

LUMINESCENCE OF WILLEMITES CONTAINING MANGENESE AND IRON

By

E. NAGY and Z. BODÓ

RESEARCH LABORATORY FOR TELECOMMUNICATION, BUDAPEST.

(Presented by Z. Gyulai — Received 28. III. 1952.)

The poisoning effect of iron is caused by several agencies.

It is shown that the iron has a concurrent absorption for 2537 Å excitation and in addition has some absorption for the emitted manganese luminescence.

Both effects are, however, inadequate to explain entirely the poisoning effect. The iron is also capable of prohibiting the radiative transition of the excitation energy absorbed previously on the manganese itself.

A formula was derived to account for the brightness of manganese and iron containing willemite at low temperatures. The agreement between measured and calculated values is quite satisfactory.

Introduction

It was established long ago that impurities of the iron group (chromium, iron, nickel, cobalt) act as poisons of luminescence in most materials. From an investigation of substances containing various amounts of activator and killer one can hope to gain some insight into the mechanism of luminescence in these materials.

The killer effect, i. e. the incorporation of foreign ions, with the resulting light output decrease, can be caused in several possible ways and therefore the relative contribution of each must be separately taken into account. We discuss here in this respect the zinc silicates activated by manganese and containing iron.

It is evident that the observed light decrease of fluorescent materials containing foreign atoms too may be caused by any of the following mechanisms :

- a) concurrent absorption of the exciting radiation,
- b) absorption of the emitted luminescence and
- c) lowering of the temperature, above which temperature quenching sets in.

d) This means, that all contributions resulting from a), b) and c) must be separately measured and taken into account, and only the remaining efficiency loss which cannot be explained by mechanisms a)–c) will be termed by us real killer effect.

a) In order to ascertain, whether the absorption of the excitation (2537 Å) is increasing due to the added killer, it was found necessary to devise a method for the determination of the absorption coefficient of substances, available only in grains of linear dimensions below 20 microns. This problem was solved by one of us [1]. The main feature of our method lies in the derivation of the diffuse reflexion, dependent on the grain size and absorption coefficient. The calculations show that the light reflected is dependent only on the product of grain size and absorption coefficient. Applying therefore a thick layer composed of grains of as homogeneous a size distribution as possible, the determination of the absorption coefficient is made possible by the measurement of the diffuse reflexion.

Having applied this method to willemites containing various amounts of manganese and iron [2] we got :

$$\mu/\text{cm} (2537 \text{ Å}) = 20 + 600 C_{Mn} + 1200 C_{Fe},$$

C_{Mn} standing for the manganese, C_{Fe} for the iron content, both expressed in weight percents.

It was found that these values show no change with temperature (between 170° and 570° K) [2].

These experiments have thus shown that the iron gives rise to a concurrent absorption, which is one of the causes of the observed light decrease. The determination of the efficiency loss caused by this concurrent absorption will be given later in this paper.

b) It was observed that the iron-containing silicates were almost colourless and the measurements showed that the absorption coefficient in the green (at the emission maximum) was so low, that no substantial light decrease could be caused by the absorption of the emitted fluorescence. This effect was in the magnitude of 20% for the powders with appr. 5% manganese or a similar amount of iron.

It was found therefore that efficiency loss could be encountered in that way too, its size, however, being quite negligible for materials containing a moderate amount of manganese or iron.

c) It must be borne in mind that the activator and killer assume random positions in the lattice, independent of each other. The experimental proof of the above assertions is furnished by the measurement of the absorption coefficient, which was found to be the simple sum of the contributions from the base lattice, activator (manganese) and killer (iron).

Moreover, the width of the emission band, and its temperature dependence, the position of band maxima are all unaffected by the presence of the killer thus showing that the levels of the activator are not modified in this case by the presence of the killer [3]. Besides the decrease in the maximum quantum effi-

ciency caused by the killer, the temperature dependence of the efficiency is greatly modified too. It is invariably found that with increasing amount of killer present, the constants C and E in the formula :

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

both decrease monotonously [3]. The first mentioned experimental data seem to indicate that the absorption of the excitation and the last phase of the emission act are insensitive to killers. The killer effect may therefore take place only after the absorption and before the emission. This effect consists of at least two separate phases. The one phase — not observable at low temperatures — is characterized by the easier conversion of energy by a radiationless process. (Decrease of E .) The exact physical significance of the exponential expression in (1) is up to now still uncertain [4].

The efficiency loss may be caused by yet another mechanism, namely by a concurrent luminescent emission of the killer itself, which was detected neither in ultra-violet, visible nor near infra-red. An eventual fluorescence in the far infra-red is also excluded by the measurement of the quantum efficiency [5], which was found to be 0, for a material containing appr. 10^{-5} Mn and $5 \cdot 10^{-3}$ Fe.

d) After taking into consideration processes *a)*—*c)* only the remainder of the efficiency loss may be termed killer effect, caused by interaction of activators and killers. This remainder is far from negligible and in fact comprises the greatest part of the observed efficiency loss.

It must be emphasized therefore that the iron is capable of prohibiting the luminescent transition within that manganese centre too, which has already absorbed the ultra-violet excitation.

We have succeeded in deriving an expression which entirely describes the efficiency dependence on manganese and iron contents at low temperatures. This derivation of the constant A in eq. (1) takes into consideration the effects *a)* and *d)*, while the effect *b)* is negligible, and *c)* is eliminated by the use of low temperatures.

Calculation of the contribution from a) and d)

From the fact, that the quantum efficiency assumes a maximum for a specific activator concentration, one may infer that the activator complexes, which lie too close to one another are unable to luminesce. This supposition, which is very similar to the explanation of the concentration quenching of fluorescent organic solutions, leads to the following derivation :

We divide the substance into cells, each having a volume v , and we suppose that only such cells are capable of luminescence which contain one, and only one manganese ion. As was shown, the absorption coefficient in the ultra-violet is linearly increasing with the manganese concentration. We denote by μ_0 the absorption coefficient of the host crystal and all the other impurities except manganese; by μ the absorption coefficient caused by a single manganese ion in a cubic centimetre, and by C the number of manganese ions present in a cubic centimetre. Then

$$\bar{\mu} = \mu_0 + \mu C. \quad (2)$$

We calculate the radiation absorbed on manganese for an infinitely thick specimen of the luminescent material by investigating a layer situated at a depth x from the surface. Denoting by I_0 the incident radiation, the following amount of radiation is absorbed in a layer of thickness dx :

$$dI = -I_0 \bar{\mu} e^{-\bar{\mu}x} dx = -I_0(\mu_0 + \mu C) e^{-\bar{\mu}x} dx. \quad (3)$$

Part of this absorption takes place on the manganese, namely:

$$dI_{Mn} = -I_0 C e^{-\bar{\mu}x} dx. \quad (4)$$

Integrating between ∞ and 0, we get:

$$\int_0^{\infty} dI_{Mn} = I_{Mn} = -I_0 \mu C \int_0^{\infty} e^{-\bar{\mu}x} dx = I_0 \frac{\mu C}{\mu C + \mu_0} = \frac{1}{1 + \frac{\mu_0}{\mu C}} I_0. \quad (5)$$

This result was already anticipated in the introduction.

We now calculate the probability of a single manganese atom occupying a cell. The unit volume contains $\frac{1}{v} = n$ cells, and C manganese ions will be distributed at random among them.

The probability that just one manganese ion gets into a specified cell is:

$$p_1 = \binom{C}{1} \frac{1}{n} \left(\frac{n-1}{n} \right)^{C-1}. \quad (6)$$

The probability that no manganese ion gets into the cell is similarly:

$$p_0 = \left(\frac{n-1}{n} \right)^C. \quad (7)$$

Thus the entire number of cells in the unit volume, each containing one manganese ion is:

$$n_1 = np_1 = n \binom{C}{1} \frac{1}{n} \left(\frac{n-1}{n} \right)^{C-1} \approx C e^{-\frac{C}{n}} \quad (8)$$

(C being large enough), whereas the entire number of cells, not containing manganese is :

$$n_0 = np_0 = n \left(\frac{n-1}{n} \right)^C = n \left(1 - \frac{1}{n} \right)^C \approx n e^{-\frac{C}{n}}. \quad (9)$$

Now the proportion of the incident radiation absorbed on the luminescent manganese and on all the manganese is :

$$\frac{n_1}{C} = e^{-\frac{C}{n}}. \quad (10)$$

Supposing that the energy absorbed in the cells containing only one manganese ion leads invariably to luminescence, while the energy absorbed anywhere else does not lead to luminescence, then the quantum efficiency of luminescence is given by :

$$\eta = \frac{1}{1 + \frac{\mu_0}{\mu C}} e^{-Cv}. \quad (11)$$

Denoting Cv by y and $\frac{\mu_0 v}{\mu}$ by α , we get

$$\eta = \frac{y}{y + \alpha} e^{-y}, \quad (12)$$

which assumes its maximum, when

$$y = \frac{\sqrt{\alpha^2 + 4\alpha} - \alpha}{2}, \quad (13)$$

and thus

$$\eta_{\max} = \frac{\sqrt{\alpha^2 + 4\alpha} - \alpha}{\sqrt{\alpha^2 + 4\alpha} + \alpha} e^{-\frac{1}{2}(\sqrt{\alpha^2 + 4\alpha} - \alpha)}. \quad (14)$$

This formula was applied to *Fonda's* measurements [6] on zinc silicates containing various amounts of manganese. As *Bodó's* investigation has shown, 1% of manganese, which is equivalent to $4 \cdot 10^{20}$ Mn atoms/cm³ gives an absorption coefficient of 600 cm⁻¹, the value of μ to be used here is $\mu = 1.5 \cdot 10^{-18} \frac{\text{cm}^{-1}}{\text{Mn/cm}^3}$. The values of μ_0 and v were chosen to give the best fit. So we have here :

$$\eta = \frac{1}{1 + \frac{60}{1.5 \cdot 10^{-18} \cdot C}} e^{-5 \cdot 10^{-22} \cdot C} \quad (15)$$

i. e. $\mu_0 = 60 \text{ cm}^{-1}$, $v = 5 \cdot 10^{-22} \text{ cm}^3 \approx (8 \text{ \AA})^3$, $\alpha = 0,02$, for $\eta_{\max} = 0,761$ at a Mn concentration of 0,66%.

It must be emphasized that $\eta_{\max}$ depends strongly on μ_0 , the contaminations influencing the position and magnitude of this maximum very markedly. It must be borne in mind too, that this formula cannot be used for any excitations approaching saturation. The measured and calculated values are compiled in Table I. It can be seen that some discrepancy exists for high manganese content, which may be caused very probably by the self-absorption of the emitted luminescence within the material itself (effect *b*).

K (Mn 0/0)	Measured	Calculated $I = 133 \eta$
0,01	12	12
0,10	80	65
0,40	96	97
0,60	98	100
0,90	100	99
1,40	96	93
2,00	90	88
4,50	44	49
5,00	34	44
9,00		20

Let us now examine the role of iron in this material. With the same notation as that used before, the proportion of the incident radiation absorbed on manganese to the entire absorbed radiation is :

$$\frac{\mu_{Mn} C_{Mn}}{\mu_0 + \mu_{Mn} C_{Mn} + \mu_{Fe} C_{Fe}}.$$

Here again μ_0 is the absorption of the host crystal and of all other contaminations (except Fe or Mn).

The number of cells each containing one manganese ion is here :

$$n_{1Mn} = C_{Mn} e^{-\frac{C_{Mn}}{n_{Mn}}} = C_{Mn} e^{-C_{Mn} v_{Mn}}. \quad (16)$$

We again subdivide the unit volume of the material, containing n_{Fe} cells, ($n_{Fe} \cdot v_{Fe} = 1 \text{ cm}^3$), and suppose that cells containing even one iron ion will be non-luminescent. Then the number of cells containing no iron is :

$$n_{0Fe} = n_{Fe} e^{-C_{Fe} v_{Fe}}. \quad (17)$$

Of all the n_{1Mn} cells containing one manganese ion each there will be $\frac{n_{0Fe}}{n_{Fe}}$ which are not killed by iron (contain no iron). The number of such cells is obviously :

$$C_{Mn} e^{-C_{Mn} v_{Mn}} e^{-C_{Fe} v_{Fe}}.$$

Now the proportion of incident radiation absorbed on the luminescent manganese and on all the manganese is :

$$\frac{C_{Mn} e^{-C_{Mn} v_{Mn}} e^{-C_{Fe} v_{Fe}}}{C_{Mn}}$$

The quantum efficiency of the material contaminated by iron is thus given by :

$$\eta = \frac{\mu_{Mn} C_{Mn}}{\mu_0 + \mu_{Mn} C_{Mn} + \mu_{Fe} C_{Fe}} e^{-C_{Mn} v_{Mn}} e^{-C_{Fe} v_{Fe}} \quad (18)$$

This formula was checked against Kröger's measurements [7]. Kröger measured the brightness of a series of luminescent willemite at -180°C each containing 0,55% Mn and varying amounts of iron. Substituting therefore our

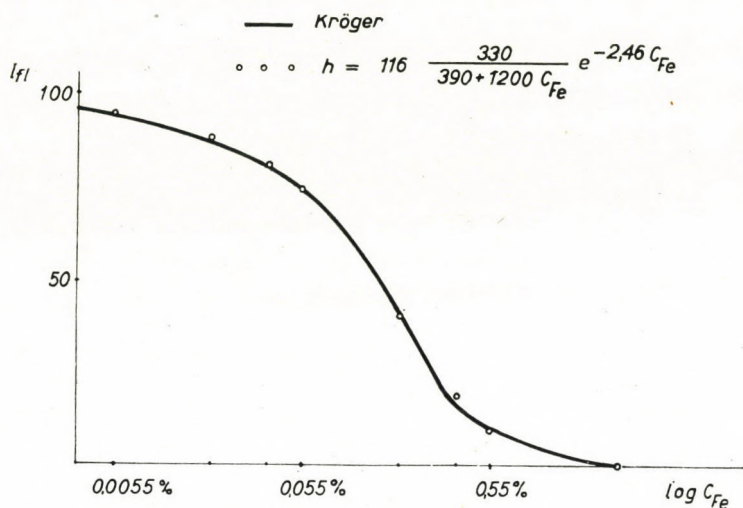


Fig. 1.

previously determined absorption coefficients into eq. (18): $\mu_0 = 60 \text{ cm}^{-1}$, $v_{Mn} = 5 \cdot 10^{-22} \text{ cm}^3$, $\mu_{Mn} \cdot C_{Mn} = 0,55 \cdot 600 = 330 \text{ cm}^{-1}$ and our experimental value for 1% Fe of 1200 cm^{-1} , it is to be seen that the entire range is accurately covered and we get for $v_{Fe} = 60 \cdot 10^{-22} \text{ cm}^3 \approx (18 \text{ Å})^3$. The measured and calculated values are plotted in Fig. 1.

It can be seen that the effect of iron is fully reproduced by an appropriate selection of v_{Fe} , all the other constants being derived from our independent absorption measurements and from the already known effect of manganese concentration upon quantum efficiency. This means that our supposition seems to be correct and the derived v_{Fe} value has a physical significance.

This formula can easily be generalized for the case of more than one contamination, and the absorption of the emitted luminescence can be accounted for by further $e^{-\mu C}$ functions.

The earlier derivations and applications of this formula are discussed by *Ewles* [8]. Recently *Johnson* and *Williams* [9] used a similar picture for the concentration dependence of $\text{KCl} \cdot \text{Tl}$ luminescence. In their calculation the absorption coefficients for host lattice and activator were selected to give the best fit to the data. Our derivation goes a step further by substituting the measured absorption coefficients and thereby reducing the number of constants freely selected.

The killer effect of iron in manganese activated zinc silicate is found to consist of two items: 1. There is a concurrent absorption and 2. the iron is capable of dissipating the energy already absorbed in the manganese. This energy dissipation takes place from a distance approx. twice as great as that between two neighbouring manganese ions. It must be emphasized that this picture is valid only for low temperatures. Our efforts to describe the temperature dependence of quantum efficiency by adequate $v_{Fe}(T)$ and $v_{Mn}(T)$ functions equally good for any willemite containing iron and manganese proved to be totally futile, and we are of the opinion that the difference in the temperature dependence is caused by a separate mechanism, which again favours the quenching by lowering the value of E in eq.(1) (effect c).

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ЛЮМИНЕСЦЕНЦИЯ ВИЛЛЕМИТОВ, СОДЕРЖАЩИХ МАРГАНЕЦ И ЖЕЛЕЗО

Е. Надь и З. Бодо

Резюме

Понижающее влияние железа на светимость при возбуждении 2537 Å может быть сведено к многим причинам.

Во-первых в отношении излучения в 2537 Å железо проявляется конкурентным абсорбентом. Во-вторых железо способно абсорбировать даже и зеленый люминесцирующий свет.

Однако эти два действия недостаточны для объяснения всего понижения светимости. Присутствие железа может препятствовать также преобразование ультрафиолетового св.та абсорбированного на марганце.

Авторы вывели формулу, которая хорошо совпадает с зависимостью светимости от содержания марганца и железа при низкой температуре. Приводится один из возможных способов вывода формулы.