ZnSe crystals is described. It is characterized by a weak zero-phonon line (ZPL) at  $\bar{\nu} = 10\,700\text{ cm}^{-1}$  ( $\lambda = 934.6\text{ nm}$ ) and 40 partially strong phonon satellites which reveal the presence of quasilocalized modes with energies of 33, 77, and  $100\text{ cm}^{-1}$ . A magnetic field does not split the ground state, indicating that this is a  $^1A_1$  state of a low-spin configuration of  $W^{2+}(5d^4)$ . The lifetime of the excited state is  $(47 \pm 2)\ \mu\text{s}$ . Intense absorption bands around  $12\,000$  and  $13\,000\text{ cm}^{-1}$  dominating the PLE spectrum are assigned to internal W transitions. Under excitation with  $9400\text{ cm}^{-1}$  ( $1.064\ \mu\text{m}$ ) a further emission appears starting at  $6655\text{ cm}^{-1}$  with a weak ZPL followed by several stronger phonon lines. The distances between these peaks coincide in some cases with the quasilocalized modes of the former emission. Therefore, this luminescence is probably also related to tungsten centres.

### 1. Introduction

ZnSe is the basic material for the intensively studied blue-light emitting laser diodes. A better understanding of the effects of dopants helps to control the optical and electrical properties of ZnSe, hoping to finally improve the performance and lifetime of such lasers.

Ions of 4d and 5d transition metals as dopants of semiconductors are only rarely investigated (Vavilov *et al* 1980, 1983, Ushakov and Gippius 1990, Näser *et al* 1995) compared with some 3d ions, e.g. Mn or Cu. One reason might be that their incorporation into the lattice is more difficult because of their ionic radii, which are often larger. The only detailed spectroscopically studied impurity is tungsten in ZnS (Heitz *et al* 1992), whose photoluminescence had for a long time been ascribed to a so-called M centre (Broser *et al* 1980), i.e. two electrons which are trapped at adjacent anion vacancies.

In the following, new near-infrared luminescence and absorption bands of ZnSe will be described and interpreted as caused by  $W^{2+}$  ions. Zeeman effect measurements will point to an electronic low-spin configuration.

### 2. Crystals

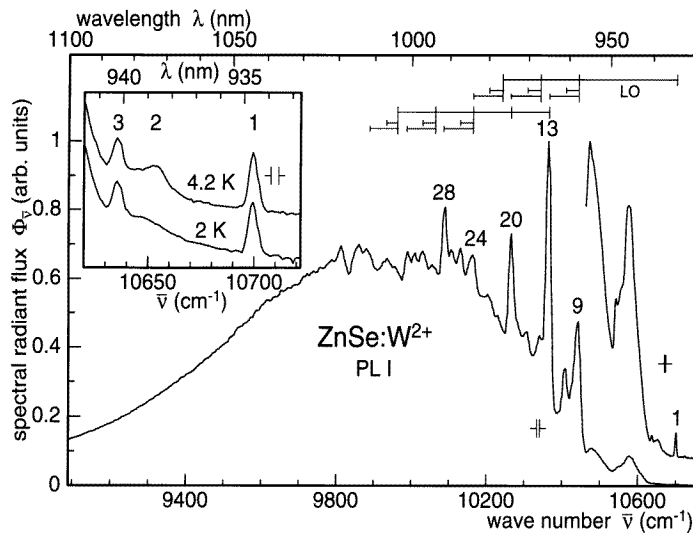
The ZnSe crystals were grown using the modified Markov or seeded chemical vapour transport (SCVT) method (Klimakow *et al* 1994) in a  $H_2$  atmosphere at  $T = 1460\text{ K}$ . The crystals are heavily doped *in situ* from an additional TiSe source with titanium which could be found in these samples in its charge states  $Ti^{2+}$  and  $Ti^{3+}$  (Klimakow *et al* 1994, Dziesiaty *et al* 1994). The tungsten ions were introduced into the samples as a codoping impurity.

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### 3. Luminescence around $10\,000\text{ cm}^{-1}$ (band I)

Under excitation with near-bandgap light a luminescence of ZnSe around  $10\,000\text{ cm}^{-1}$  or  $\lambda = 1\ \mu\text{m}$  can be observed (figure 1). This emission is characterized by weak lines in the zero-phonon (ZP) region and a bunch of strong and sharp lines superimposing the phonon sideband (table 1). There is a striking similarity between these characteristics and those of the previously studied tungsten luminescence in ZnS where the zero-phonon line (ZPL) is located at  $12\,191\text{ cm}^{-1}$  (Heitz *et al* 1992).



**Figure 1.** Photoluminescence I of  $\text{W}^{2+}$  in ZnSe crystals at 4.2 K under excitation with  $21\,837\text{ cm}^{-1}$ . The coupling to phonons is schematically sketched at the top; the numbers refer to the peak numbers used in table 1. The inset shows the temperature dependence of the zero-phonon region of this emission (excitation with  $19\,435\text{ cm}^{-1}$ ). Up to  $10\,750\text{ cm}^{-1}$  there is no further thermalized line.

Even up to  $10\,750\text{ cm}^{-1}$  there is no further thermalized peak indicating that line No 2 at  $10\,653\text{ cm}^{-1}$  is the only one with this behaviour (inset of figure 1). The emission begins immediately to rise for energies smaller than that of line No 1, thus this can be assumed as the ZPL. The behaviour of line No 2 can be tentatively explained with a stronger coupling of a phonon as the temperature is raised. In contrast to ZnS (Heitz *et al* 1992) the ZPL of the W emission in ZnSe has no thermalized line which would represent an excited state splitting. Compared with ZnS:W<sup>2+</sup> ( $12\,191\text{ cm}^{-1}$ ; Heitz *et al* 1992) the new luminescence is shifted towards lower energies due to the smaller energy gap of ZnSe.

The energetic distance between the ZPL and the strongest peak No 13 exceeds the maximum phonon energy of pure ZnSe ( $E_{LO} = 256\text{ cm}^{-1}$ ). The analysis of the peak positions yields the existence of several groups of lines which only appear for energies much lower than that of the ZPL (cf table 1 and the scheme in figure 1). The distances of approximately 33 and  $77\text{ cm}^{-1}$  (in table 1 referred to as LM1 and LM2, respectively) remain constant in each group. The line bundles are interconnected through the coupling of modes of about  $100\text{ cm}^{-1}$  (referred to as LM3 in table 1). The dominating line No 13 has the four replicas, Nos 20, 24, 29, and 34.

The phonon energies of 33, 77, and  $100\text{ cm}^{-1}$  (each with  $\pm 1\text{ cm}^{-1}$ ) which are specific

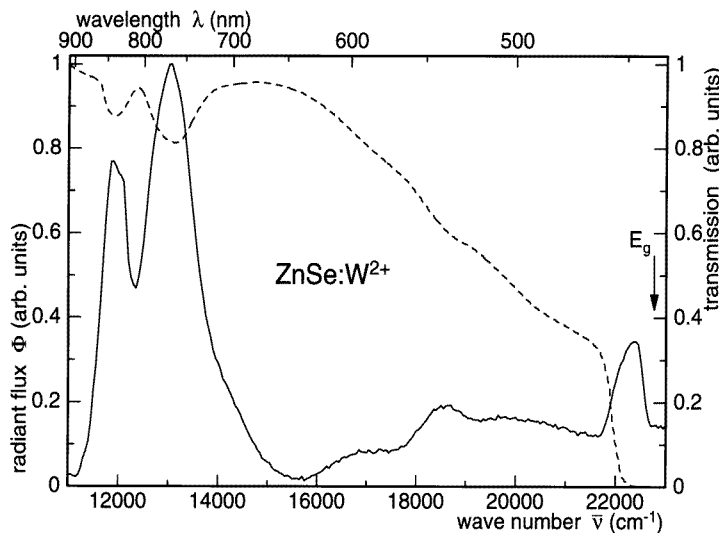
**Table 1.** Calibrated wavenumbers  $\bar{\nu}$  of the ZnSe:W<sup>2+</sup> luminescence I peaks at  $T = 4.2$  K (cf figure 1).  $\Delta\bar{\nu}$  symbolizes the energetic distance from the ZPL. The strongest lines are printed with **bold**, medium lines with *italic* letters.

No	$\bar{\nu}$ (cm <sup>-1</sup> )	$\Delta\bar{\nu}$ (cm <sup>-1</sup> )	Remark	Line group	No	$\bar{\nu}$ (cm <sup>-1</sup> )	$\Delta\bar{\nu}$ (cm <sup>-1</sup> )	Remark	Line group
1	10 699.6	0	ZPL		22	10 205	495	No 12 + 2LM3 or No 21 + LM1	A3
2	10 653	47	thermalized, TA (L)		23	10 182	518		
3	10 636	64	TA (X)		24	<i>10 163</i>	537	No 13 + 2LM3 or No 21 + LM2	A3,B1
4	<i>10 574</i>	<i>126</i>			25	10 149	551		B1
5	10 553	147			26	<i>10 130.5</i>	569	No 24 + LM1	B1
6	10 541	159			27	<i>10 104</i>	596		B1
7	<i>10 470</i>	230	LO		<b>28</b>	<b>10 086</b>	<b>614</b>	No 24 + LM2	B1
8	10 449	251	LO ( $\Gamma$ )		29	10 062	638	No 13 + 3LM3	B2
<b>9</b>	<b>10 442</b>	<b>258</b>	LO ( $\Gamma$ )	A1	30	10 049	651	No 25 + LM3	B2
10	10 434	266		A1	31	10 030	670	No 26 + LM3 or No 29 + LM1	B2
11	10 421.5	278		A1	32	10 005	695	No 27 + LM3	B2
12	<i>10 408</i>	292	No 9 + LM1	A1	33	<i>9986.5</i>	<i>713</i>	No 28 + LM3 or No 29 + LM2	B2
<b>13</b>	<b>10 363.5</b>	<b>336</b>	No 9 + LM2	A1	34	9961	739	No 13 + 4LM3	B3
14	10 358.8	341			35	9951	749	No 25 + 2LM3	B3
15	10 349	351			36	9932	768	No 26 + 2LM3 or No 34 + LM1	B3
16	<i>10 341</i>	<i>359</i>	No 9 + LM3	A2	37	9887	813	No 28 + 2LM3 or No 34 + LM2	B3
17	10 333	367	No 10 + LM3	A2	38	9874	826		
18	10 321	379	No 11 + LM3	A2	39	9855	845		
19	<i>10 307</i>	<i>393</i>	No 12 + LM3 or No 16 + LM1	A2	40	<i>9810</i>	<i>890</i>		
<b>20</b>	<b>10 263</b>	<b>437</b>	No 13 + LM3 or No 16 + LM2	A2	41	9778	922		
21	10 240	460	No 9 + 2LM3	A3					

for this luminescence I are comparable to phonons of the acoustic wing of pure ZnSe. Thus they can be assumed as quasilocalized or resonant modes due to an impurity ion which is obviously heavier than the replaced lattice ion (under the assumption of nearly unchanged force constants).

The radiant flux of the luminescence can be changed by additional unmodulated irradiation, i.e. the emission produced by the pump beam is not measured. Under excitation with  $11\,900\text{ cm}^{-1}$ , the emission intensity can be clearly decreased by a pump beam of  $22\,000\text{ cm}^{-1}$  and slightly decreased by additional light of  $15\,600\text{ cm}^{-1}$ . These observations reveal the presence of charge-transfer effects that connect the mid-gap internal electronic states of the impurity with at least one band.

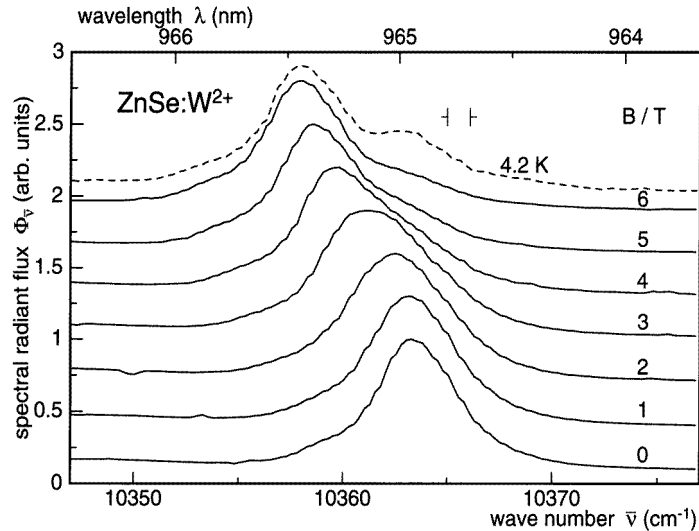
The photoluminescence excitation (PLE) spectrum (the full curve in figure 2) of the new emission is dominated by peaks that coincide exactly with absorptions in the low-temperature transmission spectrum (the broken curve in figure 2): one absorption band is located around  $12\,000\text{ cm}^{-1}$  with the onset at  $11\,600\text{ cm}^{-1}$  and a full width at half maximum (FWHM) of  $480\text{ cm}^{-1}$  and the other band is near  $13\,000\text{ cm}^{-1}$  with a starting point at  $12\,400\text{ cm}^{-1}$  and a FWHM of  $800\text{ cm}^{-1}$ . These peaks in the PLE spectrum certainly represent internal transitions of the impurity ion. For energies above  $15\,800\text{ cm}^{-1}$  and  $17\,500\text{ cm}^{-1}$ , charge-transfer processes are observed in agreement with the pump-light dependence of the emission flux. The peak at  $22\,400\text{ cm}^{-1}$  arises as the result of the excitation of excitons bound to shallow impurities. In the transmission spectrum (the broken curve in figure 2), the beginning of the charge-transfer region is demonstrated by the change of the slope of the curve at about  $15\,800\text{ cm}^{-1}$ . Furthermore, the transmission dips at  $18\,500$ , around  $20\,000$ , and at  $22\,400\text{ cm}^{-1}$  are well resolved and coincide with features in the PLE spectrum.



**Figure 2.** The excitation (PLE) spectrum of the ZnSe:W<sup>2+</sup> luminescence I around  $10\,000\text{ cm}^{-1}$  at  $4.2\text{ K}$  (full curve) and the transmission spectrum at  $2\text{ K}$  of ZnSe:W (broken curve). The PL signal for the PLE spectrum was detected between  $9800$  and  $10\,200\text{ cm}^{-1}$ .

The Zeeman effect causes a shift of the strongest line No 13 towards lower energies, but not a splitting of this peak (figure 3). For  $B = 6\text{ T}$ , two nearly equidistant thermalized lines can be identified on the high-energy shoulder of the peak (the broken curve in figure 3).

This behaviour in a magnetic field reveals the non-splitting of the ground state and the threefold splitting of the excited state with  $g = 1.7 \pm 0.1$ . These Zeeman effect properties resemble those of ZnS:W<sup>2+</sup> (Heitz *et al* 1992, Broser *et al* 1980) where the analogous  $g$  factor was measured as 1.82 (Heitz *et al* 1992) and 1.53 (here estimated from fan charts of Broser *et al* (1980)).



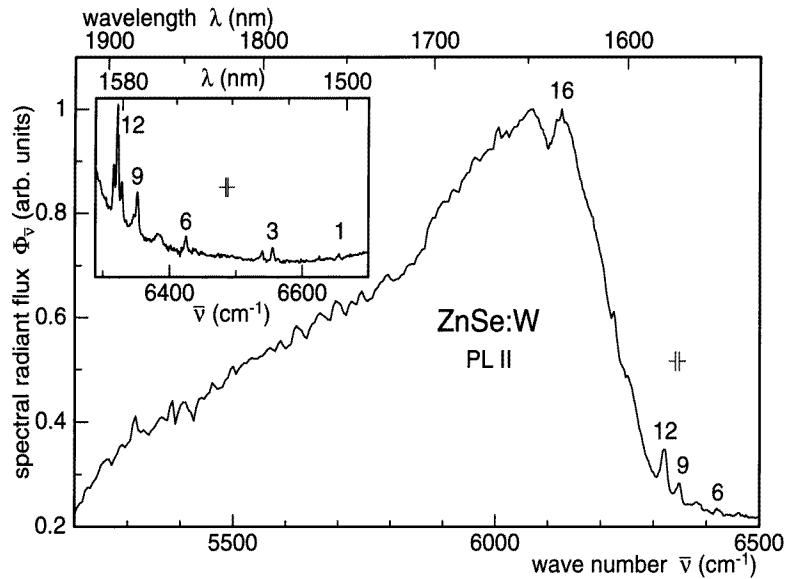
**Figure 3.** The Zeeman effect of the dominant line No 13 of the ZnSe:W<sup>2+</sup> emission I. The distance to the lower-energetic shoulder does not depend on the magnetic field. The full curves were recorded for  $T = 2$  K whereas the broken curve represents the spectrum for  $T = 4.2$  K and  $B = 6$  T. (Faraday configuration;  $B \parallel \langle 111 \rangle$ ; excitation with  $20\,141\text{ cm}^{-1}$ .)

The luminescence I decays exponentially after a pulsed excitation with  $18\,800\text{ cm}^{-1}$  or  $532\text{ nm}$  (frequency-doubled and  $Q$ -switched Nd:YAG laser) with a time constant of  $(45 \pm 2)\ \mu\text{s}$ , which is larger than that of ZnS:W ( $7\ \mu\text{s}$  (Heitz *et al* 1992)), but it is known from internal transitions of some 3d ions that analogous emissions decay faster in ZnS compared to ZnSe (Goetz and Schulz 1988).

#### 4. Luminescence around $6000\text{ cm}^{-1}$ (band II)

Under excitation with  $9400\text{ cm}^{-1}$  (Nd:YAG laser,  $1.064\ \mu\text{m}$ ) the crystals under study give rise to a rather weak further emission (figure 4) which was up to now unknown. The ZPL energy (table 2) and the shape of the sideband differ from those of an earlier observed W luminescence in ZnSe (Ushakov and Gippius 1990). In this new emission, several very weak lines in the ZP region are followed by stronger lines at the onset of the phonon sideband which has a double-band structure.

There are some remarkable similarities to the above-discussed  $10\,000\text{ cm}^{-1}$  luminescence I (cf section 3). First, the ZPL No 1 is very weak compared to pronounced phonon satellites. Second, the energetic difference between the ZPL No 1 and the most intense satellite No 12 ( $333\text{ cm}^{-1}$ ) agrees well with the corresponding value in spectrum I ( $336\text{ cm}^{-1}$ ). Third, some peaks have distances of  $100\text{ cm}^{-1}$  coinciding with a localized mode (referred to as LM3 in table 1) of the emission I. Fourth, energy shifts of  $30\text{ cm}^{-1}$



**Figure 4.** ZnSe luminescence II around  $6000\text{ cm}^{-1}$  caused by low-energy excitation with  $9400\text{ cm}^{-1}$  (Nd:YAG laser,  $1.064\text{ }\mu\text{m}$ ) of a ZnSe:W,Ti crystal. The numbers coincide with those used in table 2. The spectra were measured with PbS ( $\bar{\nu} \leq 6080\text{ cm}^{-1}$ ) and Ge photodiodes ( $\bar{\nu} > 6080\text{ cm}^{-1}$ ).  $T = 4.2\text{ K}$ .

connect some lines as in the first case where this feature was referred to the local mode LM1.

## 5. Discussion

Due to the far more available data mainly luminescence I will be discussed.

The Zeeman results give the confirmation to the presumed identity of the impurity ion as  $\text{W}^{2+}$ . Since the ground state is not split it is evidently not degenerate and must therefore be an orbital singlet ( $A_1$  or  $A_2$ ) with the spin  $1/2$ . There is no high-spin configuration of a transition ion with any d electron number that possesses a non-degenerate ground state. Only the tetrahedral  $d^4$  configuration in the strong-field approximation resulting in a low-spin configuration has such a  $^1A_1$  ground state without degeneracy (Figgis 1966). This configuration is also valid for octahedrally surrounded  $d^6$  ions, e.g. ions situated on an octahedral interstitial site in the tetrahedral ZnSe lattice. Because of the large radiant flux of the emission I and due to the lack of any polarization dependence the assumption seems reasonable that the impurity occupies a lattice site. The new luminescence differs remarkably from that of the known emissions due to  $3d^4$  ions ( $\text{Cr}^{2+}$  (Kaminska *et al* 1979) and  $\text{V}^+$  (Goetz *et al* 1994)). This is why the luminescence centre must be either  $\text{Mo}^{2+}(4d^4)$  or  $\text{W}^{2+}(5d^4)$ , both having almost the same ionic radii as  $\text{Zn}^{2+}$  (Landolt-Börnstein 1955). The similarity with the results concerning tungsten in ZnS (Heitz *et al* 1992) that are even supported by doping experiments sustain the identification of this new centre as  $\text{W}^{2+}$  occupying a cation site in ZnSe. It is noted that a previously found ZnSe emission ascribed to W (Ushakov and Gippius 1990) differs completely from this new luminescence with respect to the ZPL energy and the line shape.

**Table 2.** Wavenumbers  $\bar{\nu}$  of the lines of the ZnSe emission II around  $6000\text{ cm}^{-1}$  at  $T = 4.2\text{ K}$  (cf figure 4).  $\Delta\bar{\nu}$  represents the energy distance from the ZPL. The strongest lines are printed with **bold**, medium lines with *italic* letters. LM1 and LM3 depict quasilocalized modes observed in the luminescence I (cf table 1).

No	$\bar{\nu}$ ( $\text{cm}^{-1}$ )	$\Delta\bar{\nu}$ ( $\text{cm}^{-1}$ )	Remark
1	6655	0	ZPL
2	6625	30	LM1
3	6555	100	LM3
4	6539	116	
5	6437	218	No 4 + LM3
6	6424	231	
7	6384	271	
8	6359	296	
<b>9</b>	<b>6352</b>	<b>303</b>	
10	6346	309	
11	6328	327	No 8 + LM1
<b>12</b>	<b>6322</b>	<b>333</b>	No 9 + LM1 or No 6 + LM3
13	<i>6316</i>	339	No 10 + LM1
14	6251	404	No 12 + TA(X)
15	6224	431	No 12 + LM3
<b>16</b>	<b>6125</b>	<b>530</b>	No 12 + TO( $\Gamma$ )

Tungsten with its atomic number  $Z = 74$  has a remarkably higher mass than the replaced zinc. This large mass difference should clearly influence the local vibration properties of the lattice and should result in localized modes (Hoffmann and Scherz 1990) as observed in this case.

For high atomic numbers the influence of the crystal field as well as the spin-orbit coupling increases (Ballhausen 1962) but the electron-electron repulsion measured by the Racah parameter  $B$  decreases (Figgis 1966). In contrast to results on 4d and 5d dopants in III-V (Vavilov *et al* 1980, 1983) and 5d ions in II-VI semiconductors (Ushakov and Gippius 1990), the crystal field acting on  $W^{2+}$  in ZnSe (as well as in ZnS (Heitz *et al* 1992)) is obviously sufficiently strong to suppress the interaction of the impurity ions and to cause a low-spin configuration in which Hund's rule is no longer valid and the electron spins are ordered antiparallel. From a Tanabe-Sugano diagram for the  $d^4$  configuration (Figgis 1966) the relative strength of the crystal field can be estimated as  $Dq/B \geq 2$  (under the assumption that the ratio of the Racah parameters  $C/B$  does not differ notably from those of the ions of the Fe row).

The ground state of  $W^{2+}$  is a  $^1A_1$  term of the  $e^4$  strong-field configuration. The energetically higher-lying strong-field configurations  $t_2e^3$  and  $t_2^2e^2$  are split into terms by the interelectronic repulsion. Among the resulting terms,  $^3T_1(t_2e^3)$  has the lowest energy followed by  $^3T_2(t_2e^3)$  but the terms  $^1T_1(t_2e^3)$  and  $^5T_2(t_2^2e^2)$  come close to  $^3T_2(t_2e^3)$  (Figgis 1966). Spin-orbit coupling transforms the ground state ( $S = 0$ ) to  $\Gamma_1$ , whereas the first excited states ( $S = 1$ ) are transformed as  $\Gamma_n \otimes \Gamma_4$  resulting in  $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$  and  $\Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$ , respectively. According to the selection rules, only the transitions between  $\Gamma_5$  and  $\Gamma_1$  are electric-dipole and those between  $\Gamma_4$  and  $\Gamma_1$  are magnetic-dipole allowed. The exact prediction of the order of the excited states is prevented on the one hand by the expected strong spin-orbit coupling preferring a mixing of the states and on the other hand by the very limited knowledge of the actual quantitative relationship between crystal-field and spin-orbit coupling induced level splittings for heavy ions. The observation



of distinct absorptions is usually only possible for allowed transitions. Therefore, it can be tentatively assumed that both observed absorption bands (cf the broken curve of figure 2) connect the ground state  $\Gamma_1$  with  $\Gamma_5$ . The luminescence I could then start in a  $\Gamma_4$  state which results in a transition allowed only via the magnetic dipole operator.

In the emission I the coupling between electrons and phonons (especially quasilocalized modes) is very strong as can be seen from the intense phonon lines. This property resembles that of W in ZnS (Heitz *et al* 1992), but contrasts to W and Ta in various other II–VI compounds (Ushakov and Gippius 1990). A conceivable reason for the intense phonon satellites could also be that the local modes have symmetries which lift the basically forbidden character of the electronic transition.

Under the assumption that the force constants are not changed, the energy of a resonant impurity mode  $\hbar\omega_{imp}$  can be calculated according to (Genzel 1969)

$$\hbar\omega_{imp} = \hbar\omega_{Debye} / \sqrt{3(m_{imp}/m_0 - 1)} \quad (1)$$

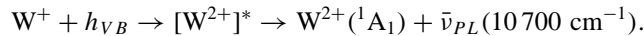
with  $\omega_{Debye}$  as the Debye frequency and  $m_{imp}$  and  $m_0$  as the masses of the impurity and of the replaced ion, respectively. Inserting the maximum energies of the phonon branches of pure ZnSe, equation (1) yields for ZnSe:W resonant mode energies of 30, 81, 91, and 110  $\text{cm}^{-1}$ . These values come close to those of the observed local modes (33, 77, and 100  $\text{cm}^{-1}$ ), but it has to be noticed that the above-made assumption of unchanged force constants after replacing  $\text{Zn}^{2+}$  by  $\text{W}^{2+}$  ions is very likely not correct due to the much larger mass of tungsten.

The shape of the charge-transfer region of the PLE spectrum (figure 2) is similar to that in ZnS:W (Heitz *et al* 1992). The two charge-transfer bands centred at 16 800 and 18 500  $\text{cm}^{-1}$  can be explained in a similar way; thus the following charge-transfer reactions can be assumed:



with a subsequent recapture of a bound (2) or free (3) hole producing the excited state  $[\text{W}^{2+}(5d^4)]^*$  and then followed by the new emission I. The binding energy of the acceptor complex  $(\text{W}^+, h_{VB})$  is approximately 1700  $\text{cm}^{-1}$ . The assumed fine structures of the bound-hole complex near 15 800  $\text{cm}^{-1}$  could not be detected because of the insufficient resolution of the monochromator used in the PLE experiments.

It is known that the  $\text{Ti}^{2+}$  and  $\text{Ti}^{3+}$  ions that are contained in the investigated crystals can easily be converted through additional light (Dziesiaty *et al* 1994). Illumination with energies exceeding 15 000  $\text{cm}^{-1}$  enhances  $\text{Ti}^{2+}$  at the expense of  $\text{Ti}^{3+}$  (Dziesiaty *et al* 1994). The resulting free holes can help to produce  $[\text{W}^{2+}]^*$  ion states from  $\text{W}^+$  after reaction (3) and consequently the new luminescence I is enhanced:



Despite some coinciding features it is all but certain that the 6000  $\text{cm}^{-1}$  emission II belongs to the same centre as the thoroughly studied high-energy luminescence I. Therefore, it can only be proposed that luminescence II is due to a  $\text{W}^{2+}$  transition which is probably forbidden.

It can be assumed that tungsten stems either from the TiSe source or from the heater wire due to the particularly high temperature of the crystal growth. All the efforts to detect tungsten with various element-sensitive methods such as particle-induced x-ray emission (PIXE), atom absorption spectroscopy (AAS), atom emission spectroscopy (AES) and energy-dispersive x-ray analysis (EDX) failed. The concentration of the incorporated

tungsten is obviously very small. The intense luminescence points to a very high oscillator strength of the studied transition.

### Acknowledgments

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