

## COMMENTS ON THE RELATION BETWEEN TEMPERATURE RADIATION AND LUMINESCENCE EMISSION

BY L. KOZMA AND J. HEVESI

Institute of Experimental Physics, University of Szeged\*

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The relation between temperature radiation and luminescence emission is investigated. It is shown that the characters of the two spectra are identical only if the active absorption is taken into account in the calculation of the temperature radiation spectrum. It follows from the experimental data that a band corresponding to the luminescence spectrum is always present in the equilibrium radiation spectrum, too.

### 1.

In examining the properties of luminescence emission, one of the first problems was to clarify the connection between luminescence emission and temperature radiation. It is sufficient to refer to Wiedemann's work [1], where luminescence emission was defined as radiation exceeding temperature radiation. This definition, completed by Vavilov [2] is also used in today's literature. The first qualitative connection between luminescence emission and temperature radiation was given in the work of Merritt [3]. These theoretical results, however, could not be checked experimentally due to the relatively low sensitivity of the experimental devices applied. In the late 1950-s the interest in this problem began to rise again. Stepanov [4], Neporent [5] and Ketskeméty [6] as well as their co-workers have shown, based on extensive theoretical work, that there exists a connection between the luminescence emission,  $f_q(\lambda)$ , and the temperature radiation spectra,  $W_q^T(\lambda)$ , which can be expressed in analytical form. The validity of these relations in the range investigated has been proved in our earlier work [7]. It was also shown there that by using the analytical relations new information about the mechanism of the processes in the luminescent centra can be obtained. At the XVIII Luminescence Conference in the Soviet Union, the necessity of casting more exact light on the nature of luminescence emission was raised by Levshin [8] again.

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\* Address: University of Szeged, Szeged, Hungary.

The aim of the present paper is to point out that, on the base of the relations given by Stepanov, Neporent and Ketskeméty, it is possible to establish that the properties both kinds of radiation have in common. According to the analytical relation mentioned above, a rigorous proportionality exists between the spectra of luminescence emission,  $f_q(\lambda)$ , and temperature radiation,  $W_q^T(\lambda)$ . Ketskeméty and co-workers [6] showed by more detailed calculations that in determining the connection between the two spectra the dependence of the luminescence quantum yield on exciting wavelength has to be taken into account. This also means, that in calculating the function  $W_q^T(\lambda)$  from Planck's or Wien's relation, instead

TABLE I

No	Substances and concentration (mole/l)	Solvent and added materials	$\lambda_g$ (nm)	$T^*$ (°K)
1	Eosine $5 \times 10^{-5}$	$C_2H_5OH$ , $5 \times 10^{-3} M/l$ NaOH	505	350
2	Rhodamin B $1 \times 10^{-4}$	60% glycerol, $H_2O$ , 3% NaOH	547	333
3	Rhodamin 6G $1 \times 10^{-4}$	$C_2H_5OH$ , 6% $CH_3COOH$	490	302
4	Chlorophyll a $1 \times 10^{-6}$	EPA	430 <sup>a</sup> 435 <sup>b</sup>	295 <sup>a</sup> 161 <sup>b</sup>
5	Al-morin $1 \times 10^{-3}$	$C_2H_5OH$ , 2% $CH_3COOH$	420	329
6	Fluoresceine $5 \times 10^{-5}$	$H_2O$ , 3% NaOH,	475	316
7	Fluoresceine $1 \times 10^{-4}$	60% glycerol, $H_2O$ , 3% NaOH, 1.995 KBr	436	305
8	Rose Bengale $5 \times 10^{-5}$	$C_2H_5OH$ , $5 \times 10^{-3} M/l$ NaOH	540	395
9	Chlorin $e_6$ $1 \times 10^{-6}$	EPA	390 <sup>a</sup> 410 <sup>b</sup>	328 <sup>a</sup> 186 <sup>b</sup>
10	Methylene blue $7.1 \times 10^{-6}$	$H_2O$ , $3.5 \times 10^{-3} M/l$ NaLS	560	378
11	Erythrosine $5 \times 10^{-5}$	$C_2H_5OH$ , $5 \times 10^{-3} M/l$ NaOH	510	403
12	Pheophytin a $1 \times 10^{-6}$	EPA	405 <sup>b</sup>	177 <sup>b</sup>

<sup>a</sup>  $T = 298^\circ K$ , <sup>b</sup>  $T = 77^\circ K$

of the absorption spectrum  $k(\lambda)$ , the active absorption spectrum  $\eta(\lambda) \cdot k(\lambda)$  has to be used. (Here the function  $\eta(\lambda)$  gives the dependence of the luminescence quantum yield on the exciting wavelength.) It is, however, possible, in most cases to get very useful information concerning the common properties of both kinds of radiation by using the less complex Stepanov's relation.

## 3.

In the following, some of the data of our earlier experiments as well as part of our numerous recent results are presented. The experimental luminescence emission spectra plotted in the figures were determined by the methods described in [9]. The composition of the systems examined, the exciting wavelength, and the local temperature of the excited molecules calculated from Stepanov's relation are listed in Table I. The functions  $W_q^T(\lambda)$

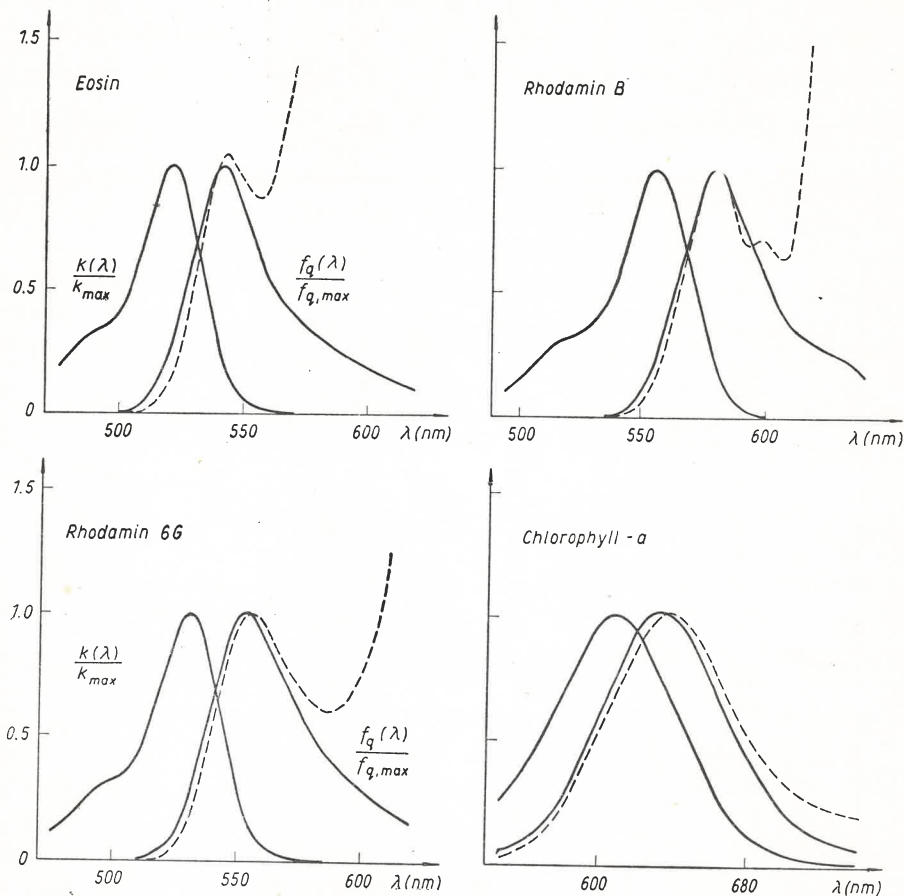


Fig. 1. Absorption and luminescence spectra (—), and temperature radiation (---) of Eosine, Rhodamin B, Rhodamin 6G and Chlorophyll a

were calculated from Wien's relation using the macroscopical temperature of the systems examined. The spectra were normalized to the maximum of the luminescence emission spectra.

Fig. 1 shows the spectra  $k(\lambda)$  of absorption,  $f_q(\lambda)$  of luminescence emission and  $W_q^T(\lambda)$  of temperature radiation for four of the systems examined. It can be seen from the figure that the character of the functions  $f_q(\lambda)$  and  $W_q^T(\lambda)$  is the same for the major part of the

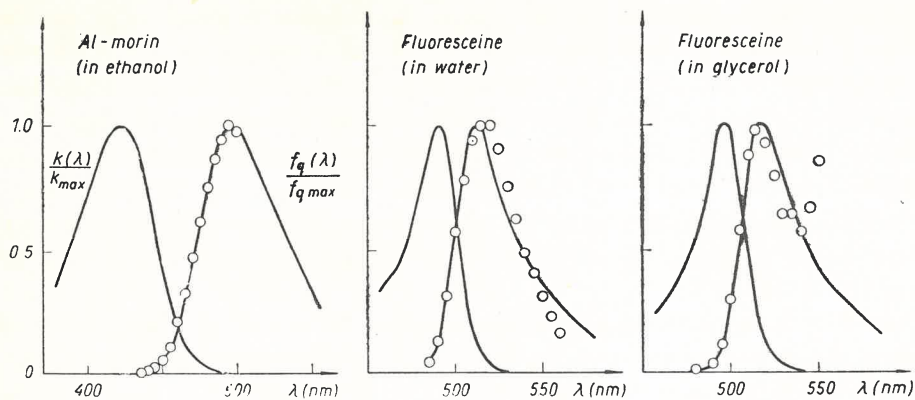


Fig. 2. Absorption and luminescence spectra (—) and temperature radiation (○○○) of Al-morin and of Fluoresceine in different solvents

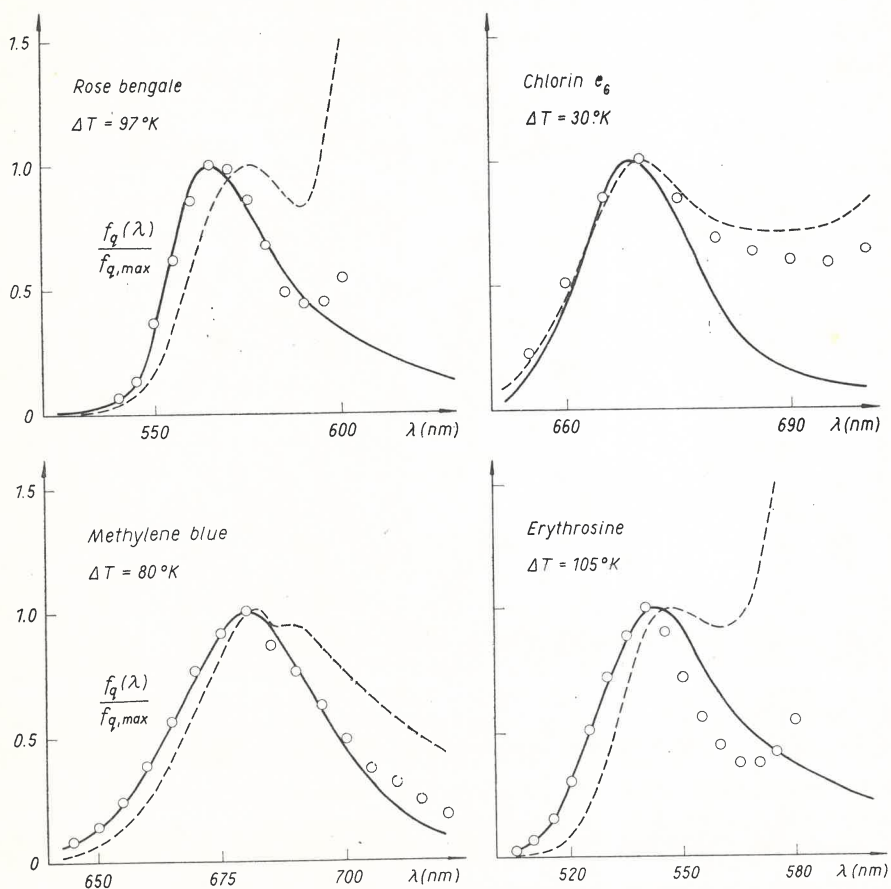


Fig. 3. Absorption and luminescence spectra (—), and temperature radiation  $W_q^T(\lambda)$  (---) and  $W_q^{T*}(\lambda)$ , (○○○) of Rose Bengale, Chlorin e<sub>6</sub>, Methylene Blue and Erythrosine

total range of the luminescence emission spectra. The identity in character of both spectra cases to continue only at the longer wavelengths, where the temperature radiation spectrum shows a very fast increase. It can be also seen from the figure that, in most cases, the sites of the maxima of the functions  $W_q^T(\lambda)$  are shifted towards longer wavelengths.

In Fig. 2 the spectra of such systems are shown, for which the active absorption spectra had to be taken into account in calculating  $W_q^T(\lambda)$ , in order to obtain good coincidence between  $f_q(\lambda)$  and  $W_q^T(\lambda)$ . The figure also shows the coincidence of the maximum sites of the temperature radiation spectra calculated in the above manner, and those of the luminescence emission spectra.

According to the results of our measurements mentioned above [6]–[7], [9] by using the experimentally determined spectra, a local temperature ( $T^*$ ) belonging to the luminescent centrum can be determined. The value of this local temperature is, in most cases, higher than the macroscopical temperature ( $T$ ) of the system. In Fig. 3 some results are plotted as examples for which the difference  $\Delta T$  between the calculated effective (local) temperature and the macroscopical temperature of the system is comparatively high. It can be seen from Fig. 3 that in these cases the sites of the maxima of the functions  $f_q(\lambda)$  and  $W_q^T(\lambda)$  do not coincide. However, if instead of the macroscopical temperature ( $T$ ) of the system,

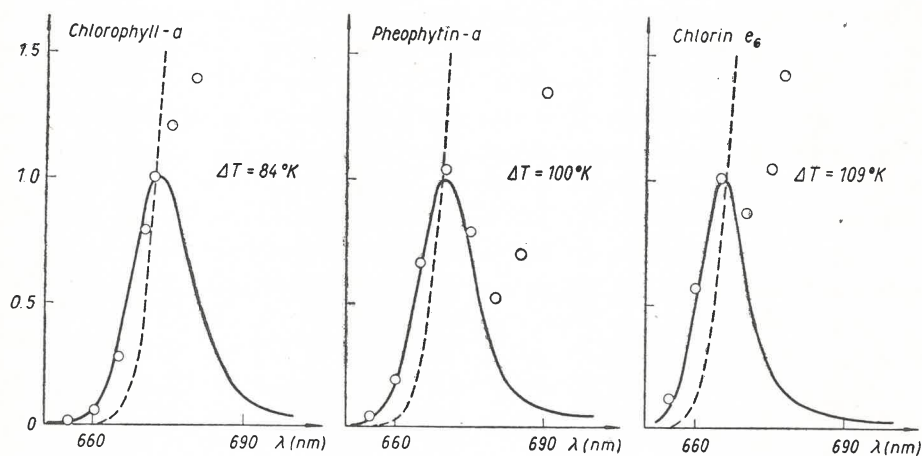


Fig. 4. Luminescence spectra (—), temperature radiation  $W_q^T(\lambda)$  (---) and  $W_q^{T^*}(\lambda)$ , (○○○) of Chlorophyll a, Pheophytin a and Chlorin  $e_6$  at 77°K

the higher local temperature ( $T^*$ ) in the Wien-relation is used in the calculations, then the calculated curve  $W_q^{T^*}(\lambda)$  is shifted towards longer wavelengths, and in this manner the course of luminescence emission and that of temperature radiation coincides. The validity of this result is well illustrated by the spectra plotted in the figure.

Fig. 4 shows the functions  $f_q(\lambda)$ ,  $W_q^T(\lambda)$  and  $W_q^{T^*}(\lambda)$  for chlorophyll a and two of its derivatives, measured and calculated, respectively, for 77°K. These results clearly show that with decreasing temperature of the system the difference in temperature  $\Delta T = T^* - T$  increases, and therefore the above shift of the spectra becomes more significant. This also

means that, at low temperatures, the character of  $W_q^{T^*}(\lambda)$  becomes identical to that of the curve  $f_q(\lambda)$ , rather than to that of  $W_q^T(\lambda)$ . This conclusion is also well supported by the spectra plotted in the figure.

## 4.

On the base of the results mentioned above it can be concluded that the spectral distribution of the luminescence emission corresponds to the spectral distribution of the local temperature ( $T^*$ ) belonging to the excited states of the molecules taking part in the luminescence emission, rather than to that of the temperature radiation corresponding to the macroscopical temperature ( $T$ ) of the system. This result supports the conclusions drawn from the measurements mentioned above [7], [9], according to which the effective temperature of the excited molecules is higher than the macroscopical temperature of the system.

On the base of the above considerations the following conclusions concerning the definition of the luminescence given by Wiedemann and Vavilov can be drawn: the equilibrium temperature radiation process belonging to the local temperature ( $T^*$ ) and the nonequilibrium luminescence emission at the same temperature are of the same character. Disruptions of the thermodynamical equilibrium condition of the system which do not change the optical properties of the molecules, *e. g.* optical excitation, enhance the population of the upper energy level as compared to the equilibrium state, therefore an excess in the emission transition appears. This excess radiation, defined as luminescence emission, differs from temperature radiation in its finite lifetime, as well as in its state of polarization resulting from the latter, and in its behavior manifested against quenching of luminescence. The contradiction that the spectral distribution of the luminescence emission is similar to that of temperature radiation of essentially higher temperatures, is only apparent. Our experimental results prove that a band corresponding to the luminescence spectrum is always present in the spectrum of the equilibrium radiation, too, though its intensity is so low that its demonstrations by experimental methods encounters difficulties.

## REFERENCES

- [1] E., Wiedemann, *Wied. Ann.*, **34**, 446 (1888).
- [2] S. I., Vavilov, *Izv. Akad. Nauk SSSR*, **9**, 277 (1945).
- [3] E. Merritt, *Phys. Rev.*, **23**, 684 (1926).
- [4] B. I. Stepanov, *Dokl. Akad. Nauk SSSR*, **112**, 839 (1957); *Izv. Akad. Nauk SSSR*, **22**, 1367 (1958).
- [5] B. S. Neporent, *Izv. Akad. Nauk SSSR*, **22**, 1372 (1958); *Dokl. Akad. Nauk SSSR*, **119**, 682 (1958).
- [6] I. Ketskeméty, J. Dombi, R. Horvai, *Acta Phys. Hungar.*, **12**, 263 (1960); **14**, 165 (1962); *Ann. Phys.*, **3**, 342 (1961).
- [7] J. Hevesi, L. Kozma, *Optika i Spektrosk.*, (in press).
- [8] V. L. Levshin, *Izv. Akad. Nauk SSSR*, **34**, 476 (1970).
- [9] J. Hevesi, L. Kozma, *Acta Phys. Hungar.*, **20**, 351 (1966); *Acta Phys. Chem. Szeged*, **3**, 103 (1962).