Evidence of Refrigerating Action by Means of Photon Emission in Semiconductor Diodes

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More than 90% of the photons emitted from forward-biased GaAs diodes have energies $h\nu$ higher than the applied voltage V. Thus, a portion of the energy of these photons must come from lattice heat. This portion is 3% of $h\nu$ for photons at the peak of the incoherent emission spectrum. An upper limit of $(h\nu-qV)$ is estimated from thermodynamics. This difference is larger at 78 than 27°K, in agreement with theory. Also, the dependence of the effect on voltage and current is in fair agreement with expectations. At high forward currents, near the threshold for stimulated emission, $h\nu$ is about equal to qV. The removal of heat, in the form of photon energy from the crystal, should in principle lead to refrigeration. The main requirement for net cooling is a quantum efficiency (photons/electron) higher than 0.97. At 10 mA, with an assumed quantum efficiency of 0.99, the heat removal rate (per diode) is estimated as 3×10^{-4} W compared to a Joule heating rate of 5×10^{-5} W.

In recent studies of recombination radiation in GaAs diodes[1] it was observed that the photon energy of the incoherent emission peak was larger than the applied voltage. The difference $\Delta(=h\nu-qV)$ decreases with increasing current so that at high currents, near lasing threshold, $h\nu$ is about equal to qV. Earlier work by Keyes and Quist[2] has shown that the high-energy tail of the GaAs emission line contained photons with $h\nu>qV$. It was proposed that part of the energy of these photons came from lattice heat, so that the process may be considered as a basis for refrigerating action. The number of these high-energy photons, however, was very small.

That the energy of the main peak itself is larger than qV implies a more substantial removal of energy from the lattice than one would expect from the earlier evidence on photons from the high-energy tail. A limit is estimated for Δ in terms of lattice temperature, quantum efficiency and photon density (or photon temperature). The predictions of this computation are compared with the data and an estimate is given for the heat removal rate.

More than 90% of the photons emitted by the GaAs diodes have energies higher than the applied voltage (Fig. 1). Also, a photon with the energy of the emission peak draws from the lattice 3% of $h\nu$, an appreciable amount. The thermodynamics of processes of this type have been discussed.[2–6] Let Q be the heat removed from the lattice per recombining electron, and V the battery voltage. From the first law, and in view of energy losses, one concludes that $h\nu\leq qV+Q$. The quantity Q can be estimated from the second law; the entropy change associated with the absorption of heat Q by the electron is $-Q/T$. The entropy increase due to the production of a photon is $h\nu/T^*$, where T^* is the photon temperature. Thus $Q\leq T(h\nu)/T^*$, and

$$\Delta=h\nu-qV\leq kT(h\nu/kT^*). \quad (1)$$

The photon temperature T^* can be related to the number of photons N in an electromagnetic mode by the relation

$$N=[\exp(h\nu/kT^*)-1]^{-1}. \quad (2)$$

So that

$$\Delta\leq kT\ln(1+1/N)\sim kT\ln(1/N), \quad (2a)$$

since $N\ll1$ below lasing threshold. At low injection, $T^*\sim T$, and Δ can be large, but near lasing threshold, Δ goes to zero. Δ represents the heat removed from the lattice per photon, and it goes to zero as T goes to zero or as T^* becomes large. The process removes heat from a reservoir at temperature T to another one at higher temperature T^*.

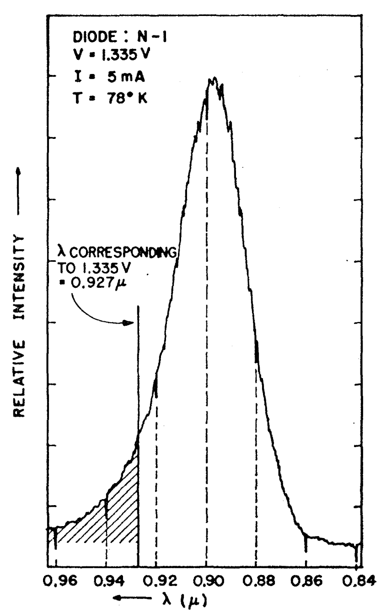

FIG. 1. An emission line from a GaAs diode, forward biased, showing only a small shaded region (low-energy tail) where the photon energy is smaller than the applied voltage.

[1] G. C. Dousmanis, C. W. Mueller, and H. Nelson, Appl. Phys. Letters **3**, 133 (1963).
[2] R. T. Keyes and T. M. Quist, Proc. I.R.E. **50**, 1822 (1962).
[3] F. E. Williams, Bull. Am. Phys. Soc. **5**, 70 (1960).
[4] M. A. Weinstein, J. Opt. Soc. Am. **50**, 597 (1960).
[5] A. Rose, J. Appl. Phys. **31**, 1640 (1960).
[6] D. F. Nelson, M. Gershenzon, A. Ashkin, L. A. D'Asaro, and J. C. Sarace, Appl. Phys. Letters **2**, 483 (1963).

We need to relate $\triangle$ to our other measured quantities, current I and applied voltage V. N is proportional to the intensity of the emission which in our GaAs diodes is approximately proportional to I. Thus,

$$N=\text{const}\times\text{intensity}=\alpha\eta I\,, \tag{3}$$

where α is a constant, and η the quantum efficiency or yield (photons/electron). From (2a) and (3),

$$\triangle\leq kT\ln(1/\alpha\eta I)\,. \tag{4}$$

Thus, $\triangle$ should decrease slowly with current in agreement with the data, as will be seen below. The rate of

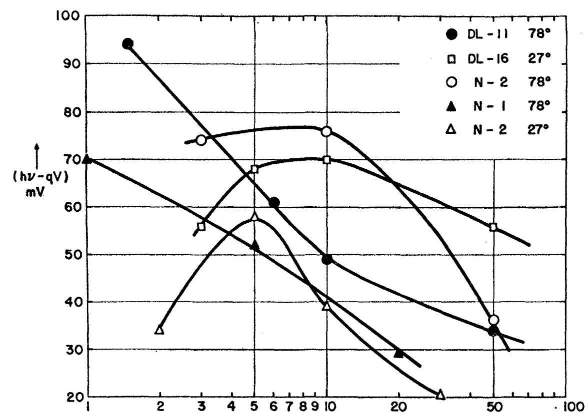

FIG. 2. $\triangle=(h\nu-qV)$ versus current in GaAs electroluminescent diodes at 27 and 78°K. $h\nu$ is the energy of the peak of the incoherent emission spectrum. Diodes N-1 and N-2 are of Type II, the others of Type I (see text). The area of all diodes is about 10^{-3}cm^2.

change of $\triangle$, qualitatively, can be obtained by using the equality sign in (4):

$$\partial\triangle/\partial I=-kT/I-(kT/\eta)(\partial\eta/\partial I)\,. \tag{5}$$

The term in $\partial\eta/\partial I$ can be important if η varies with I. The proportionality of intensity to current, in our current range, suggests that $\partial\eta/\partial I\sim 0$, and this term can be neglected.

In GaAs diodes there is a shift of the incoherent emission peak to shorter wavelength with increasing current, for currents below lasing threshold.[1,7,8] The energy of the peak is related to I by the relation:

$$I=I_0\exp(h\nu/E_0)\,, \tag{6}$$

where E_0 is a constant independent of temperature, which is larger in heavier doped samples. From (4) and (6) we obtain

$$qV\geq h\nu+kT(h\nu/E_0)+kT\ln(\alpha\eta I_0)\,. \tag{7}$$

[7] J. I. Pankove, Phys. Rev. Letters **9**, 283 (1963); R. Braunstein, H. Nelson and J. I. Pankove, Appl. Phys. Letters **3**, 31 (1963).

[8] R. J. Archer, R. C. C. Leite, A. Yariv, S. P. S. Porto, and J. M. Whelan, Phys. Rev. Letters **10**, 483 (1963).

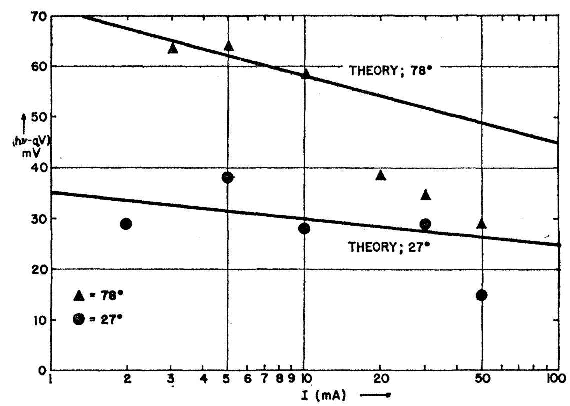

FIG. 3. $(h\nu-qV)$ versus current averaged over several diodes at 27 and 78°K. The two straight lines are theoretical curves.

Thus V is a linear function of $h\nu$, and

$$[\partial(qV)/\partial(h\nu)]_\eta\sim 1+kT/E_0\,. \tag{8}$$

The heavier doped samples (large E_0) should have the smaller variation of V with $h\nu$, as well as smaller values of $\triangle$.

The energy of the incoherent emission peak has been measured as a function of current and voltage across the diode. Figure 2 shows $\triangle$ as a function of I. Figure 2 includes data with $I\leq 50$ mA to minimize errors due to the IR drop for which no correction has been made. Because of the small magnitude of $\triangle$, the data points are considerably scattered. Two types of diodes have been examined. Type I are diffused, and Type II are solution grown and diffused. Their preparation has been described elsewhere.[1] All diodes of Type I show $\triangle$ positive ($h\nu>qV$). Each of these diodes has a surface Zn concentration of 5×10^{19}/cm^3 and a donor concentration in the 10^{17} to 3×10^{18}/cm^3 range. Type II diodes have a bulk Zn concentration of 10^{19} to 3×10^{19}, and the donor concentration is somewhat

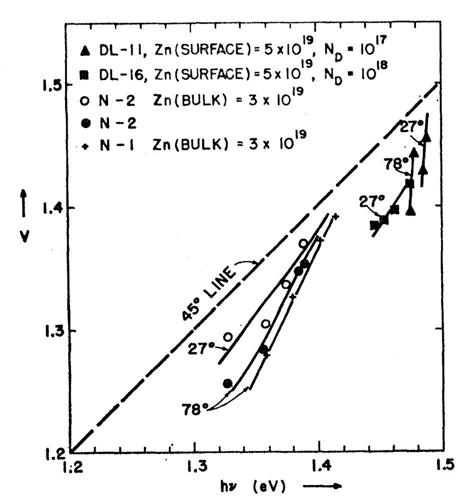

FIG. 4. The applied voltage versus $h\nu$ in different diodes at 27 and 78°K.

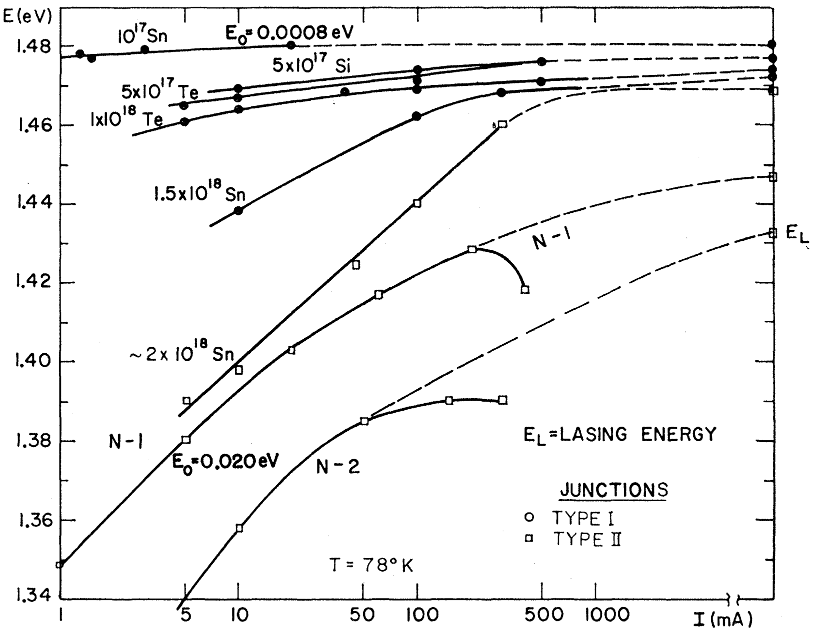

FIG. 5. Energy of incoherent emission peak versus current in GaAs diodes. (Data of Ref. 1). Diodes whose $h\nu$ versus I slopes are large in this figure, are those with small slopes of qV versus $h\nu$ in Fig. 4.

larger than in Type I. Some of these diodes show also a positive Δ, but for others $\Delta<0$. We do not know why this latter group shows a different behavior than the other diodes. We will not discuss them here any further, but note that the IR drop in these diodes may be larger, and this might obscure the effect observed in the others. One has to have nearly ideal diodes to correct properly for this drop.

The value of Δ at each value of the current averaged over many diodes (including those of Fig. 2) are shown in Fig. 3. This figure also shows two theoretical lines from (4) (using the equality sign). The factors multiplying I are adjusted so that the theoretical lines agree with the data within experimental errors in the 1–10 mA current range. The deviations of the experimental points at higher currents are in the direction one expects from the increasing IR drop. Both the magnitude of the effect, i.e., Δ and $\partial\Delta/\partial I$, are smaller at 27°K than 78°K as expected from (4) and (5).

The accuracy of Δ is about ± 20 mV, without corrections for the IR drop. This is at most 25 mV (at 50 mA) and would increase Δ, bringing the experimental points closer to the theoretical ones at high current values.

Figure 4 shows V versus $h\nu$. The slopes of the curves differ from one diode to the next as expected from Eq. (8). This is due to the different values of E_0. This constant measures the energy shift of the emission peak with current. For comparison, Figure 5 shows these current-induced shifts as measured earlier[1] for many diodes, including some whose V versus $h\nu$ curves are shown in Fig. 4. Equation (8) suggests that diodes with large slopes in Fig. 2 should have small slopes in Fig. 5, in agreement with the data.

We make some further comments on Fig. 1. The emission peak has a wavelength of 8970 Å while the applied voltage corresponds to 9270 Å. About 94% of the photons have energies higher than qV.

With $\Delta\sim 60$ mV at 78°K, one computes from (2) $T^*\leq 2000$°K. At 27°K, with $\Delta\sim 30$ mV, one obtains $T^*\leq 1300$°K. One notes that the upper limit for the photon temperature is much larger in both cases than lattice temperature, although the current is one to two orders of magnitude below lasing threshold.

Some small and unexplained differences between $h\nu$ and qV were reported by Archer *et al.*[8] The process discussed here would account, qualitatively, for the fact that $h\nu$ is larger in their work by about 14 mV than qV at 78°K. Their result that $h\nu < qV$ at lower temperatures is still unaccounted for.

Taking the magnitude of Δ as 60 mV at 78°K one sees that $\Delta/h\nu$ is about 0.03, so 3% of the photon energy comes from the lattice. If the quantum yield is small, *net* cooling of the lattice is not obtained. The fraction of electrons that do not emit a photon yield a large amount of energy ($qV\sim h\nu$) to the lattice. The quantum yield in fact has to be about 0.97 for net cooling to occur. The rate of energy extraction from the lattice for $\Delta/h\nu=0.03$, with a quantum yield, for example, of 0.99, is 0.02 $h\nu\, I/q$. The I^2R loss is equal to this, with $R\sim 0.5\ \Omega$, at $I=30$ mA. Thus, below 30 mA, the cooling effect overcomes heating. At 10 mA, the cooling rate is 3×10^{-4} W, whereas I^2R is 5×10^{-5} W. This, of course, assumes a 0.99 quantum efficiency. Diodes with high quantum yield are required for direct experimental observation of the cooling effect.

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