THERMODYNAMIC LIMIT OF THE LUMINESCENCE EFFICIENCY

Yu. P. Chukova
All-union Illumination-engineering Research Institute
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L. D. Landau has shown [1] that an efficiency in excess of unity is thermodynamically permissible in the case of luminescence, but he considered this excess to be negligible and its observation unlikely. We derive here a formula for the maximum luminescence efficiency with allowance for the characteristics of the exciting radiation and the luminescence light, and estimate its absolute magnitude. We use the following symbols: W_{ex} - exciting-radiation power absorbed per unit surface of the luminescent body, W_ℓ - luminescence-radiation power emitted by a unit surface of the luminescent body, Q - heat-flux power delivered to the body by heat conduction, S_{ex} - entropy of the exciting radiation, S_ℓ - entropy of luminescent radiation, T - ambient temperature.

For a system consisting of an ambient, a luminescent body in thermal equilibrium with the ambient, the exciting radiation, and the luminescent light, we have in the stationary state:

$$\dot{W}_{ex} + \dot{Q} - \dot{W}_\ell = 0, \tag{1}$$

$$\frac{dS_{ex}}{dt} + \frac{\dot{Q}}{T} - \frac{dS_\ell}{dt} \geqslant 0, \tag{2}$$

with Eq. (2) satisfied only for reversible processes; the entropy increment due to the irreversible processes is positive in any macroscopic section of the system. These relations have been written out under the assumption that the energy and entropy contained in the absorbed and reflected parts of the radiation of the surrounding space, incident on the luminescent body, can be neglected, i.e., they are valid when the luminescence intensity is many times the absolute black-body intensity at room temperature. From (1) and (2) we obtain for the maximum luminescence efficiency

$$\eta < 1 + \frac{T}{\dot{W}_{ex}}(\dot{S}_\ell - \dot{S}_{ex}) = \frac{T^\ell_{eff}}{T^\ell_{eff} - T}\left(1 - \frac{T}{T^{ex}_{eff}}\right). \tag{3}$$

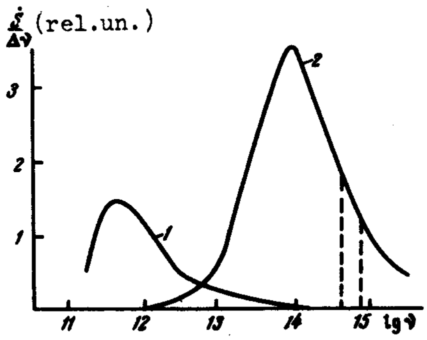
Here

$$\eta = \frac{\dot{W}_\ell}{\dot{W}_{ex}}, \quad T^\ell_{eff} = \frac{\dot{W}_\ell}{\dot{S}_\ell} \text{ and } T^{ex}_{eff} = \frac{\dot{W}_{ex}}{\dot{S}_{ex}}.$$

Consequently, in all cases when $S_\ell > S_{ex}$, the limiting luminescence efficiency will exceed unity. When $S_{ex} = 0$, formula (3) goes over into the formula derived by Weinstein [2]. The entropy flux of unpolarized radiation through a unit surface per unit time is determined by the well known Bose-statistics formula [3]

$$\dot{S} = \frac{2\pi k}{c^2}\int\left[\left(1 + \frac{c^2E_\nu}{2\pi h\nu^3}\right)\ln\left(1 + \frac{c^2E_\nu}{2\pi h\nu^3}\right) - \frac{c^2E_\nu}{2\pi h\nu^3}\ln\left(\frac{c^2E_\nu}{2\pi h\nu^3}\right)\right]\nu^2 d\nu, \tag{4}$$

where E_ν is the spectral density of the radiation. When E_ν is constant in some narrow frequency band, the function S/W has a maximum at the same frequency as the entropy maximum. The figure shows the spectral density of the entropy flux as a function of the frequency (curves 1 and 2 correspond to $E_\nu = 4.6 \times 10^{-2}$ and 4.6×10^{-5} erg/cm^2, respectively). If E_ν of the exciting light and of the luminescence light are of the same order of magnitude, then at all intensities of interest (up to $E_\nu = 10^{-3}$ erg/cm^2), for excitation in the Stokes region, we have $S - S_{ex} > 0$ and increasing with decreasing exciting-light wavelength, i.e., $\eta > 1$.



Spectral density of entropy flux vs. frequency for two values of the energy-flux spectral density. The dashed lines are the boundaries of the visible spectrum.

This calculation shows that in the case of excitation in the anti-Stokes region, where the searches for above-unity efficiencies have been made so far, such efficiencies can be obtained either at an excitation spectral density exceeding 10^{-3} erg/cm^2, or by excitation of a very narrow spectral line. For example, to obtain η = 130% for photoluminescence of brightness 300 nit in the visible range, the excitation line width must be smaller than 10^{-4} Å. This explains the failure of numerous attempts to observe above-unity luminescence efficiency.

In the case of excitation in the Stokes region, to the contrary, using a feasible line width, the thermodynamic efficiency limit can reach 160%. The most realistic way of obtaining it is presumably the experimentally observed mechanism of photon multiplication [4], or else other mechanisms that ensure a quantum field in excess of unity.

For luminescence excitation in the radio band (electroluminescence), the limiting efficiency exceeds unity almost regardless of the type of exciting field.

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[1] L. D. Landau, J. Phys. USSR, 10, 503 (1946).
[2] M. A. Weinstein, J. Opt. Soc. Am. 50, 597 (1960).
[3] M. Planck, Theory of Thermal Radiation (Russ. transl.) M., 1956.
[4] In: Fotonnoe umnozhenie v kristallakh (Photon Multiplication in Crystals), Tr. IFA, AN ESSR 34, (1966).