

strength increases considerably as a result of internal oxidation. The incoherency due to the presence of dispersed oxide particles strengthens the otherwise soft matrix, and this type of composite alloys may prove to be useful for high temperature applications.

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SENSITIZATION IN CaS : Zr, Mn PHOSPHORS

D. R. BHAWALKAR AND K. MULEY

Solid State Physics Laboratory, Department of Physics, University of Saugar, Saugar

ABSTRACT

CaS : Zr, Mn phosphor system was found to present an interesting case of sensitized luminescence and hence was investigated in detail. Absorption, excitation and emission spectra along with thermoluminescence and decay characteristics were studied. The results indicate resonance transfer of excitation energy from Zr to Mn. Sensitizer-sensitizer transfer also appears to be appreciable. The trap-depths calculated from thermoluminescence and decay studies show good correlation, thus justifying the use of the simple theory of Randall and Wilkins which neglects retrapping. Perturbed levels of the lattice lying quite close to luminescence centres appear to act as traps. A plausible energy level diagram is proposed to explain the luminescence mechanism.

INTRODUCTION

SENSITIZATION is transfer of excitation energy from one luminescence centre to another. It was first investigated by Tomaschek¹ and Rothschild² in alkaline earth sulphides. Numerous studies were made afterwards but a majority of them have been on non-photoconducting phosphors. For photoconducting phosphors, the work has recently started and considerable work has been done on alkali halides too. However, in alkaline earth sulphides, this phenomenon has not been sufficiently studied.

Divalent Mn is known to give rise to appreciable luminescence only by sensitization when incorporated in inorganic phosphors. It has been reported to give orange red luminescence in CaS lattice when excited in the host crystal absorption band.^{3,4} Since the transition involved is a forbidden one, luminescence appears only with the host excitation. It is found that this Mn emission is sensitized by zirconium. Zr when introduced in the CaS lattice creates its own absorption band on the long wavelength side of the host absorption, and excitation in this band gives rise to its

TABLE I

Phosphor	Absorption band peaks eV	Region of strong absorption eV	Excitation band peaks eV (for 2.24 eV emission)	Remarks
†CaS	5.16, 4.65, 3.98	5.10-4.25	5.10*, 4.60, 3.91*, 3.61*, 3.16*	Increase in Zr concentration in general increases the absorption. With increase in Zr concentration weak 4.25 eV band is strengthened, additional 4.40 eV band is developed, 3.52 eV band increases in strength as well as in extension and 2.90 eV band, while increasing in strength, shifts to 2.71 eV. Gradual addition of Mn to CaS : Zr phosphors decreases the absorption, 5.36 eV shifts to 5.43 eV. In CaS : Mn phosphors with increase in Mn concentration 5.16 shifts to 5.43 and additional weak bands at 3.61 and 3.24 eV are developed. 4.60 eV excitation band is the strongest one
CaS : Zr (0.12%)	5.16, 4.57, 4.25*, 3.52*, 3.33*, 2.90	5.10-3.98	5.10, 4.60, 4.40, 3.85, 3.61, 3.28, 3.16	
CaS : Zr (0.95%)	5.36, 4.65, 4.40, 4.25, 3.61, 2.71, 2.05	5.10-3.42	5.10, 4.60, 4.40, 3.85, 3.61, 3.28, 3.16	
CaS : Zr (0.95%) Mn(0.02%)	5.36, 4.60, 4.25, 3.61, 2.71, 2.05	5.10-3.42	5.10, 4.60, 4.40, 3.85, 3.61, 3.16	
CaS : Zr (0.95%) Mn(2.3%)	5.43, 4.53, 4.25, 3.61*, 2.05	5.10-3.85	5.10, 4.60, 4.40, 3.85*, 3.61*, 3.30*, 3.16*	
†CaS:Mn (1.2%)	5.32, 4.65, 4.04*	5.10-3.98	5.10, 4.60, 3.91*, 3.61*, 3.16*	
†CaS:Mn (9%)	5.43, 4.57, 3.61*, 3.24*	5.10-3.98	5.10, 4.60, 4.00*, 3.83*, 3.61*, 3.16*	

* Weak.

† Absorption in the visible region not studied.

own luminescence. However, when Mn is present along with Zr, transfer of excitation energy takes place and Mn emission is obtained. With a view to studying this energy transfer, absorption, excitation and emission spectra of CaS : Zr, CaS : Zr, Mn and CaS : Mn phosphors were studied. To have an idea about the nature and distribution of trapping states in these phosphors, phosphorescence decay and thermoluminescence measurements were also made. This article presents a summary of the results of these studies. The phosphors (in all about 40) were prepared by the method developed in this laboratory and all the studies were made at room temperature.

RESULTS AND INTERPRETATION

(a) *Absorption and Excitation.*—Table I summarizes the results of absorption and excitation of a few representative samples. 5.43-5.16 eV absorption is attributed to host lattice, 4.40 eV to Zr levels perturbed by the host lattice and 4.25 eV to Zr ions embedded in the CaS lattice. Strong absorption starting from 5.1 eV is attributed to the first exciton excitation of the crystal and 4.65-4.53 eV to the levels of the host lattice perturbed by the incorporation of flux. Studies of Levshin and co-workers and Tomar⁴ also support these views. 3.51, 3.61 eV absorption appears to be due to the defect centres (Ca²⁺ vacancies or other localized levels) produced so as to effect charge com-

pensation. 2.90-2.71 eV absorption is attributed to aggregates of defect centres, 2.05 eV to some localized levels introduced by Zr at high concentration and 3.61 eV observed at high Mn concentration to electron transition in MnS lattice perturbed by the surrounding Ca ions. The excitation bands do not exactly coincide with the absorption bands but nevertheless lie in the region of strong absorption.

(b) *Emission, Sensitization and Transfer of Energy.*—Table II summarizes the results of emission. 3.33 eV emission is attributed to some unknown impurity, 2.80 eV along with 2.05 eV to Zr impurity, 1.86 eV to Mn²⁺ centres and 2.12 eV to defect centres. In CaS : Zr, Mn phosphors, with 240.7, 265.5 and 281.4 mμ excitations, the Zr emission is gradually replaced by Mn emission as the Mn concentration increases. It therefore appears that the energy is transferred to Mn²⁺ centres. With 319.1, 338.5, 380.6 and 391.1 mμ excitations, with increase in Mn concentration, though 2.74-2.47 eV region and also the 2.24 eV emission get quenched, this energy does not appear on the long wavelength side, i.e., transfer from defect centres to Mn²⁺ ones is not a probable one.

With 240.7, 265.5 and 281.4 mμ excitations, the emission produced is similar and is the emission attributed to Zr impurity. It is therefore proposed that the transitions corresponding to these excitations occur to some

TABLE II

Phosphor	Exciting wavelength $m\mu$	Emission band peaks eV	Remarks
CaS	240.7	3.33, 2.80, 1.86	Very weak fluorescence. Except 265.5 $m\mu$, emission excited by all other wavelengths is very, very poor in intensity. 3.33 and 2.80 eV bands are very weak compared to 1.86 eV band
	265.5	3.33, 2.80, 1.90	
	313	2.80, 2.09	
	338.5	2.80, 2.12	
	391.1	2.09	
CaS : Mn (0.02%)	240.7	3.33, 2.80, 1.86	CaS : Mn phosphors are weak ones. With increasing Mn concentration, luminescence intensity decreases. 240.7 and 265.5 $m\mu$ lines excite similar emission but that excited by 319.1, 338.5 and 391.1 $m\mu$ lines is different. 3.33 and 2.80 eV bands in the emission excited by 240.7 and 265.5 $m\mu$ lines are very weak compared to 1.86 eV band
	265.5	3.37, 2.80, 1.86	
	319.1	3.37, 2.80, 2.09	
	338.5	2.80, 2.09	
	391.1	2.09	
CaS : Mn (9%)	240.7	3.33, 2.80, 1.86	CaS : Mn phosphors are weak ones. With increasing Mn concentration, luminescence intensity decreases. 240.7 and 265.5 $m\mu$ lines excite similar emission but that excited by 319.1, 338.5 and 391.1 $m\mu$ lines is different. 3.33 and 2.80 eV bands in the emission excited by 240.7 and 265.5 $m\mu$ lines are very weak compared to 1.86 eV band
	265.5	3.37, 2.80, 1.86	
	319.1	3.33, 2.80, 2.12	
	338.5	2.80, 2.12	
	391.1	2.11	
CaS : Zr (0.12%)	240.7	3.33, 2.80, 2.05	CaS : Zr phosphors are quite strong ones. 240.7, 265.5 and 281.4 $m\mu$ lines give similar emission, the 2.80 eV band being not resolved at low Zr concentration with 265.5 and 281.4 $m\mu$ excitations. 319.1, 338.5 and 391.1 $m\mu$ excitations give similar emission which is different from that excited by 240.7, 265.5 and 281.4 $m\mu$ excitations
	265.5	3.33, 2.05	
	281.4	3.33, 2.05	
	319.1	3.33, 2.12	
	338.5	2.80, 2.12	
CaS : Zr (0.95%)	240.7	3.33, 2.80, 2.05	CaS : Zr phosphors are quite strong ones. 240.7, 265.5 and 281.4 $m\mu$ lines give similar emission, the 2.80 eV band being not resolved at low Zr concentration with 265.5 and 281.4 $m\mu$ excitations. 319.1, 338.5 and 391.1 $m\mu$ excitations give similar emission which is different from that excited by 240.7, 265.5 and 281.4 $m\mu$ excitations
	265.5	3.33, 2.80, 2.05	
	281.4	3.33, 2.80*, 2.05	
	319.1	2.80, 2.24*, 2.12	
	338.5	2.80, 2.24*, 2.12	
CaS : Zr (0.95%) Mn (0.02%)	240.7	3.33, 2.80, 1.92	Gradual addition of Mn to CaS : Zr phosphors produces the following effects: (1) Reduction in intensity of the 2.80 eV band (for 265.5 and 281.4 $m\mu$ excitations) (2) Quenching of emission lying between 2.74 and 2.47 eV (for all excitations) (3) Gradual shifting of the peak from 2.05 to 1.86 eV (for 240.7, 265.5 and 281.4 $m\mu$ excitations) (4) Disappearance of the indicated 2.24 eV band (for 319.1, 338.5 and 391.1 $m\mu$ excitations)
	265.5	2.80, 1.96	
	281.4	3.33, 2.80, 1.96	
	319.1	2.80, 2.24*	
	338.5	2.80, 2.12	
CaS : Zr (0.95%) Mn (2.3%)	240.7	2.80, 1.86	Gradual addition of Mn to CaS : Zr phosphors produces the following effects: (1) Reduction in intensity of the 2.80 eV band (for 265.5 and 281.4 $m\mu$ excitations) (2) Quenching of emission lying between 2.74 and 2.47 eV (for all excitations) (3) Gradual shifting of the peak from 2.05 to 1.86 eV (for 240.7, 265.5 and 281.4 $m\mu$ excitations) (4) Disappearance of the indicated 2.24 eV band (for 319.1, 338.5 and 391.1 $m\mu$ excitations)
	265.5	3.33, 2.80, 1.86	
	281.4	2.80, 1.86	
	319.1	2.80, 2.12	
	338.5	2.80, 2.12	
391.1	2.12		

* Indication only. Not clearly resolved.

It has been found that 240.7, 265.5 and 281.4 $m\mu$ excitations give strong fluorescence and a very weak phosphorescence, whereas reverse is the case with 319.1, 338.5 and 391.1 $m\mu$ excitations.

localized level below the conduction band, the holes left thus migrate to Zr centres, thereby producing the Zr emission. The probability of transfer of excitation energy from this level to Mn^{2+} centres is quite high. The present data are not sufficient to decide between the two mechanisms, viz., the resonance transfer and the movement of charged carriers. However, the reported fact that appreciable photoconductivity is observed in CaS : Cu phosphors when light is absorbed in the defect centres absorption band superimposed on the

long wavelength tail which give rise to strong phosphorescence³ and our observation that 319.1, 338.5, 380.6 and 391.1 $m\mu$ excitations give strong phosphorescence, suggest resonance transfer to be the predominant mechanism of energy transfer. Mn emission is found to increase with increase in Zr concentration and this suggests appreciable sensitizer-sensitizer transfer. Approximate position of Mn absorption lies between 450–500 $m\mu$. Excitation by 466 $m\mu$ line of mercury gives not the Mn emission but an emission similar to that

obtained when phosphors are excited in the aggregates of defect centres absorption band. This suggests that the exchange interactions between defect centres and Mn ions are not possible.

(c) *Decay.*—The results of decay studies indicate a hyperbolic decay which can be represented by an equation of the type $I_t = I_0 t^{-b}$ where b is the decay constant. It was possible to break up the decay curve into three exponentials and the trap-depths corresponding to these were calculated. Only one group of traps was found to be effective. The trap-depths appear to decrease with increasing Mn concentration, but do not vary significantly with Zr concentration.

(d) *Thermoluminescence.*—With 0.05°K/sec. heating rate, the glow intensity was quite low and the curves showed only one broad peak which did not show any appreciable variation with increase in Mn concentration. With 0.2°K/sec. , the glow curves are quite broad

and nearly all the samples, except those with high Mn concentration, showed the presence of two peaks. With 0.61°K/sec. heating rate, glow intensity obtained is quite high and the glow curves have a single comparatively sharp peak. With the latter two heating rates, the peak temperature shifts to high temperature side and the intensity of thermoluminescence emission becomes weak as Mn concentration increases. It was not possible to detect glow emission, if any, for phosphors having Mn concentration greater than 0.2%. The trap-depths were calculated by the formula given by Curie.⁶ They were found to be slightly higher than those found from decay. This is expected, since phosphors were allowed to decay to a very low intensity before the heating was started. The trap-depths, however, appear to increase with increase in Mn concentration which is in contrast to the results obtained from decay and can be explained by taking into consideration,

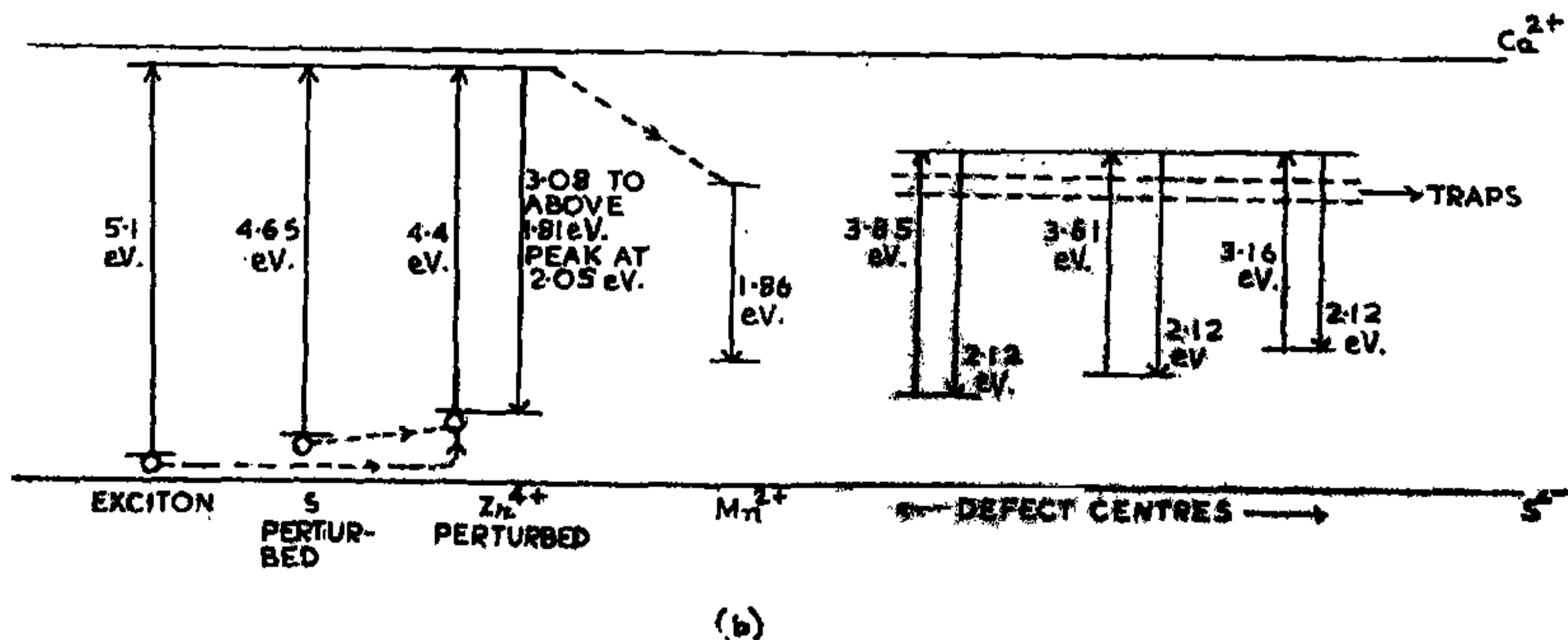
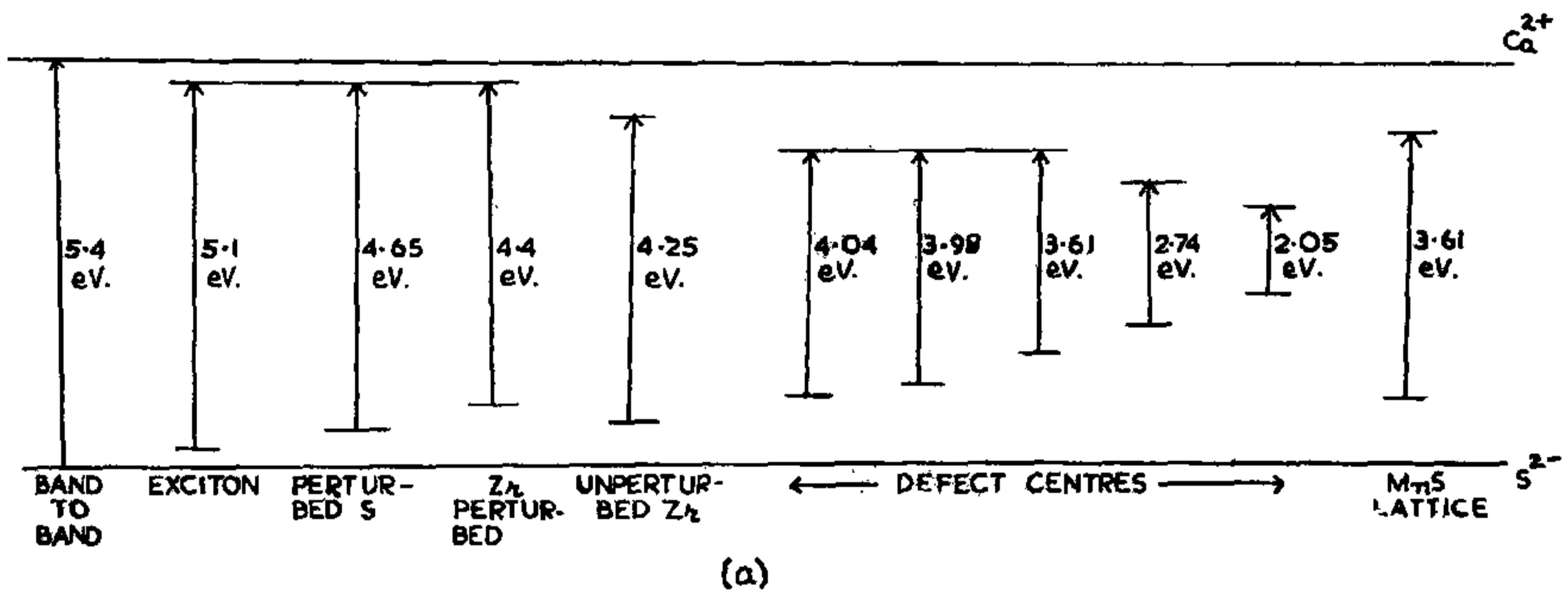


FIG. 1 a, b. Energy level diagram for the CaS : Zr, Mn phosphor system, Readjustment of levels during emission not shown in the figure,

the different decay rates of the two emission bands, the quenching of 2.74–2.47 eV emission with increase in Mn concentration and the maximum sensitivity of the detector phototube in the blue region. However, the trap-depths calculated with the low heating rate were found to agree quite well with those corresponding to the slowest exponential in phosphorescence decay, thus justifying the use of Randall and Wilkins' theory of phosphorescence decay in CaS : Zr, Mn phosphors.

Zr by itself has been reported to introduce no new trapping states. In phosphors containing high Mn concentration, traps due to Mn will predominate, but no thermoluminescence is observed in the temperature range studied for phosphors with high Mn concentration. The glow peaks attributed to traps formed by Mn in different phosphor systems have been reported to be below room temperature only. Most of the investigations in this laboratory on CaS phosphors activated with different activators and prepared with different fluxes revealed a group of traps lying between 0.6 and 0.8 eV. We may therefore say that the traps observed in the present system are typical of the host lattice itself.

Our experimental results of decay and thermoluminescence studies are quite well explained by the simple theory of Randall and

Wilkins which neglects retrapping. This combined with the observation that CaS phosphors are photoconducting when excited in the defect centres absorption bands corresponding to long-lasting phosphorescence suggests that the traps are the perturbed levels of the lattice lying quite close to luminescence centres. Their size has been estimated to be of the order of 10^{-17} cm.^{2,8}

The above-shown energy level diagram (Fig. 1, a and b) has been proposed for the CaS : Zr, Mn phosphor system.

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ON THE OCCURRENCE OF THE DEEP-WATER SQUALOID SHARK *SQUALUS FERNANDINUS* MOLINA FROM THE CONTINENTAL SLOPE OFF THE WEST COAST OF INDIA*

E. G. SILAS† AND N. K. PRASAD‡

Central Marine Fisheries Research Institute, Mandapam Camp, S. India

ABSTRACT

During exploratory trawling from the upper continental slope in depths between 290 and 325 metres off the south-west coast of India, a specimen of the Squaloid shark *Squalus fernandinus* Molina was obtained. This species is a new distributional record for Indian Seas and it is described and illustrated.

ON 7-8-1969 the Indo-Norwegian Project Fishing Vessel M.V. *Velameen* while trawling on the upper continental slope off Quilon between 290 and 325 metres obtained one specimen of a species of squaloid shark

which is identified here as *Squalus fernandinus* Molina. Up to now no representative of the genus *Squalus* Linnaeus popularly known as the 'Spiny dogfish' has been reported from the Indian Seas. In view of the fact that species of *Squalus* are of considerable economic importance in some areas constituting sizable fishery, the present record is of special interest. A description of this new record along with a taxonomic discussion is given below;

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† Present address: Central Marine Fisheries Research Substation, Gopala Prabhu Cross Road, Ernakulam Cochin-11.