DIRECT CURRENT ELECTROLUMINESCENCE AND SPECTRAL INTENSITY
IN ERBIUM-DOPED ZINC SULPHIDE THIN FILMS

G.Z. Zhong* and F.J. Bryant

Department of Physics
University of Hull, Hull, U.K.

* Changchun Institute of Physics, Changchun, China.

A simple technique of simultaneous co-evaporation has been used
to form thin films of Er-doped ZnS which give good DCEL. For
transitions from excited states to the $^4I_{15/2}$ ground state of the
Er^{3+} ion theoretical calculations of oscillator strengths have
been compared with those determined experimentally from observ-
ations of spectral intensities of DCEL. The good agreement
noted between experiment and theory gives further support for a
previous finding that in rare-earth ZnS thin films the hot
electrons exciting DCEL follow a Boltzmann distribution.

Electroluminescent ZnS thin films were developed as long ago as 1968 [1,2] but
most of these films were ACEL (alternating current electroluminescence) devices.
We have studied electroluminescent ZnS thin films but have paid more attention to
DCEL (direct current electroluminescence) devices [3,4] because they are simple
and convenient both for studying the electroluminescence mechanism and for the
particular application in which a d.c. source or a pulse voltage can be used.

The spectral intensities of rare earth ions have been investigated theoretically
by Judd [5] and Ofelt [6]. As an expression for the oscillator strength Judd gave

$$P' = \sum_{\lambda=2,4,6} T_\lambda \nu \left(\psi_J \| U^{(\lambda)} \| \psi'_{J'} \right)^2 \tag{1}$$

where ν is the wavenumber in cm^{-1} and $\left(\psi_J \| U^{(\lambda)} \| \psi'_{J'} \right)$ are the matrix elements.
Comparisons of experimentally-observed absorption spectral intensities of rare
earth ions in solutions with intensities calculated from the theoretical
expressions have been reported [5,7]. In the DCEL of rare earth doped ZnS thin
films the rare earth spectral intensities should correlate not only with the
theoretical oscillator strengths but also with the energy distribution of the hot
electrons which excite the luminescence centres. This energy distribution has
been shown to follow a Boltzmann distribution [4]. In the present work
theoretical values of the DCEL spectral intensities have been calculated using the
Judd expression and compared with experimental measurements.

The method of fabricating the ZnS:Cu:Er:Cl thin films was similar to that reported
for DCEL thin films of ZnS:Cu:Nd:Cl [3]. The Er-doped thin films gave green DCEL
only when the voltage was applied to reverse bias the cells. The DCEL spectrum of
these ZnS:Cu:Er:Cl films contained the ten groups of lines listed in the table and
is clearly the typical emission of Er^{3+} ions. Fig. 1(a) shows that when the
applied voltage was increased the shorter wavelength emission intensities
increased more rapidly than the longer wavelength emission intensities. This fact
revealed that the electroluminescence in these thin films is excited by direct
impact of hot electrons on the Er^{3+} ions, as concluded for Tb^{3+} by Krupka [8].

The DCEL spectral intensities due to transitions to the $^4I_{15/2}$ ground state from
different excited states were measured with the device at various temperatures, T,
between ~10 K and room temperature. Fig. 1(b) shows that the intensities due to

| Transition	Wavelength /nm	Emission energy/cm^{-1}	ΔE/eV	Relative intensity at $\sim$ 10 K
$^4G_{11/2}-^4I_{15/2}$	385	26000	3.22	11.3
$^2G_{9/2}(^2H_{9/2}^*)-^4I_{15/2}$	411	24300	3.01	20.8
$^4F_{3/2}+^4F_{5/2}-^4I_{15/2}$	457	21900	2.71	17.0
$^4F_{7/2}-^4I_{15/2}$	495	20200	2.50	33.0
$^2H_{11/2}-^4I_{15/2}$	532	18800	2.33	188
$^4S_{3/2}-^4I_{15/2}$	552	18100	2.25	6145
$^4F_{9/2}-^4I_{15/2}$	666	15000	1.86	2323
$^4I_{9/2}-^4I_{15/2}$	809	12400	1.53	899
$^4I_{11/2}-^4I_{15/2}$	985	10200	1.26	8880
$^4I_{13/2}-^4I_{15/2}$	1540	6500	0.81	
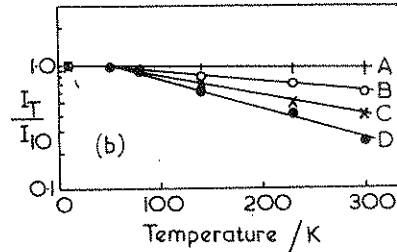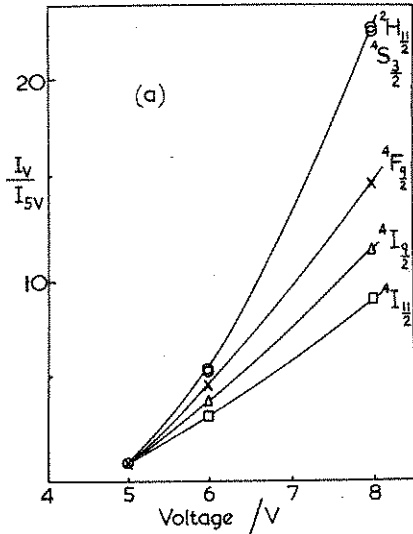
Fig.1(a) The variation of the ratio I_V/I_{5V} with the applied voltage V for the DCEL device at $\sim$ 293 K. For each transition from the labelled excited state to the ground state $^4I_{15/2}$. I_V and I_{5V} are the spectral intensities at applied voltages V volts and 5 volts respectively. (b) The variation of the ratio I_T/I_{10K} with the temperature of the DCEL device. I_T and I_{10K} are spectral intensities with device at T K and $\sim$10 K respectively. For transitions to the $^4I_{15/2}$ ground state from (A) excited states $^4F_{5/2}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$, (B) excited state $^4F_{7/2}$, (C) excited state $^2G_{9/2}$ ($^2H_{9/2}^*$) (D) excited state $^4G_{11/2}$.

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transitions from the $^4F_{5/2}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ excited levels did not change significantly in the 10-295 K range. The same figure shows that for the excited levels $^4G_{11/2}$, $^4G_{9/2}$ $(^2H_{9/2}^*)$ and $^4F_{7/2}$ the emission intensities decreased as the sample temperature was increased. Such a temperature-dependent decrease in emission intensity could be due to non-radiative decay from these levels. In contrast to the results of fig. 1(b), the emission intensities of the transitions from the $^4S_{3/2}$ and $^2H_{11/2}$ levels behave very distinctively. With increasing temperature transitions from the $^4S_{3/2}$ level to the $^4I_{15/2}$ level decreased whereas the $^2H_{11/2}$-$^4I_{15/2}$ transitions increased. The sum of these two spectral intensities would be expected to remain constant when the temperature was increased from ∿10 K to 295 K, and this was in fact observed. In order to exclude the effects of non-radiative decay evident in fig. 1(b), it is reasonable to use, in the comparison of experimental spectral intensities with theoretically calculated values, the spectral intensity data observed at ∿ 10 K.

The spectral intensities of the transitions to the $^4I_{15/2}$ ground state from the various excited states in DCEL of ZnS:Cu:Er:Cl at ∿ 10 K are shown in the table. By the use of some suitable approximations it has been shown [4] that the spectral intensity of the rare earth DCEL in thin films can be written as

$$I \propto \exp\left(-\frac{\Delta E}{E_0}\right) \frac{(P_{down})^2}{\nu^3} \tag{2}$$

where E_0 is the mean energy of the hot electrons, ν is the wavenumber and P_{down} is the transition probability from the excited state to the ground state. Dieke [9] has shown that $P_{down} \propto \nu^2 P'$, where P' is the calculated oscillator strength given in (1). Relationships (1) and (2) can be combined to give

$$I \propto \exp\left(-\frac{\Delta E}{E_o}\right) \nu^3 \left[\sum_{\lambda=2,4,6} T_\lambda \left(\psi_J \| U^{(\lambda)} \| \psi_{J'}'\right)^2\right]^2 \tag{3}$$

Introduction of a constant, K, the value of which depends on the experimental system and the magnitude of the applied voltage, allows (3) to be written as

$$I^{\frac{1}{2}} \exp\left(\frac{\Delta E}{2E_o}\right) \Delta E^{-\frac{3}{2}} = K \sum_{\lambda=2,4,6} T_\lambda \left(\psi_J \| U^{(\lambda)} \| \psi_{J'}'\right)^2 \tag{4}$$

The left hand side of (4) can be evaluated from the experimental data. The matrix elements used for evaluating the right hand side of (4) have been calculated for Er^{3+} (see Table X of ref. [7]). In our calculation two approximations have been made. Firstly, excited levels $^4F_{3/2}$ and $^4F_{5/2}$ have been combined because they were very close together in energy. Secondly, as the sample temperature was varied the sum of the spectral intensities for transitions from the $^2H_{11/2}$ and $^4S_{3/2}$ excited levels stayed almost constant so that they were considered to be one term in the calculation. On previous work [4], with an applied voltage of 13 V, the mean free energy of the electrons, E_o, was taken to be 0.15 eV. For each transition to the $^4I_{15/2}$ ground state from an excited state the value of the expression on the left hand side of (4) was found, using experimentally-determined parameters. The best fit of experimental values with the theoretically-calculated values of the right hand side of (4) was obtained for the parameters
$T_2 = 3.9 \pm 1.4$, $T_4 = 0.94 \pm 0.32$, $T_6 = 1.52 \pm 0.69$ and $K = 10^4$.

The energy level scheme of the Er^{3+} levels is shown in fig. 2(a) and alongside, in fig. 2(b), is shown the comparison with experimental values of the calculations in which the T_λ values have the above T_2, T_4 and T_6 values. In fig. 2(b), at the energy value corresponding to a transition from a particular level, experimental values have been represented by horizontal lines drawn to the left of the y-axis and calculated values by lines to the right of the y-axis. Perfect agreement between theory and experiment would be indicated for each transition by a line symmetrical about the y-axis. Fig. 2(b) shows that good agreement between theory and experiment was obtained for all transitions to the $^4I_{15/2}$ ground state except that from the $^2G_{9/2}$ level. It may be that there was a difference between the calculated energy levels for $^2G_{9/2}$ and $^2H_{9/2}^*$.
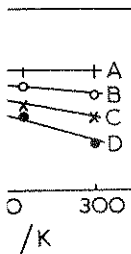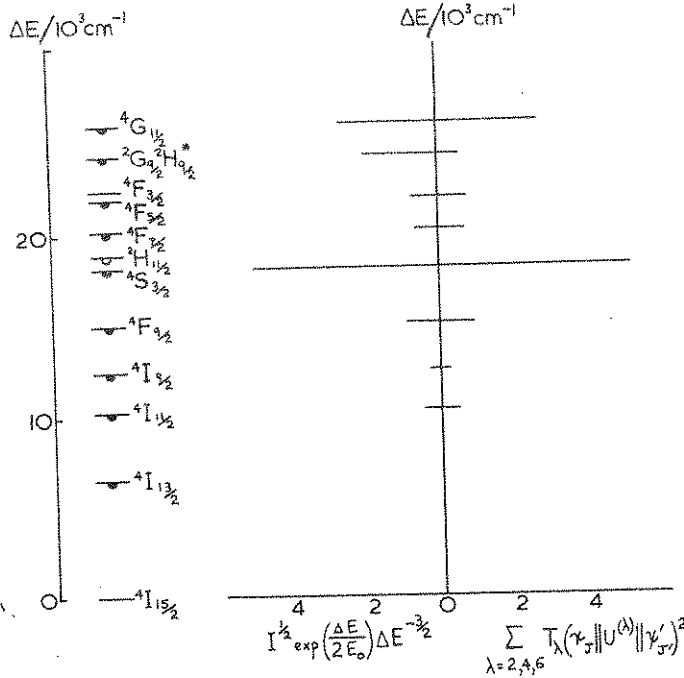
Fig. 2.(a) Energy level scheme of the trivalent erbium ions. (b) Comparison between experimentally measured values of $I^{\frac{1}{2}} \exp(\Delta E/2E_0) \Delta E^{-3/2}$ and theoretical calculations of oscillator strengths for the various transitions to the $^4I_{15/2}$ ground state. For this figure $E_0 = 0.15$ eV and $K = 10^4$.

Good Er^{3+} DCEL has been observed in ZnS:Cu:Er:Cl thin films made by simultaneous co-evaporation of fired ZnS:CuCl powder and erbium metal. Non-radiative processes have been found to be unimportant so that DCEL could be obtained up to room temperature, with external power efficiencies as much as 10^{-4} W/W. Experimental and theoretical oscillator strengths for transitions from Er^{3+} levels have been evaluated and their comparison, by use of (4), shows good agreement. In addition, the existence of such good agreement supports the previous finding [4] that the energy distribution of hot electrons in high electric field regions in rare earth ZnS thin films followed a Boltzmann distribution, $\exp(-\Delta E/E_0)$. For the present thin films of ZnS:Cu:Er:Cl, E_0 was ~ 0.15 eV.

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