

TEMPERATURE-DEPENDENCE OF WILLEMITE LUMINESCENCE

(RECEIVED: 15. XII. 1951)

In previous communications it was reported [1], [2], [3] that the temperature dependence of willemite luminescence may be described by a formula:

$$(1) \quad \eta = \frac{A}{1 + C e^{-\frac{E}{kT}}}.$$

It was also established that by varying the activator concentration $\log C$ and E change in a similar manner. The present paper deals with a generalization of the above assertion. 24 willemites, containing various amounts of manganese activator (0,001, 0,01, 0,1, 0,7, 2 and 5%) and iron killer (0,001, 0,01, 0,1, 1%) were investigated. It was found that the temperature dependence of the luminescence for all the specimens could be described by a modification of formula (1), namely:

$$(2) \quad \eta = \frac{A}{1 + C_1 e^{-\frac{E_1}{kT}} + C_2 e^{-\frac{E_2}{kT}}}.$$

The values of the exponentials in the denominator group themselves into two distinct classes. For the first exponential, C_1 is appr. 10^2 – 10^3 and E_1 0,2–0,4 e. v., for the second, C_2 appr. 10^9 , E_2 1–1,4 e. v. This means, that the second exponential cannot be observed below appr. 600° K, and therefore, in materials containing substantial amounts of manganese or iron, it must have escaped attention. The effect of iron can be studied thus only on the first exponential with the result that increasing amounts of iron monotonously lower both C_1 and E_1 . The same holds for manganese above the optimum concentration. The constants of the second exponential, C_2 and E_2 , may be determined, but less accurately, though the magnitude mentioned is undoubtedly correct.

There seems to exist a definite correlation between the corresponding activation energies (E) and constants C . Plotting $\log C$ as a function of E , ($\log C_1$ vs. E_1 and $\log C_2$ vs. E_2), we get quite an accurate straight line (Fig. 1.). This relationship can therefore be expressed thus: $^{10}\log C = a + bE$. The existence of this relationship is not destroyed by possible errors in the determination of the corresponding C and E , for the eventual variations in C and E merely cause a shift of the locus almost exactly parallel to the above line.

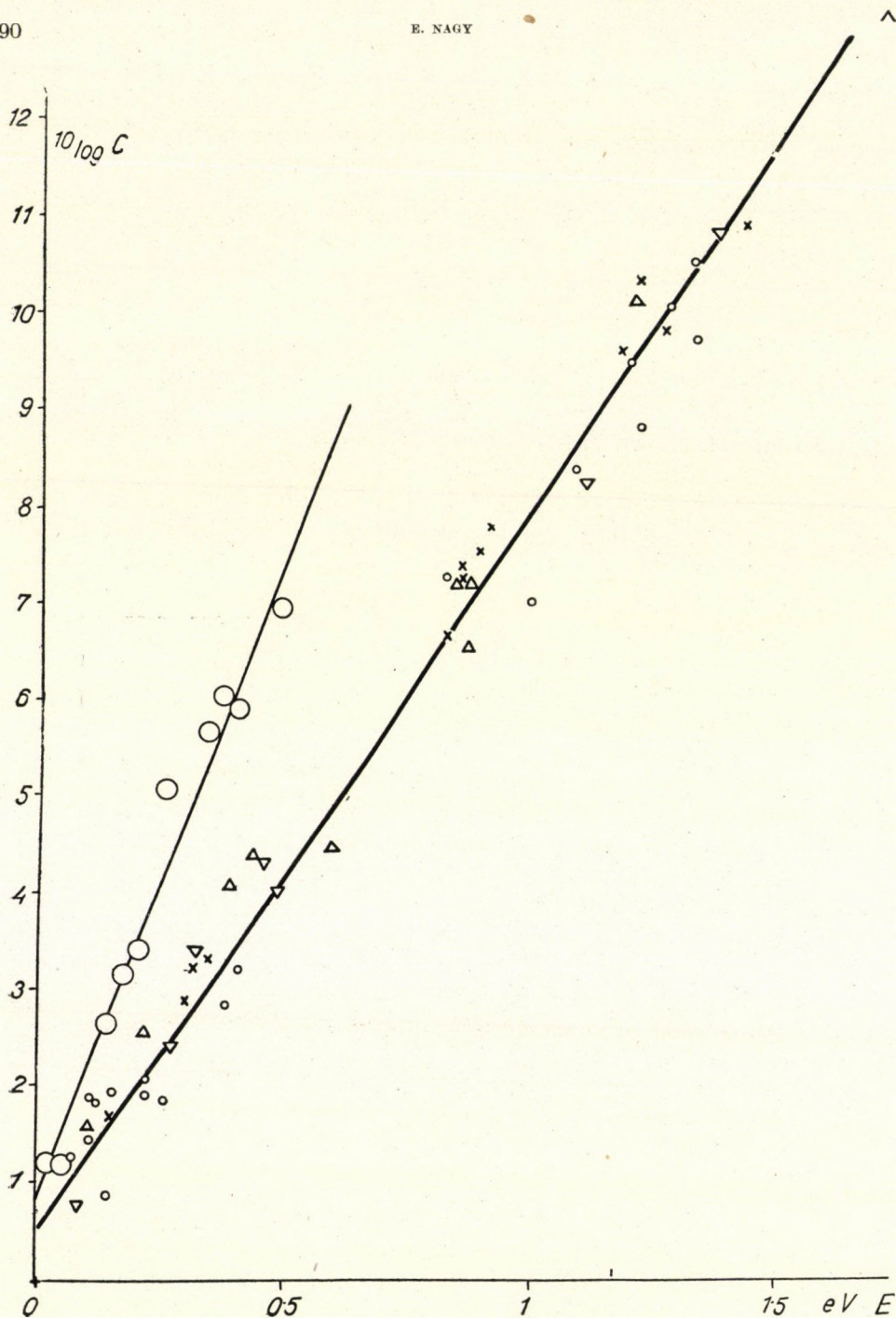


Fig. 1. E and $\log C$ for various luminescent materials.

Our measurements: $\circ$ best values, $\times$ possible values.

- Kröger and Hoogenstraaten: $\times$ fluorescence of zinc silicate,
 $\triangle$ temperature dependence of the phosphorescent decay,
 ∇ fluorescence in the green band of zinc beryllium silicate.
 $\circ$ ZnS · Ag · Co, according to Hill and Klasens.

As an indication that this relation is a general one, the same figure contains the C and E values, calculated from the published curves of *Kröger* and *Hoogenstraaten* [4], [5]. Moreover, the data of the last named authors, on the green band of various zinc beryllium silicates, analysed as in the previous case, are also plotted.

This correlation between C and E seems to be true not only for the green band of zinc silicates, but for a much wider class of luminescent materials too. For ZnO [6], for the green and blue bands of copper activated ZnS [7] the data of *Vergunas* and *Gavrilov* fall again on a straight line. For ZnS containing Ag and Co, the data of *Hill* and *Klasens* [8] show the same relationship, and in this latter case, for the materials having the same heat treatment, both C and E monotonously decrease with increasing cobalt concentration. (Fig. 1.) The values of the constants are summarized in the following table :

TABLE I

Material	a	b
Zn silicate (Mn, Fe)		
ZnBe silicate (Mn), green band accord. to Nagy, Kröger, et al.	0,5	7,1
ZnO [6]	0,8	16,7
ZnS · Cu [7] blue band	0,8	16,7
ZnS · Cu [7] green band	0,7	8,3
ZnS · Ag · Co [8]	0,8	13

Similar relationship was established for the conductivity of some semiconductors by *Meyer* and *Neldel* [9], by *Busch* in the case of SiC [10]. *Busch* has offered an explanation by assuming that below a specific temperature (T_c) the irregularities of the crystal lattice, increasing in number towards higher temperatures according to a Boltzmann-relation, are frozen in. The temperature T_c can be determined in this case by b.

This explanation would lead in our case to a T_c which is apparently too low.

Another explanation would be possible, by assuming that the relationship is caused by the linear dependence of the activation energy on temperature, $E = E_0 (1 - \alpha T)$, C being invariant. This assumption leads directly to

$$(3) \quad C e^{-\frac{E}{kT}} = C_0 e^{-\frac{E_0 - E_0 \alpha T}{kT}} = C_0 e^{\frac{E_0 \alpha}{k}} e^{-\frac{E_0}{kT}} \quad \text{i. e.} \quad \log C = \log C_0 + \frac{E_0 \alpha}{k}.$$

Taking into consideration that the willemite mentioned were all prepared by the same schedule (base lattice composition, firing temperature) and were excited in course of the measurements by the same amount of 2537 Å u. v.

energy, it seemed desirable to extend these investigations by varying the conditions of manufacture, the $\text{ZnO} : \text{SiO}_2$ proportion, and the excitation intensity. These investigations are at present in progress.

The author recognizes with thanks the help of Mr. G. Bauer in performing the spectrum measurements.

Elemér Nagy

Research Laboratory for Telecommunication, Budapest

REFERENCES

1. G. Szigeti, E. Nagy, *Műegyetemi Közlemények*, 1948.
2. E. Nagy, *J. Opt. Soc. Am.* **39**, 42, 1949.
3. E. Nagy, *Acta Physica Hung.* **1**, 115, 1951.
4. F. A. Kröger, W. Hoogenstraaten, *Physica*, **14**, 425, 1948.
5. F. A. Kröger, W. Hoogenstraaten, *Physica*, **15**, 557, 1949.
6. Ф. И. Вергунас, Ф. Ф. Гаврилов, Д. А. Н. **57**, 31, 1947.
7. Ф. И. Вергунас, Ф. Ф. Гаврилов, Ж. Э. Т. Ф. **20**, 224, 1950.
8. C. G. A. Hill, H. A. Klasens, *J. Electrochem. Soc.* **96**, 275, 1949.
9. W. Meyer, H. Neldel, *Zs. f. tech. Phys.* **18**, 588, 1937.
10. G. Busch, *Helv. Phys. Acta*, **19**, 189, 1946.