The region of thermodynamic admissibility of light efficiencies larger than unity

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The dependence of the thermodynamic limit of the optical efficiency of luminescence on the frequency and spectral density of the exciting and luminescent radiations is analyzed in terms of effective temperatures. It is shown that the limiting efficiency of photoluminescence cannot be larger than the thermodynamic limit on the efficiency of electroluminescence. A graphical characterization of the limiting-efficiency surface is given, and of the region in which the thermodynamic limit on the efficiency of electroluminescence exceeds unity. The way this region and the limiting-efficiency surface are deformed on changing to photoexcitation is investigated, and the effects of all the parameters of the radiation exciting photoluminescence on the value of the limiting efficiency are demonstrated.

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In recent years the problem of optical cooling and of the limiting efficiencies of luminescence has again attracted the attention of both theorists and experimenters. First formulated about fifty years ago and known as the Vavilov-Pringshein controversy,[1-3] it has been examined theoretically on the molecular level[4,5] and by thermodynamic methods. A rigorous examination of the stationary process of transformation of electromagnetic radiation by a luminescent body showed that thermodynamics in principle admits the possibility of the existence of systems with light efficiencies larger than unity.[6-8]

The relation between the light efficiency and the refrigeration coefficient of an ideal luminescent radiator is discussed in a paper by the present writer.[9] A number of systems have been proposed for conducting experiments to observe optical cooling,[10,11] and the opinion has been expressed that it is possible for cooling effects to be very large in absolute value.[12] So far, however, direct experiments have not given the desired result, and only the work of Kushida and Geusic[13] can be regarded as an indirect confirmation of the existence of optical cooling.

This makes us turn again to an examination of the thermodynamic restrictions on the value of the efficiency of an ideal luminescent radiator. The problem of the present paper is to make a general study of the functional dependence of the light efficiency η of an ideal luminescent radiator on the frequency ν and the spectral intensity E_ν of the radiation, in order to determine the boundaries of the region of thermodynamic admissibility of efficiencies larger than unity.

1. GENERAL RELATIONS

In its most general form the derivation of the formulas for the limiting efficiency of luminescence has been given by a number of authors.[8,14,15] For the treatment of our problem it is convenient to use an expression obtained previously[15]:

$$\eta \leqslant 1+\frac{T}{T_{\text{eff}}^{\text{lu}}-T}\frac{T_{\text{eff}}^{\text{ex}}-T_{\text{eff}}^{\text{lu}}}{T_{\text{eff}}^{\text{ex}}}, \tag{1}$$

which fixes the thermodynamic limit on the efficiency η of luminescence in terms of the characteristics of the exciting radiation and of the luminescence light; we shall mark all quantities relating to the excitation with an index "ex," and those relating to the luminescence with "lu." In Eqs. (1) the effective temperature T_{eff} is defined as the ratio of the rate $\dot{W}$ at which the body absorbs (or emits) energy to the rate $\dot{S}$ at which it acquires (or loses) entropy:

$$T_{\text{eff}}=\dot{W}/\dot{S}; \tag{2}$$

The luminescence efficiency η is introduced, as usual, as the ratio

$$\eta=\dot{W}_{\text{lu}}/\dot{W}_{\text{ex}}. \tag{3}$$

Equation (1) was derived by consideration of a closed system including the luminescing body, the absorbed part of the exciting radiation, and the luminescence radiation, and also a surrounding medium at temperature T, with which the luminescing body is in thermal contact. Only one restricting condition, in addition to the assumption of a quasistationary state, was introduced: it was assumed that the intensity of the luminescence is much higher than that of the black-body radiation at temperature T in the same spectral region.

In what follows we shall consider the excitation of luminescence by an electromagnetic field only, excluding luminescence excited by electrons and other particles. Then the luminescence and exciting radiation may be regarded as a photon gas which obeys Bose-Einstein statistics, so that the entropy flux of unpolarized radiation with a uniform angular distribution can be calculated from the formula

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

where

$$\rho=c^2E_\nu/2\pi h\nu^3 \tag{5}$$

is the spectral density function of the radiation E_ν, with which the radiation power is connected by the relation

$$\dot{W}=\pi\int E_\nu d\nu. \tag{6}$$

Using Eqs. (1)–(6), we can find the limiting light efficiency of luminescent radiation with arbitrary spectral characteristics of the exciting radiation and the luminescence. However, because of the complexity of the solution of the general problem our further argument will be confined to the case of quasimonochromatic radiation; that is, we shall assume that the quantity E_ν is nonzero and constant only within a narrow

wavelength interval ($\Delta\nu$). This decidedly simplifies the calculation of the entropy flux. The analysis made earlier[14] of the properties of the entropy of quasimonochromatic radiation showed that $\dot{S}$ at constant E_ν has as a function of frequency a maximum whose position on the ν axis depends on the quantity E_ν.

Owing to the fact that $\dot{S}$ is expressed in terms of transcendental functions, the condition for the maximum of $\dot{S}$ is also rather complicated. By approximate methods it can be found that $\dot{S}$ takes its maximum value for $\rho = 0.191$. This makes it possible to establish the connection between E_ν and ν at the point of maximum value of the entropy. From the fact that $\dot{S} = \dot{S}(\nu)$ is an extremum it follows that the inverse of the effective temperature of quasimonochromatic radiation also has its maximum at the same value of the frequency ν as the entropy. Figure 1 shows the frequency dependence of the inverse of the effective temperature for some fixed values of E_ν, which is measured in erg/cm^2 ($E = 0.24$; 1.9×10^{-3}; 6.9×10^{-4}; 7.1×10^{-5}; 3×10^{-5}; 8×10^{-6}; 1.9×10^{-6}; and 4.7×10^{-7} for curves 1 to 8, inclusive).

Knowledge of the effective temperature makes it possible to determine the thermodynamic limit on the efficiency. However, as can be seen from Eq. (1), to do this it is necessary to know two effective temperatures: that of the exciting radiation and that of the luminescence. The complexity of the solution of the problem in general form is due to the fact that there exists no general quantitative law for the spectral transformation of radiation. Even Stokes' law, which is the past served as an approximate criterion of frequency change, is now known to be subject to many exceptions. The law of the spectral transformation of light is determined by the specific mechanism of luminescence and is very sensitive to the conditions of preparation of the phosphor and to external conditions. Therefore we can find η only by prescribing a definite law of spectral transformation of the radiation. There is only one case in which η can be defined without knowledge of the spectral transformation of the radiation by the phosphor. We consider this case in the next section.

2. THE THERMODYNAMIC LIMIT OF THE EFFICIENCY OF LUMINESCENCE EXCITED BY RADIATION WITH SMALL ENTROPY (ELECTROLUMINESCENCE)

From Eq. (1) it can be seen that if

$$T_{\text{eff}}^{\text{ex}} \gg T_{\text{eff}}^{\text{lu}}, \tag{7}$$

then the second factor can be set equal to unity, and the limiting efficiency of the luminescence will be

$$\eta^* \leqslant 1 + T/(T_{\text{eff}}^{\text{lu}} - T). \tag{8}$$

The effective temperature increases with increasing $\dot{W}$ and with decreasing $\dot{S}$. For $\dot{S} \to 0$ the effective temperature goes to infinity.

A strictly zero entropy value is possible only for exactly monochromatic radiation, which is not found in practice. There are, however, a number of cases in which the entropy can be set equal to zero without appreciable error, for example the excitation of electroluminescence of photodiodes by a constant current. This is the case for which Weinstein[7] made a calculation. His result [Eq. (8)], however, also holds for electroluminescence excited by an alternating current. We have previously[15] made a calculation of the entropy and the effective temperature of an alternating current exciting luminescence of p-n junctions, and showed that although $\dot{S}_{\text{ex}} \neq 0$, and $T_{\text{eff}}^{\text{ex}}$ has a finite value, this value is so large that the second factor in Eq. (1) can be set equal to unity. Then the value of η, which we shall call η^* in this case, will depend only on the effective temperature of the luminescent radiation.

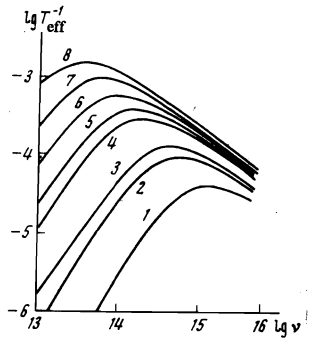

FIG. 1

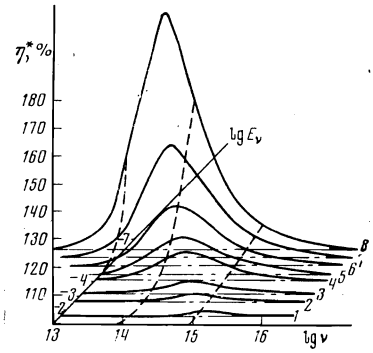

FIG. 2

FIG. 1. Frequency dependence of the inverse of the effective temperature.

FIG. 2. Limiting-efficiency surface of electroluminescence.

Using values of $T_{\text{eff}}^{\text{lu}}$ corresponding to definite frequencies and spectral densities of the luminescent radiation, we can find the values of η, which are shown in the form of a surface in Fig. 2. The frequency (in Hz) is plotted in a logarithmic scale along the x axis, lg E_ν^{lu} is plotted along the y axis (E_ν^{lu} is measured in erg/cm^2), and along the z axis is plotted the efficiency η, measured in percent. In Fig. 2 intersections of the limiting-efficiency surface with planes of constant spectral density E_ν^{lu} are shown as solid curves: $E_\nu^{\text{lu}} = 0.24$ erg/cm^2; 1.9×10^{-3}; 6.9×10^{-4}; 7.1×10^{-5}; 3×10^{-5}; 8×10^{-6}; 1.9×10^{-6}; and 4.7×10^{-7} for curves 1 to 8, inclusive; the dot-dash lines show the intersections of these planes with the log ν, log E_ν^{lu} plane; and dashed lines show the intersections of the surface with planes of constant frequency (10^{13}, 10^{14}, and 10^{15} Hz). It can be seen from Eq. (1) that η can only be smaller than η^*, since effective temperatures are always positive, but even for η^* values above 100% are thermodynamically admissible only in a limited region of frequencies and spectral densities. With increase of the spectral density η^* approaches 100%, and decrease of the spectral density is limited by our assumption that the intensity of the luminescence is much larger than that of the radiation from an ideal black body.

Accordingly, Fig. 2 gives the surface of the thermodynamic limit on the efficiency of electroluminescence. As can be seen from this diagram, for an electroluminescent radiator the region where light efficiencies larger than unity are thermodynamically admissible is very extensive and reminiscent of a mountain ridge, beginning at $\nu \approx 10^{15}$ Hz and $E_\nu^{\text{lu}} = 10^{-2}$ erg/cm^2 and developing in the direction of decreasing E_ν^{lu} with a slow shift to frequency 10^{13} Hz.

A physical model in which the highest efficiencies can be realized is the luminescence of p-n junctions. The positive Peltier effect, which with nonradiative recombination heats the p-n junction, should lead under

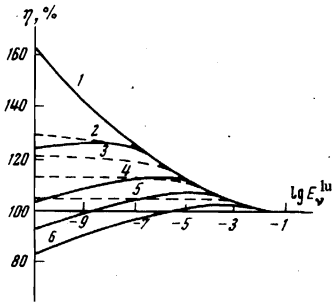

FIG. 3. Thermodynamic limit on the efficiency of luminescence of YAl–d for various conditions of excitation.

conditions of radiative recombination (if all the radiation passes out into the surrounding medium) to cooling of the junction. This makes it possible for a p-n junction in thermal contact with the surrounding medium to take energy from it, which for the act of radiation can be regarded as additional to the energy of the external electric field.

3. PHOTOLUMINESCENCE

An examination of the process of photoluminescence shows that as a rule the entropy of the exciting radiation is of the same order of magnitude as the entropy of the luminescence. Therefore the second factor in Eq. (1) must be taken into account. Since the connection between T_{eff}^{ex} and T_{eff}^{lu} is governed by the actual mechanism of the luminescence, we cannot draw a surface of limiting efficiency of photoluminescence, but we can note some features: 1) taking T_{eff}^{ex} into account can only decrease the values of the limiting efficiency: 2) the more nearly equal the values of T_{eff}^{ex} and T_{eff}^{lu}, the more strongly η will differ from η^*; 3) for $T_{eff}^{ex} = T_{eff}^{lu}$ the limiting efficiency of photoluminescence will be 100%; 4) if the effective temperature of the luminescence is higher than that of the exciting radiation, the thermodynamic limit on the efficiency of photoluminescence is less than unity. These fundamental points can be verified with a number of concrete examples of photoluminescence.

We shall consider two cases of anti-Stokes luminescence, since it provides the possibility of the clearest demonstration of how strong an influence the characteristics of the exciting radiation have on the thermodynamic limit on the efficiency. As before, we confine ourselves to the case of quasimonochromatic radiation. This means that in what follows we have to do only with radiation of a fixed wavelength, which corresponds in the diagram of Fig. 2 to a single definite dashed line.

As the first example let us consider the luminescence of the trivalent neodymium ion in the single-crystal YA1G-Nd. The most intense luminescence is that of the line 946 nm. This is a transition from the $^4F_{3/2}$ level to $^4I_{9/2}$. (We use throughout the Russell-Saunders classification in the notation.) If luminescence with this wavelength is produced with strictly monochromatic exciting radiation, the limiting efficiency of the luminescence will not depend on the wavelength of the exciting radiation, but will be a function of the spectral density function. It is given by Curve 1 in Fig. 3. In practice, however, the radiation with wavelength 946 nm is obtained only by using exciting radiation with a finite band width, although when laser radiation, for example YA1-Nd, is used this width may be very small. Let us assume that the wavelength of the exciting radiation is 1064 nm. This corresponds to transition of electrons to the $^4F_{3/2}$ level not from the ground state, but from the $^4I_{11/2}$ level, to which they can be raised by thermal motion.

The larger the bandwidth of the radiation used, the higher its entropy (at constant spectral density E_ν^{ex}) and the lower the value of the limiting efficiency. The dashed curves 2–5 (Fig. 3) show the limiting efficiency of such luminescence for excitation by a line with its center at 1064 nm and widths 10^7, 10^8, 10^9, and 10^{10} sec^{-1}. In all of these cases of anti-Stokes luminescence (λ_{ex} = 1064 nm, λ_{1u} = 946 nm) the limiting efficiency of the luminescence is higher than 100%. It was on this luminescence that the experiment of Kushida and Geusic[13] was based, in which a latent cooling was established. The reasons that a manifest cooling of the YA1G-Nd crystal was not achieved are analyzed in a paper by the present writer,[16] and are probably connected with the use of an excessive power $\dot{W}$.

The dashed curves in Fig. 3 give an idea of the influence on the limiting efficiency of the spectral density E_ν^{ex} and of $\Delta\nu_{ex}$. Let us see how the limiting efficiency changes if we change the frequency of the exciting radiation. Let us increase the anti-Stokes shift, using as the exciting radiation the wavelength 1337 nm (the transition $^4I_{13/2} - {}^4F_{3/2}$) with bandwidths 10^7, 10^8, 10^9, and 10^{11} sec^{-1}. The limiting efficiency of the luminescence in this case has the values shown in Fig. 3 by the corresponding solid curves 2, 4, 5, 6. The change of wavelength of the exciting radiation has led to a strong lowering of η at small spectral densities of the luminescence. For bandwidths 10^{10} and 10^{11} Hz the limiting efficiency as a function of the spectral density of the luminescence can have values both above and below 100%, dropping almost to 80%. It must be emphasized that such narrow bandwidths (10^{10}–10^7 Hz) can be obtained only with laser radiation. When the bandwidths used are wider, or comparable with the luminescence bandwidth, which in the present case is 2.7×10^{11} Hz, the efficiency is always below 100%.

Up to this point we have chosen for the excitation lines lying in the anti-Stokes region. If the exciting line is in the Stokes region and its width does not exceed that of the luminescence line, the values of the limiting efficiency will be closer to the ideal case of excitation by a monochromatic line, i.e., the region of thermodynamic admissibility of light efficiencies larger than unity is not so much deformed in this case. However, the Stokes region is at present not suitable for conducting experiments, since we cannot find a physical mechanism which with excitation in the Stokes region would secure the removal of heat from the surrounding medium. With anti-Stokes excitation this extra energy is drawn from the vibrational energy of a crystal or molecule. Even when thermodynamics permits an efficiency larger than unity and there exists a mechanism providing the supplying of energy from the surrounding medium, experiments on optical cooling can give negative results. An example of this is the anti-Stokes resonance of ruby. For luminescence of ruby with wavelength 6931.6 Å, excited by radiation of wavelength 6944 Å, there are thermodynamically allowed efficiencies larger than unity at temperatures not far from room temperature. In this case, however, the anti-Stokes shift of the radiation is so small that an appreciable excess of the efficiency over unity is possible only

for a quantum yield larger than unity, which cannot be realized in the actual scheme of the luminescence of the Cr^{3+} ion.

The Nd^{3+} ion in YA1G can have a large anti-Stokes shift, which is enough to give an efficiency larger than unity even with a quantum yield smaller than unity. The physical reason for the absence of any manifest cooling of the luminescent system YA1G-Nd is probably the fact that with laser excitation the rate at which the level $^4I_{11/2}$ gets emptied is larger than the rate at which it gets filled owing to thermodynamic processes. Such effects are often encountered with laser excitation and are known as "bottleneck" effects.

All of the results given here have been obtained by the consideration of quasimonochromatic spectra. Equations (4) and (6) can be used for calculations for any spectral distribution of the intensities of the exciting and luminescent radiations. It should be noted that the error made by using the quasimonochromatic approximation is in most cases small, except for very broad spectra.

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