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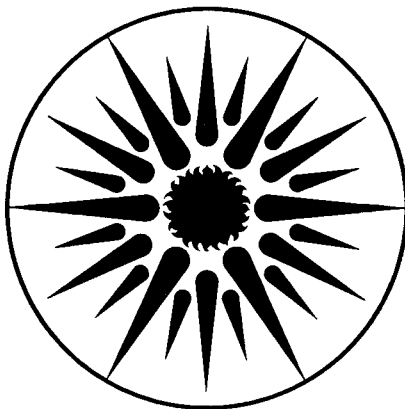
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RADIANT REFRIGERATION BY SEMICONDUCTOR DIODES[*]

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Abstract

Dousmanis *et al.* demonstrated that GaAs light emitting diodes could produce a cooling effect if the quantum efficiency (ratio of photon flux to junction current) is very close to unity (e.g., >0.97). Here, it is pointed out that for narrow-bandgap semiconductors, the quantum efficiency need not be so high to produce cooling. Also, for narrow-bandgap semiconductors there is an additional cooling mode in which the reverse-biased diode cools its radiant environment by absorbing infrared radiation. Maximum cooling rates per unit of junction area are on the order of $n^2 \sigma T^4$, where n is the index of refraction, σ is the Stefan-Boltzmann constant, and T is the temperature. For small cooling rates the efficiency for cooling can approach the limit imposed by the second law of thermodynamics.

I. INTRODUCTION

It has been known for some time that a forward-biased p-n junction can in principle produce a cooling effect.[1-6] The carrier recombination due to minority carrier injection causes a Peltier-effect heating. However, if the recombination mechanism is primarily radiative, the emitted radiant energy can exceed the externally provided electrical energy, thereby cooling the p-n junction. The paper by Dousmanis *et al.*[6] on the emission spectrum of GaAs diodes demonstrated clearly that the average emitted photon energy E was greater than qV, for small bias voltages, and that consequently a net cooling effect would be produced if diodes with sufficiently high quantum efficiency η_q could be made. The estimated minimum

value of η_q required to produce cooling was 0.97 (at 78K with a current density of about 6 A cm^{-2}), because the cooling effect per photon was about 3%.

The general thermodynamics of light emitting processes has been addressed by a number of authors.[7-13] The review article by Landsberg and Tonge[13] contains a summary of this literature. It has been established that the second law of thermodynamics permits luminescent sources, such as p-n junctions, to have technical efficiencies (ratio of output photon energy to input electrical energy) which exceeds unity. A portion of the radiated energy comes from the general thermal environment (the diode's heat sink); the entropy associated with this thermal input energy is radiated away with the luminescence. Since the luminescence must carry entropy, it cannot be arbitrarily intense. For example, laser emission in one or a few photon modes carries very little entropy per photon (the radiation "temperature is high) and, therefore, a technical efficiency which exceeds unity is precluded. On the other hand, less intense diffusely emitting radiation sources emit more entropy per photon and consequently can be more energy efficient. Weinstein[8] gives an efficiency limit of 160% for room temperature visible light sources of "practical" brightness.

In much of the prior work, the cooling effect is a by-product of a hyper-efficient luminescence process. For this paper, however, I wish to focus attention on the refrigeration, or heat pump effect, itself. The thermodynamic figure of merit is the coefficient of performance (COP), defined as the ratio of cooling effect produced to external (electrical) work required. This difference in emphasis leads to consideration of a technique for cooling using reverse-biased diodes as well as forward-biased diodes, and to consideration of semiconductors with narrow energy gaps, comparable to kT.

The term "photodiode" will be used in what follows in a generalized way to represent both a reverse-biased semiconductor diode which absorbs photons accompanied by electron-hole pair production (the usual definition), and also, to

represent a forward-biased light emitting diode. In the most general sense, such a diode is a device which produces excess electrons and/or holes (compared to thermal equilibrium) when current flows through it in the forward direction, and which produces a deficit of electrons and/or holes when current flows through it in the reverse direction. The excess (or deficit) of charge carriers can produce luminescence (or "negative luminescence"). The term "negative luminescence" refers to a reduction in the luminescence compared to that produced under conditions of thermal equilibrium. The same excess (or deficit) of change carriers is responsible for the lower (higher) resistance of the diode for current flow in the forward (reverse) direction. For concreteness one can consider the device to be a p-n junction.[14] It is a type of radiant heat engine.

An ordinary radiant heat engine may be defined as a Carnot heat engine in which one heat sink is an ordinary radiating surface obeying Kirchhoff's law and the other heat sink is at temperature T. Work can be performed by such a radiant heat engine if the incident radiant energy received by the radiating surface differs from blackbody radiation of temperature T. Either a hot source (e.g., solar energy conversion) or a cold source can be used to perform work. A radiant heat engine can also absorb work and produce radiant fluxes larger or smaller than that of a black body at the temperature T. In these modes, the device is a radiative heat pump. It is the heat pump modes of an infrared photodiode which are treated in this paper. Kirchhoff's law is, however, not directly applicable to the photodiode because internal thermal equilibrium is disturbed by the applied electrical bias. Nevertheless, in the next section it is shown that the idealized narrow-band photodiode is equivalent to a Carnot engine coupled to a radiative heat exchanger. Subsequently, the simplifying narrow-band assumption is relaxed and the available cooling capacity is computed as a function of semiconductor energy gap, coefficient of performance, and reservoir temperatures.

II. AN IDEALIZED NARROW-BAND PHOTODIODE

To employ the simplest non-trivial model of an idealized photodiode, we assume that the diode can only absorb (and emit) photons with energies in the narrow range $\left[E, E + \Delta E\right]$, $\Delta E \ll E$. Each absorbed photon produces an electron-hole pair; each emitted photon is the result of electron-hole recombination. The electrons and holes remain in kinetic thermal equilibrium with the semiconductor lattice at temperature T. *It is not assumed that kT is small compared to E.* The only bulk mechanisms for changing the *numbers* of electrons and holes are radiative recombination and radiative generation. For this reason the numbers of electrons and holes need not be equal to their absolute equilibrium values. The carrier concentrations may be disturbed from their equilibrium values by application of an applied electrical bias. Assuming that all of the externally applied voltage V will appear across the diode junction, the effective or quasi Fermi levels for electrons and holes (on both sides of the junction) are displaced from one another by the energy qV. Thus qV is the external electrical energy which must be supplied to produce an electron-hole pair. If it is further assumed that the only bulk mechanisms for the production and destruction of photons are the electron-hole processes already mentioned, then the photon number is otherwise conserved. Consequently, the non-equilibrium but steady-state occupation numbers of the photon modes are given by Bose-Einstein statistics as

$$N(E) = \left\{ \exp\left[\beta(E - qV)\right] - 1 \right\}^{-1} \tag{1}$$

where $\beta = (kT)^{-1}$. That is, the energy qV plays the role of a chemical potential for the photons.

The net radiative heat transfer to the diode (per unit area and time), Q, is now easily obtained from Eq. (1) for the physical configuration shown in Fig. 1. For simplicity, it is assumed that the index of refraction of the diode is unity (no reflection at the vacuum/diode interface), and that the external emitter/absorber has an emissivity of unity for photon energies near E. Accounting for the density of states

of the photons and performing the trivial angular integrations one has

$$Q = -\left(\frac{2\pi}{h^3 c^2}\right) E^3 \Delta E \left\{ \frac{1}{e^{\beta(E-qV)}-1} - \frac{1}{e^{\beta_e E}-1} \right\} \tag{2}$$

where $\beta_e = (kT_e)^{-1}$. the first term represents the voltage-dependent emission from the diode and the second term, the absorption by the diode. The emission term has been previously given by Würfel,[15] as a consequence of his proposed generalized Kirchhoff's law.

The current density, j, for the diode can now be computed from the fact that the quantum efficiency of the diode must be unity: for a net transfer of one photon into the diode, one electron-hole pair is produced, and, in a stationary state, one charge must circulate in the external circuit. Thus one has

$$j = -q \ Q/E \tag{3}$$

This current/voltage relation is essentially identical to that given by DeVos and Pauwels,[16] for photovoltaic conversion, obtained from a microscopic derivation.

Several differences with conventional equations for photodiodes deserve comment. It is often assumed that a diode is in equilibrium when j=V=0 and in the absence of "external" radiation. This idea is certainly correct when the photon energy is much larger than typical thermal energies, $\beta E \gg 1$, but for our case, thermal equilibrium requires that the external and internal temperatures be equal, $\beta_e = \beta$. In the absence of external radiation, the photodiode is not in thermal equilibrium; it can do work on its external electrical circuit. A related fact is that the reverse saturation current (limit of Eqs(2,3) for V → −∞) depends not on the diode's temperature, but on the external temperature, and is not small unless $\beta_e E \gg 1$. Note that the limit qV → E is the laser threshold.

Equations (2) and (3) contain enough information to permit the analysis of the photodiode as a radiant heat engine. The net radiant heat transfer per unit area to

the diode is Q; electrical work per unit area (on the diode) is jV; and the sum appears in the heat sink:

$$Q_{sink} = jV + Q \qquad (4)$$

If jV < 0, the diode performs work on its external circuit. For example, if T_e > T, heat from the radiant source can be converted to electricity. Photovoltaic conversion of sunlight is an example of this process. If T_e < T, heat from the diode's heat sink can be radiated away, accompanied by the production of electricity. If jV > 0, the diode functions as a type of heat pump.

For j > 0, E > qV > 0, the diode is a net emitter of electromagnetic radiation, i.e., it is a "light" emitting diode. Each emitted photon carries energy E but requires an electrical input energy of only qV, thus cooling the heat sink. Finally, consider the case j < 0, qV < 0, for which the diode is a net absorber of external radiation, passing both the heat Q and the work jV on to the heat sink. This heat pump mode seems not to have been discussed previously, perhaps because the reverse saturation current of diodes (and the corresponding magnitude of Q) is exponentially small when the photon energy E is large compared to kT. Thus, in what follows, the case E/kT ~ 1 is of special interest.

Before examining the capacity of radiative heat pumps in more detail, it is of interest to note the correspondence of the idealized narrow-band photodiode model with a Carnot engine coupled to a radiative heat exchanger. The heat exchange rate Q is just that which would take place in the energy interval ΔE between two blackbody radiators, one at temperature T_e and the other at an "apparent radiant temperature"

$$T^* = T(1-qV/E)^{-1}. \qquad (5)$$

A heat engine with heat input rate Q at temperature T^* and heat output rate Q_{sink} at temperature T has a rate of entropy increase

$$dS/dT = Q/T^* - Q_{sink}/T, \qquad (6)$$

which Eqns (3) and (4) show is equal to zero. Thus, the idealized narrow-band photo-

diode is equivalent to a radiative heat exchanger at temperature T^* coupled to a Carnot heat engine. Entropy increase is associated only with the exchange of radiation with the external radiant environment, not with the internal operation of the diode. If T^* approaches T_e, the entropy increase associated with the radiant transfer becomes small, and the radiant heat engine becomes thermodynamically reversible.

III. MAXIMUM AVAILABLE COOLING RATES

To permit the calculation of the cooling effect available from reverse and forward biased photodiodes, it is necessary to remove the restriction that all the photon energies are within ΔE of E. Consider an optically thick semiconductor with bandgap E_g. All incident photons with $E > E_g$ are absorbed. The generalization of Eq.(2) is straightforward. Introducing dimensionless variables $x = \beta E$, $x_g = \beta E_g$, $v = \beta q V$, and $\tau = T/T_e$, one obtains for the net radiant energy flow per unit area:

$$Q = - \frac{15}{\pi^4} \sigma\, T^4 \int_{x_g}^{x_m} dx\ x^3 \left\{ \frac{1}{e^{x-v} - 1} - \frac{1}{e^{\tau x} - 1} \right\} \tag{7}$$

where $\sigma = 2\pi^5 k^4 / 15\, h^3 c^2$ and $x_m = v/(1-\tau)$, a cut-off to be explained shortly. The corresponding equation for the product of the current density and applied voltage is:

$$jV = \frac{15}{\pi^4} \sigma\, T^4 v \int_{x_g}^{x_m} dx\ x^2 \left\{ \frac{1}{e^{x-v} - 1} - \frac{1}{e^{\tau x} - 1} \right\} \tag{8}$$

The significance of Eqs.(7)and(8) will be illustrated with specific examples.

Consider cooling in the reverse bias mode ($v < 0$), referring to Fig. 1. The external emitter/absorber is to be cooled. Its temperature T_e is less than T ($\tau > 1$), and it is desired to pump the heat "uphill" in the direction of positive Q. For small reverse bias, $x_m < x_g$, and heat flow, if permitted, occurs in the wrong direction.

Above the threshold $-v > (\tau-1)x_g$, the radiant heat flow occurs in the correct direction in the photon energy interval $x_g \leq x \leq x_m$. For $x > x_m$, the heat flow is counterproductive. Thus, it is desired to prevent the radiant flow of photons with dimensionless energies $x > x_m$. A suitable filter on the surface of the diode or suitable selectively emitting coating on the external emitter/absorber could be used to provide the cut-off x_m. For values of $-v$ just above the threshold the radiative transfer occurs in a small photon energy range between x_g and x_m, and we recover the narrow-band photodiode model with its Carnot performance.

The available cooling rate Q clearly depends upon the bias voltage; if $-v >> x_g$ emission from the diode is insignificant and the cooling rate is determined by the rate at which the external emitter can radiate ($\sigma\, T_e^4$ for $x_g = 0$). In principle, cyrogenic temperatures can be produced. However, the cooling Q and the coefficient of performance, Q/jV, both become small at low temperatures. For the special case $\tau = 1.1$, the available cooling obtained numerically from Eqs.(7)and(8) is shown in Fig. 2 as a function of $x_g = E_g/kT$ for several coefficients of performance. For this case the Carnot COP is $(\tau-1)^{-1}=10$. The bias voltage is determined from the specified COP. For T=300K, T_e=273K, and a COP of 1.25, the highest cooling rates occur for energy gaps of 0-2kT (0 to 52 meV) and are roughly 250 Wm^{-2}. Better thermodynamic performance ($COP = 5$) requires the use of larger energy gaps (2-4kT) and permits smaller maximum cooling rates ($\sim 45\ Wm^{-2}$).

The available cooling effect for the forward bias mode is shown in Fig. 3. In this mode the diode is cooled as it radiates energy to the external emitter/absorber. The same Eqs.(7)and(8) apply but now $\tau = T/T_e = (1.1)^{-1} < 1$ and $v > 0$. The corresponding Carnot COP is $(\tau^{-1}-1)^{-1}=10$. The cooling effect is, due to heat extracted from the sink,

$$-Q_{sink} = -(Q+jV) \tag{9}$$

For T_e=300, T=273, and a COP of 1.25, Fig. 3. shows that the best energy gaps are in

the range of 3-5 kT (78 to 130 meV) yielding a maximum cooling rate of over 650 Wm^{-2}. A COP of 5 also requires energy gaps in the range of 3-5 kT, with the maximum cooling being about 65 Wm^{-2}.

IV. DISCUSSION

The available cooling rates determined by Eqs. (7) and (8) represent absolute maximum values for an idealized photodiode composed of a semiconductor with a single energy gap, in radiative contact with a passive emitter/absorber across a macroscopic vacuum gap. However, larger cooling rates are available if the dimension d in Fig. 1 is comparable with the typical thermal photon wavelength hc/kT. Consider the effect of the finite index of refraction n > 1. The density of states for photons internal to the semiconductor is increased by a factor of n^3 and the velocity of the photons, neglecting dispersion, is proportional to n^{-1}, so that internal radiative energy fluxes are increased by the factor n^2. This fact does not in itself permit the attainment of higher radiative transfer rates and hence higher cooling rates, because the phenomenon of total internal reflection limits the external radiative transfer; the upper limits for cooling remain unchanged. However, if the dimension d is small (less than several microns at 300K), and if the emissive coating on the external emitter/absorber has an infrared index matched to that of the semiconducting diode, then the "tunneling" of radiation across the gap defeats total internal reflection and leads to higher energy transfer rates. If $d \ll hc/kT$, the energy transfer and corresponding maximum available cooling rates are increased by the factor n^2.

It may appear that, if high thermodynamic efficiency is not required, very high cooling rates can be obtained in the forward biased mode by using "wide" bandgap semiconductors ($E_g/kT \gg 1$) with bias voltages near the laser threshold $qV = E_g$. However, these large cooling rates are the difference between very large numbers, the emitted photon energy flux and the input electrical energy. Even weak parasitic mechanisms can eliminate the cooling effect. For example, suppose that the

quantum efficiency η_q, the ratio of the net numbers of photons emitted from the diode to number of charges passing through the junction, is less than unity, due to non-radiative recombination and generation of charge carriers. An approximate solution can be obtained by simply assuming that the required current (Eq.(8)), to support a given radiative flux, is increased by a factor of η_q^{-1}. For $\eta_q = \frac{1}{2}$, the results are shown in Figure 4. Now there is a maximum cooling rate of about 0.62 $\sigma\, T^4$ occurring at $E_g = 3.6\,kT$ and $qV = 1.8\,kT$, and the available cooling for $E_g/kT \gg 1$ is exponentially small.

The effect of parasitic loss mechanisms on the reverse bias cooling mode is much less dramatic than for the forward bias cooling mode. Excess entropy production causes the release of heat in the diode which can be passed to the heat sink without subtracting directly from the cooling effect. Thus, the cooling rates shown in Fig. 2 are still achievable, but the coefficients of performance will be smaller by the factor η_q.

Returning now to the paper by Dousmanis et al. [6] on forward biased GaAs diodes, we observe that the cooling effect Δ (per emitted photon) can be inferred from the difference between the emitted photon energy and the corresponding bias voltage. Typically Δ was about 3% of the photon energy, which leads to their estimate of the required 97% quantum efficiency to produce net cooling. Their fit to their data has the form

$$\Delta = kT \ln\left(\frac{j_0}{\eta_q\, j}\right),$$

(10)

where j_0/η_q is a parameter. Thus Δ decreases slowly as the current density j increases and is (roughly) proportional to temperature. The fit for 78K yields

$$j_0/\eta_q = 5.6 \times 10^4\, A\ cm^{-2},$$

(11)

with the experimental uncertainty of 20 meV in Δ leading to a factor of 20 uncertainty in j_0/η_q. A value of j_0 derived from Eqs. (7,8) can thus be used to produce an order-of-magnitude estimate of η_q.

To obtain Eq. (10) from Eqs. (7) and (8) we compute

$$\Delta = -q \ Q/j - qV$$

for $x_g \gg 1$, $x_g - v \gg 1$, $\tau = 1$ and obtain

$$\Delta = kT \ (x_g - v + 1).$$ (12)

Also one has

$$j = \frac{15}{\pi^4} \sigma \ T^4 \left(\frac{q}{kT}\right) x_g^2 \ e^{v - x_g}$$ (13)

It is necessary to adjust Eq. (13) to account for the fact that the quantum efficiency is not unity. This adjustment increases j by a factor of η_q^{-1}, but does not change (12). Also, for a real semiconductor with a refractive index n greater than one, j must be increased by the factor n^2 as discussed above. Performing these adjustments and eliminating $v - x_g$ between Eqs. (11) and (12), we recover Eq. (10), with the parameter j_o having the value

$$j_o = \frac{15e}{\pi^4} n^2 \sigma \ T^4 \left(\frac{q}{kT}\right) x_g^2 \ .$$ (14)

For GaAs at 78K (E_g = 1.52 eV, n = 3.55), the value of j_o is 8,430 A cm^{-2}. The measured value (11) of j_o/η_q thus yields the reasonable value 0.15 for the quantum efficiency. Due to the experimental inaccuracies and the highly simplified form of the theory (which ignores all details of the GaAs bandstructure) no quantitative conclusions can be drawn. However, it has been shown that the present theoretical results are consistent with the observations of Dousmanis *et al.*

The development of thermodynamically efficient cooling devices requires the use of materials in which excess carrier concentrations relax toward equilibrium primarily by emitting photons and in which deficit carrier concentrations relax toward equilibrium primarily by the absorption of photons. The various non-radiative recombination mechanisms include Auger recombination, Shockley-Read recombination, and recombination with phonon emission. The inverse processes lead to non-radiative carrier generation. The Auger process is particularly important, in which the recombination energy appears in the form of an energetic elec-

tron or hole. It tends to be most important in narrow-bandgap semiconductors at high temperatures, which is the parameter range of primary interest here, and it is an intrinsic mechanism. For any given material, there will be a temperature, which one might call the Auger temperature, at which Auger and radiative recombination proceed at equal rates. Since the 3-body Auger recombination rate should increase more rapidly with temperature than the 2-body radiative recombination rate (due to thermal excitation of electrons and holes), a given material can produce cooling efficiently only below its Auger temperature.

V. SUMMARY AND CONCLUSIONS

Semiconductor diodes have the potential to provide radiant refrigeration. An applied electrical bias produces an excess or deficit of electrons and holes, which in turn produces an excess or deficit of infrared radiation compared to the radiation present in thermal equilibrium. A device operating in this way is a solid state radiative heat pump.

The maximum available cooling rates per unit of junction area are on the order of $n^2 \sigma\, T^4$. The thermodynamic efficiency can approach the Carnot value in an ideal material. In particular the limitations of Peltier effect coolers, due to heat conduction in the thermal elements, are circumvented. However, various loss mechanisms are present, and therefore a net cooling effect may be first observed using a reverse-biased diode to cool a nearly object by absorption of its thermal radiation, rather than by a forward-biased diode.
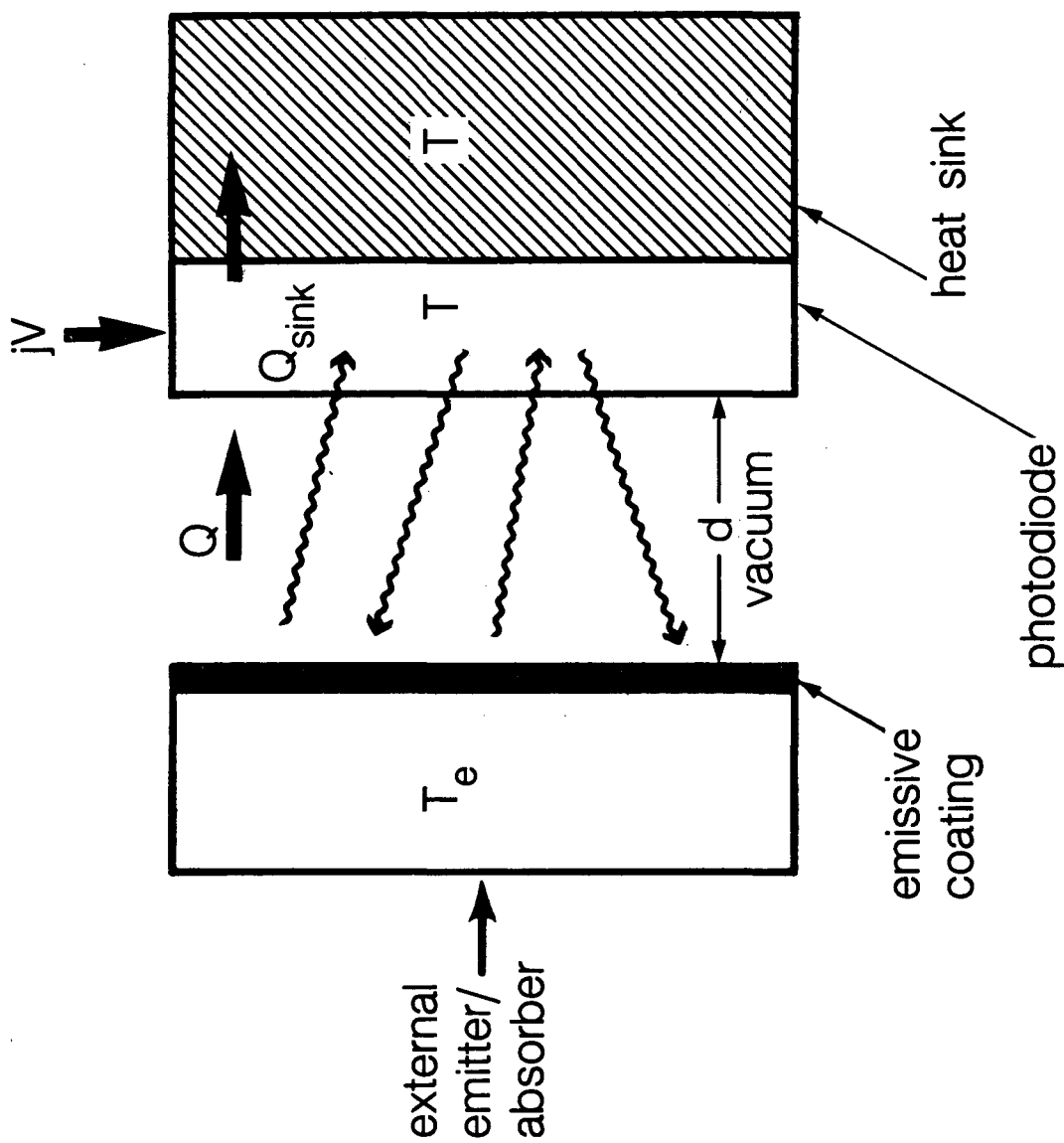
VI. ACKNOWLEDGEMENTS

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14. Other physical configurations can lead to thermodynamically similar devices. One example of interest is a thin semiconducting layer in a parallel magnetic field, whose two surfaces are treated to have very different recombination rates. If electrical current is passed through such a layer, transverse to the magnetic field, the resistance is low in one direction and high for the other polarity. Positive luminescence due to carrier recombination is seen for forward bias and negative luminescence for reverse bias. See, for example, S.S. Bolgov, V. K. Malyutenko, and V. I. Pipa, *Sov. Phys. Semicond. 17*, 134-137 (1983); T. Morimoto and M. Chiba, *Phys. Lett. 85A*, 395-398 (1981); F. R. Kessler and J. W. Mangelsdorf, *Phys. Stat. Sol. B 105*, 525-535 (1981).

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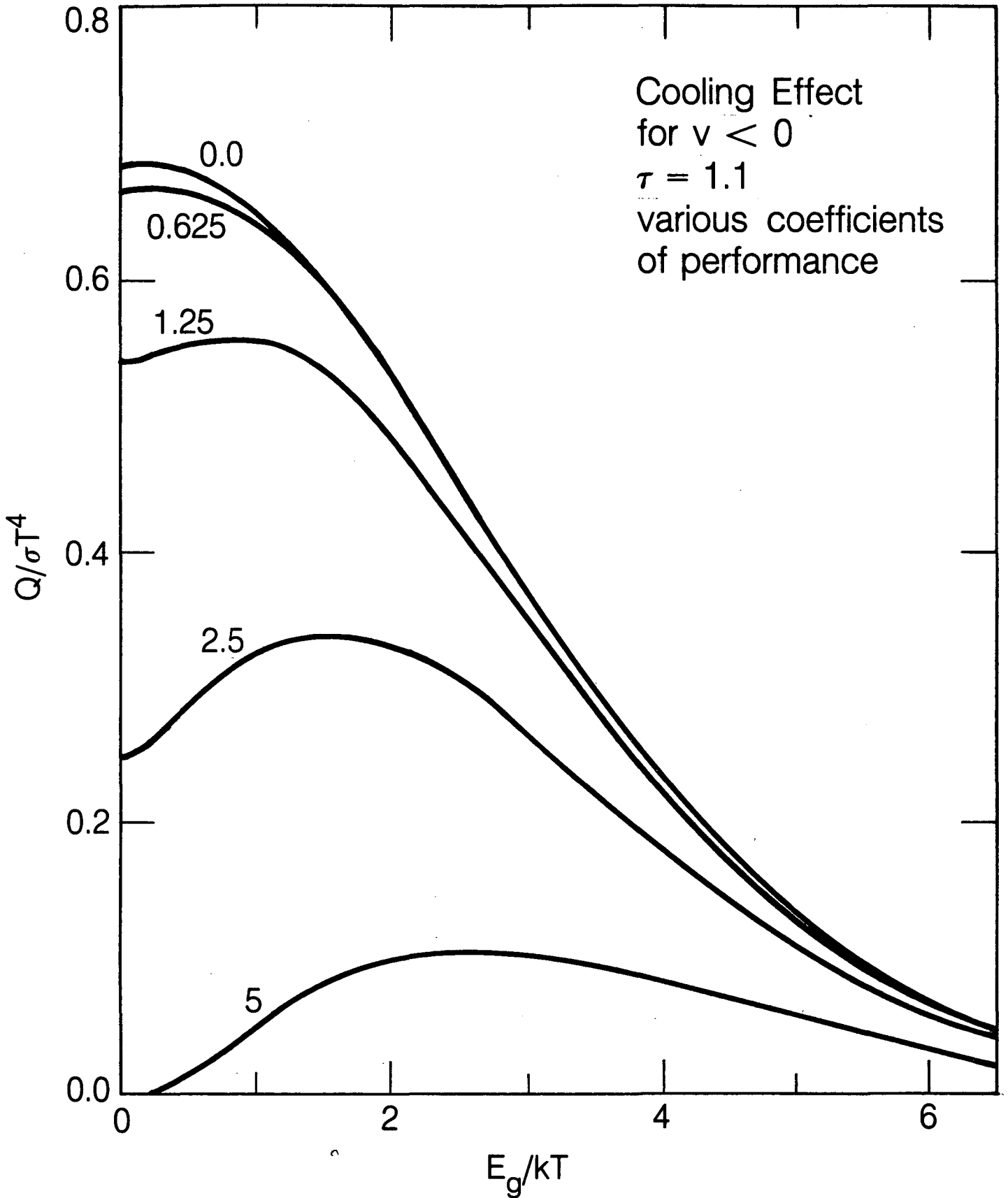16. De Vos, A. and H. Pauwels, *Appl. Phys.* *25*, 119-125 (1981).

FIGURE CAPTIONS

1. Physical configuration of the photodiode, which exchanges radiation with an external emitter/absorber. The signs of Q, Q_{sink}, and jV are defined as positive for the directions shown.

2. The cooling effect for a reverse-biased photodiode. The coefficients of performance are Q/jV.

3. The cooling effect for a forward-biased photodiode. The coefficients of performance are $-Q_{sink}/jV$.

4. Cooling effect as in Fig. 3, but with the quantum efficiency η_q reduced from 1 to 0.5.

Fig. 1

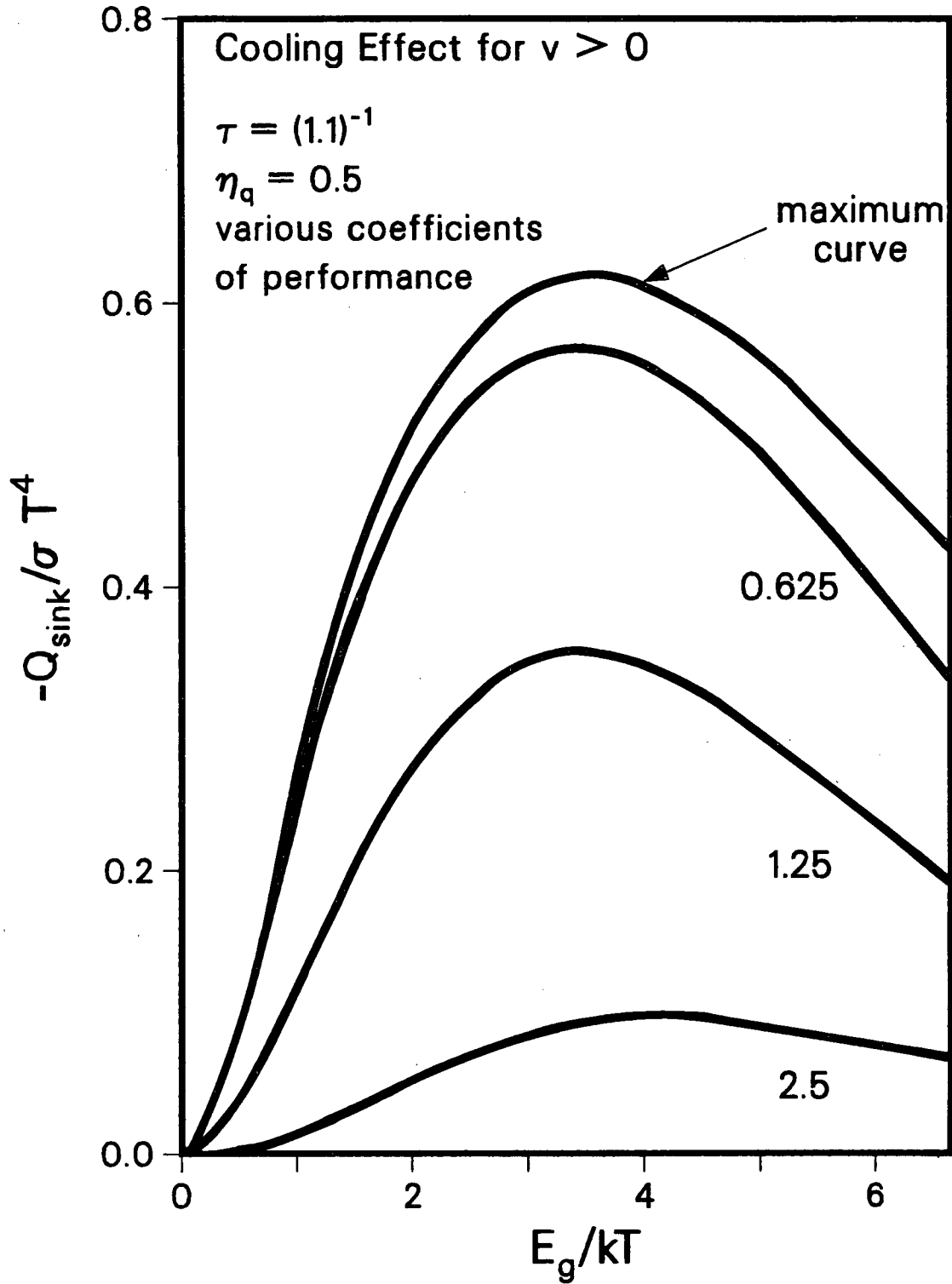XBL 849-8715

Fig. 2

XBL 849-8717

Fig. 3

XBL 849-8716

Cooling Effect for $v > 0$

$\tau = (1.1)^{-1}$
$\eta_q = 0.5$
various coefficients
of performance

maximum
curve

0.625

1.25

2.5

E_g/kT

$-Q_{sink}/\sigma T^4$

XCG 8410-13331

Fig. 4