

## A PROPOSED MODEL FOR THE PHOTOLUMINESCENCE OF ZnS: CdS(Ag, Ni) PHOSPHORS

BY M. S. ELMANHARAWY

Physics Unit, Department of Radiology, The Cancer Institute, Cairo University\*

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Phosphors with 41% ZnS, 59% CdS, 0.009% Ag and containing various concentrations of Ni dopant are investigated with regard to the fundamental photoluminescence processes involved. The wavelengths of maximum emission intensities in the spectral distributions of excitation and emission remain unaltered with increase in nickel concentration. Thus the energy level structures with the silver impurity centres are not affected by the nickel content. A striking new feature found for these phosphors is their ability to give a thermoluminescence peak at temperatures above those at which their fluorescence has fallen to zero. This peak has been identified as specifically due to trapping states associated with nickel impurity and has an energy depth of 0.78 eV. An energy band model is proposed to explain this phenomenon. It is suggested that the nickel impurity centres provide the energy levels at which recombination processes responsible for this thermoluminescence take place.

### 1. Introduction

Impurity-activated zinc and cadmium sulphides, with and without an additional nickel dopant as a luminescent-quencher, were carefully studied by a number of workers [1-7]. As a result of these investigations, the physical model of the zinc sulphide-type phosphors became more and more developed; and at the same time, knowledge about the chemical nature of the various centres, traps and "quenchers" increased. Nevertheless, luminescence mechanisms in these phosphors are still somewhat controversial subjects; the difficulty arises in explaining a great number of experimental observations by a simple energy model with only one or two levels in the forbidden band gap.

Zinc and cadmium sulphides form a mixed crystal system over all ranges of composition. With increasing cadmium content, the emission spectra of the system shift to longer wavelengths. The mixed system assumes the hexagonal form and the spectral shifts show a reasonably linear relation between the cadmium sulphide content and wavelength. The trapping states also alter regularly with the CdS content [7, 8, 9].

Cobalt, nickel and iron impurities are known to be the most efficient sources of non-radiative centres in zinc sulphide-type phosphors. Bube and his co-workers [10] have

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\* Address: The Cancer Institute, Cairo Univ., Cairo, Egypt.

suggested that these atoms can absorb energy directly, interact with deep activator centres causing them to become non-radiative, and form deep trapping states. Hoogenstraaten [7] has also pointed out that the quenching phenomenon in phosphors containing Co, Ni or Fe impurities could be explained by the formation of deep trap levels with radiationless recombination mechanisms. It has been established for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  ions that they give rise to quite well-defined trapping states. Those produced by cobalt and nickel are evident in thermoluminescence curves [7, 8]. In case of iron, they are inferred from the slow build-up of fluorescence in previously unexcited phosphors.

The present work is an attempt to investigate silver-activated zinc-cadmium sulphides with additional nickel dopant, with respect to the fundamental photoluminescence mechanisms involved.

## 2. Experimental

### 2.1. Phosphors

Phosphors with a host matrix lattice composition of 41% ZnS : 59% CdS, activated with 0.009% Ag and containing varying concentrations of nickel dopant were investigated. All were in powder form, manufactured and supplied by Thorn Electrical Industries Ltd. (England). The chosen host matrix lattice concentration is of interest for two reasons [8]

(a) A cadmium sulphide concentration of 59% in the matrix lattice represents the threshold concentration at which the thermoluminescence peak due to trapping states associated with nickel impurity appears. Below this concentration, detection of this peak by thermoluminescence measurements is not possible for reasons which will be given later.

(b) The fluorescence of phosphors with the above-mentioned host matrix lattice composition shows a marked temperature-dependence at temperatures similar to that of the human body. This behavior has an applicational significance when the phosphors are used to measure tumour temperatures and to provide a topograph of body temperatures in an imaging device.

### 2.2. Measurements

The phosphor specimens were mounted in vacuum on the thermally-insulated copper finger of a cryostat. The temperature could be varied from 77°K to more than 600°K by means of liquid nitrogen and a heating element. Two exciting sources were available: a straight filament tungsten lamp and a 125 watt low pressure mercury lamp. A Chance OX1 filter and a copper chloride solution were used to select the 3650 Å radiation from the mercury lamp.

The spectral distributions of excitation and emission were measured using the conventional chopper disc system techniques [9]. To measure excitation spectra, radiation from the tungsten lamp was chopped and then scanned by a Barr and Stroud double prism monochromator equipped with calcium fluoride prisms. Any emission from the sample was detected by an RCA 1P 21 photomultiplier, amplified by an a.c. tuned amplifier and finally recorded.

Emission spectra were measured by first exciting the sample with the 3650 Å radiation. The light emitted by the specimen was then scanned by the monochromator, detected, amplified and finally recorded. The measured excitation and emission spectra were both corrected for the non-linear variations in response of the apparatus with wavelength.

Temperature-dependence of fluorescence efficiency curves as well as thermoluminescence curves were measured using the 3650 Å radiation for excitation. The emission from the sample was focused onto the cathode of the photomultiplier and the output signal was amplified by a d.c. amplifier and finally recorded. Suitable Wratten filters were used to select the emission band of the phosphor and remove any undesired radiation such as that scattered by the phosphor during irradiation. The temperature of the phosphor was measured by means of a copper — constantan thermocouple and the accuracy of the measured temperature readings was of the order of  $\pm 3^\circ\text{K}$ .

A heating rate of  $2.5^\circ\text{K}/\text{sec}$  was always maintained during the warming process and curves with the best linear heating rates were selected. Full details of the experimental techniques employed for measuring thermoluminescence and temperature-dependence of fluorescence efficiency curves have been published elsewhere [8].

### 3. Results

Figure 1 shows the variation of excitation efficiency with wavelength of the exciting radiation of a constant intensity. The curves were recorded at liquid nitrogen and room temperatures. Excitation occurs in two bands: the fundamental absorption band and a second band of longer wavelength. The curves recorded at room temperature show some indication of tails extending into longer wavelength regions of the spectra, possibly caused by a perturbation of the silver activator centres by nickel. The excitation efficiency decreases

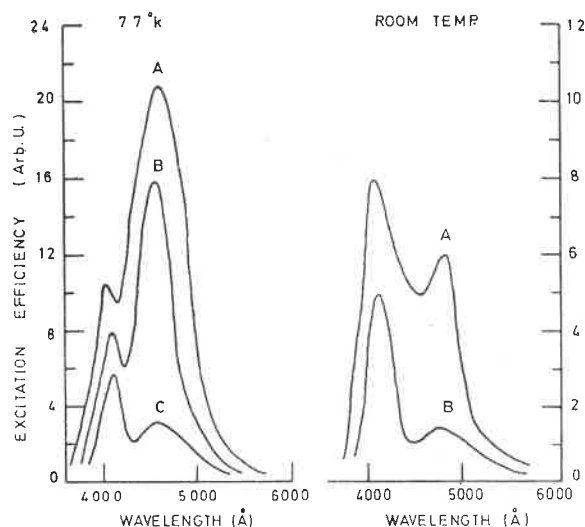


Fig. 1. Excitation spectra for 41% ZnS : 59% CdS (0.009% Ag,  $x\%$  Ni) phosphors; A)  $x = 0.00065$ ; B)  $x = 0.0065$ ; C)  $x = 0.0325$

with rise in temperature from 77°K to room temperature and with the increase in nickel concentration. This quenching of emission is caused by positive hole migration, which is effective at elevated temperatures. The increase in nickel content seems to have no influence on the wavelength of maximum excitation efficiency.

Emission spectra recorded at 77°K and room temperature under steady ultra-violet irradiation are illustrated in Fig. 2. The spectral distribution of emission is unaltered by

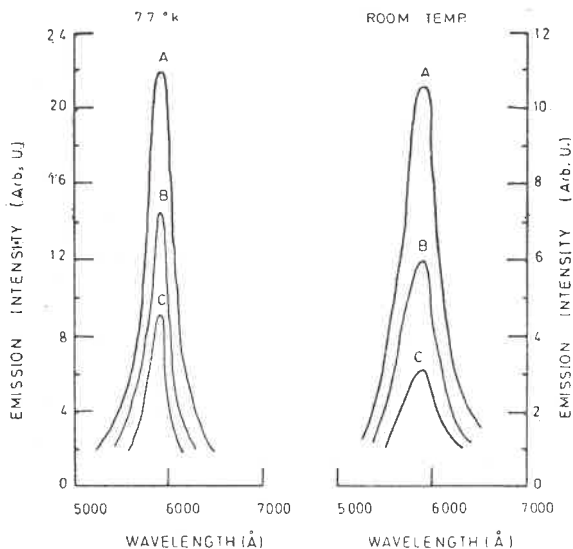


Fig. 2. Emission spectra for 41% ZnS : 59% CdS (0.009% Ag,  $x\%$  Ni) phosphors; A)  $x = 0.00065$ ; B)  $x = 0.0065$ ; C)  $x = 0.0325$

the nickel content. The wavelengths of the silver emission band are very similar to those in ZnS:CdS(Ag) phosphors of similar host matrix lattice compositions [11, 12, 13, 14]. No new emission that may be attributed to nickel is found in the wavelength range of 4000–9000 Å. It is clear that both a rise in temperature and an increase in nickel concentration cause the emission intensity to decrease.

Fig. 3. shows temperature-dependence of fluorescence efficiency curves. The efficiency at a certain temperature is the *ratio* of the fluorescence intensity at that temperature to the fluorescence intensity at liquid nitrogen temperature. At 77°K, positive hole migration is practically negligible and the efficiency of the phosphor is unity. It is found that with an increase in nickel concentration, the whole curve shifts to lower temperatures, the temperature of complete fluorescence-quenching is lowered and the value of the calculated thermal activation energy for the quenching process is decreased. Thermal activation energy values were calculated from the slope of the straight line resulting when  $\ln\left(\frac{1}{\eta} - 1\right)$  was plotted against the reciprocal of the phosphor temperature over the falling part of the temperature-efficiency curve;  $\eta$  being the phosphor efficiency [15]. For the nickel-free phosphor, an activation energy of 0.53 eV was calculated which decreased gradually with the increase

in nickel content, reaching a value of 0.31 eV for a nickel concentration of 0.001%; the average standard error being  $\pm 0.01$  eV. The observed effects of nickel are similar to those of cobalt in ZnS:CdS(Ag,Co) phosphors [7, 16]. Such a lowering of thermal activation energy values cannot be attributed primarily to the presence of nickel, since no shift of the silver emission towards shorter wavelengths was found with the increase in nickel content.

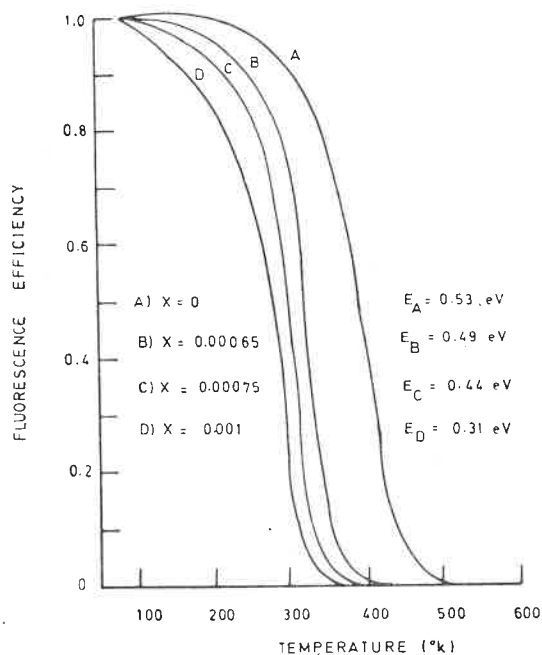


Fig. 3. Temperature — dependence of fluorescence efficiency curves for 41% ZnS : 59% CdS (0.009% Ag, x% Ni) phosphors

It is possible, however, that deep electron traps, known to be present in these phosphors, are responsible for the changes observed. There is no doubt that these electron traps affect the equilibrium between free electrons, holes and centres.

Thermoluminescence curves for phosphors with varying nickel concentrations are shown in Fig. 4. Each curve exhibits three well-separated peaks, which have been identified as due to trapping states associated with chlorine, cadmium and nickel impurities. The variation of the heating rate method, suggested by Hoogenstraaten [7], was used to estimate the energy depths of the traps; and the respective values of 0.26 eV, 0.52 eV and 0.78 eV were found. The energy depths of the traps associated with chlorine and cadmium are very similar to those reported in ZnS:CdS(Ag, Co) phosphors [7].

It is of interest to mention that the thermoluminescence peak due to trapping states caused by nickel impurity has been found to appear only when the cadmium sulphide concentration in the matrix lattice is 59% or more. The absence of this peak from thermoluminescence curves of phosphors with lower cadmium sulphide content is mainly due to the fact that such a peak would appear at very high temperatures (800°K in the case of ZnS(Ag, Ni) phosphor, as estimated from the peak shifting rate of 8°K/Mole% CdS).

At these high temperatures, any luminescence would no longer exist because of the excessive thermal quenching. It has been established that the increase in the cadmium content of the matrix lattice of the present phosphors has little or no effect on the temperature-dependence of fluorescence, but shifts thermoluminescence peaks to lower temperatures [8]. It is therefore expected that the thermoluminescence peak associated with nickel impurity will only appear when the cadmium sulphide content of the lattice has reached a threshold

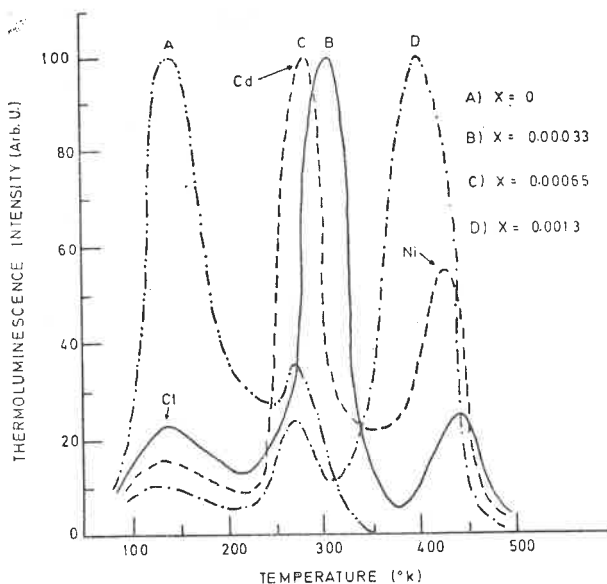


Fig. 4. Thermoluminescence curves for 41% ZnS : 59% CdS (0.009% Ag,  $x\%$  Ni) phosphors

value sufficient to shift the peak to low enough temperatures. In this case, its detection by thermoluminescence measurements will be feasible.

It is also observed that with increase in nickel concentration the thermoluminescence intensity of the peak caused by nickel increases, while those of peaks associated with chlorine and cadmium decrease. This is due to the resulting increased degree of retrapping, into the deeper nickel trapping states, of electrons released from shallower traps during the heating process. Direct observation of such retrapping by nickel has not been previously reported.

Two striking new features have been found for the phosphors presently studied, these are:

(1) Their ability to give thermoluminescence emission at temperatures above those at which their fluorescence efficiency has fallen to zero. The result of measuring a temperature-dependence of fluorescence curve in the conventional way under steady ultra-violet excitation is shown in Fig. 5. Once the fluorescence intensity had fallen to zero, excitation was terminated, the heating process was continued and the thermoluminescence curve was immediately measured. The maximum fluorescence intensity was found to be  $3 \times 10^3$  times greater than that of thermoluminescence.

(2) The glow colour is yellow at temperatures where the chlorine and cadmium peaks appear. However, the emission colour changes to red at temperatures where the nickel glow peak appears [17]. If the recombinations responsible for this thermoluminescence take place between electrons thermally released from trapping states caused by nickel and empty silver centres, then for phosphors with host matrix lattice compositions of 41% ZnS: 59% CdS such recombinations would give a yellow glow. The observation of a red glow colour is thus a surprising and interesting difference from expectation.

#### 4. Discussion and conclusion

During the preparation process of these phosphors, the silver impurity ion enters the lattice to form a luminescent centre in accordance with Kroger's theory of charge compensation [18]. A monovalent positive silver ion replaces a divalent positive zinc or cadmium ion and the missing positive charge is compensated by monovalent chlorine ions replacing a divalent negative sulphur ion. When the phosphor is excited with 3650 Å radiation, an electron from the  $S^{2-}$  ion is brought to a state in which it can move freely through the lattice, *i.e.* it is raised to the conduction band. Moreover, excitation also takes place in a second absorption band on the longer wavelength side of the fundamental absorption. These bands are similar to those reported in ZnS(Cu) phosphors where excitation is known to produce conductivity [19]. The fluorescence of ZnS:CdS(Ag,Ni) phosphors will therefore result from the reverse process, that is:

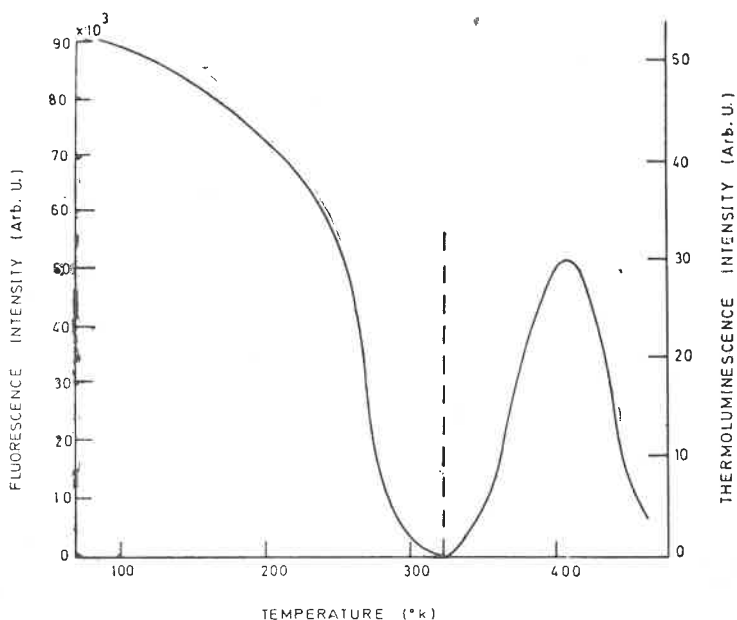
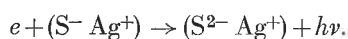


Fig. 5. Temperature — dependence of fluorescence curve and thermoluminescence curve for 41% ZnS : 59% CdS (0.009% Ag, 0.0013% Ni) phosphor. The thermoluminescence curve was immediately measured after the fluorescence intensity had dropped to zero

The form of the temperature-dependence of fluorescence efficiency curve is in agreement with the simple thermal quenching theory of Klasens and his co-workers [15]. When the falling part of the temperature-efficiency curve was replotted, a linear relation existed between  $\ln\left(\frac{1}{\eta} - 1\right)$  values and the reciprocal of the phosphor temperature;  $\eta$  being the phosphor efficiency. A detailed account of the experimental investigation of Klasens' theory will appear elsewhere [20]. The activation energy for the quenching process decreases with the increase in nickel concentration, but these changes are primarily due to the presence

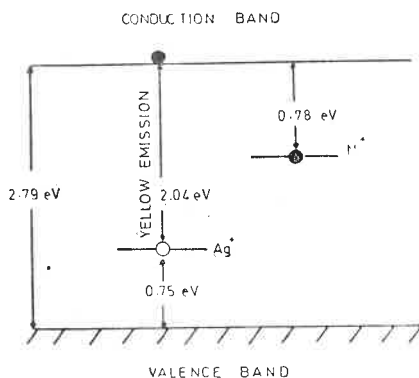


Fig. 6. The conventional energy model

of deep electron traps. Since the number of these traps is directly related to the nickel concentration, it is therefore expected that the number of electrons trapped will increase with the increase in nickel content. Consequently, fewer electrons will be available in the conduction band for recombination with empty silver centres to produce the observed fluorescence. This will cause a shift of the whole temperature-dependence curve, leading to a change in its slope and thus to a change in the calculated activation energy. This suggestion is similar to that made by Hill and Klasens [16], to explain the changes in thermal activation energy values with increase of cobalt content in their ZnS(Ag, Co) phosphors.

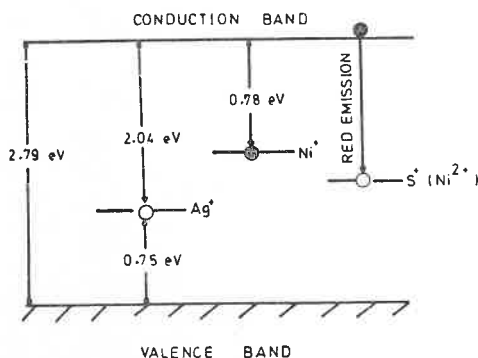


Fig. 7. The proposed energy model



They attributed these changes to the presence of deep electron traps caused by cobalt impurity. This proposal, however, needs quantitative elaboration.

Thermoluminescence measurements have revealed a thermoluminescence peak due to trapping states associated with nickel impurity. The nickel centres are known to be situated as divalent ions at normal  $\text{Zn}^{2+}$  sites in the lattice. Since nickel centres give rise to trapping states, the electronic level of the nickel ion must, therefore, lie below the  $\text{Zn}^{2+}$  band, in which case the trapping by nickel can be represented as:



If the glow peak due to traps caused by nickel is to be associated with recombinations of thermally released electrons with empty silver centres, then such recombinations should give a yellow emission at temperatures where this peak appears. This is understood from consideration of the conventional energy model in Fig. 6, where the energy values have been estimated from the measured spectral distributions of excitation and emission spectra. However, the observed colour during thermoluminescence was found red, so it seems improbable that the recombination processes responsible for the nickel glow take place through the silver centres. It is possible, however, that the nickel impurity centres can provide the alternative levels at which such recombinations occur. This situation is illustrated qualitatively in Fig. 7.; and the mechanisms involved can be described in the following way:

A filled trap associated with nickel ( $\text{Ni}^{+}$  at  $\text{Zn}^{2+}$  site) constitutes an effectively negative nickel centre ( $\text{Ni}^{-}$ ), which may produce its own kind of activator level — like the activator  $\text{Ag}^{-}$ ; ( $\text{Ag}^{+}$  at  $\text{Zn}^{2+}$  site) — by lifting an occupied level from the valence band. Let this new level, from which an electron may be excited to the conduction band by ultra-violet irradiation, be denoted as  $\text{S}(\text{Ni}^{-})$ . It is not entirely improbable that an occupied trap with a thermal activation energy of only 0.78 eV can show absorption for the 3650 Å radiation, since filled traps due to cobalt in ZnS phosphors with smaller thermal activation energy (0.50 eV) have shown absorption for the same radiation [7]. Apart from freeing an electron, the result of such excitation is a new state of the centre,  $\text{S}^{+}(\text{Ni}^{-})$ , which represents an empty level below the filled trap level. This direct result,  $\text{S}^{+}(\text{Ni}^{-})$ , of the optical excitation may be considered as a trapped exciton since it consists essentially of an electron-hole pair trapped at a nickel site. Annihilation of this exciton, leading to an empty state, will be accompanied by liberation of energy which is the excess of the short wavelength quantum over the energy needed for direct optical transition of a trapped electron to the conduction band. This excess energy may either be radiated as fluorescence or it may be used to bring the  $\text{Ni}^{-}$  atom, which is reformed in the process, into one of its characteristic exciting states. Thus on exciting the phosphor, electrons are trapped in states caused by  $\text{Ni}^{2+}$  at  $\text{Zn}^{2+}$  sites. On subsequent warming, recombinations of the thermally released electrons will take place — *via* the conduction band — at  $(\text{S}^{+} \text{Ni}^{-})$  levels, producing the red thermoluminescence.

#### REFERENCES

- [1] H. A. Klasens, *Nature* (London), **158**, 306 (1946).
- [2] G. F. J. Garlick, A. F. Gibson, *J. Opt. Soc. Amer.*, **39**, 935 (1949).
- [3] W. E. Nail, F. Urbach, D. Pearlman, *J. Opt. Soc. Amer.*, **39**, 690 (1949).

- [4] S. Roberts, F. E. Williams, *J. Opt. Soc. Amer.*, **40**, 516 (1950).
- [5] H. Eder, *Z. Phys.*, **166**, 328 (1962).
- [6] H. Eder, *Z. Phys.*, **166**, 386 (1962).
- [7] W. Hoogenstraaten, *Philips Res. Rep.*, **13**, 515 (1958).
- [8] M. S. Elmanharawy, *Rev. Roum. Phys.*, **14**, 1245 (1969).
- [9] M. S. Elmanharawy, *Czech. J. Phys.*, **B20**, 746 (1970).
- [10] R. H. Bube, H. Larach, R. E. Schrader, *Phys. Rev.*, **92**, 1135 (1953).
- [11] W. Van Gool, *Philips Res. Rep.*, **13**, 157 (1958).
- [12] W. Van Gool, *Philips Res. Rep.*, Suppl. No. 3 (1961).
- [13] E. Grillot, *J. Phys. Rad.*, **17**, 624 (1956).
- [14] H. P. De La Garanderie, *Ann. Phys. (France)*, **9**, 649 (1964).
- [15] H. A. Klasens, W. Ramsden, Chow Quantie, *J. Opt. Soc. Amer.*, **38**, 60 (1948).
- [16] C. G. A. Hill, H. A. Klasens, *J. Electrochem. Soc.*, **96**, 275 (1949).
- [17] M. S. Elmanharawy, *Int. J. Appl. Rad. Isotopes*, **22**, 9 (1971).
- [18] F. A. Kroger, *Brit. J. Appl. Phys.*, Suppl. No. 4 (1955).
- [19] J. H. Gisolf, W. De Groot, F. A. Kroger, *Physica*, **8**, 805 (1941).
- [20] M. S. Elmanharawy, *Rev. Roum. Phys.*, (1971), to be published.