Title

STATE OF THE ART OF NEGATIVE LUMINESCENCE

Authors

Berdahl, P.
Malyutenko, V.
Morimoto, T.

Publication Date

1988-04-01

LBL-25244 c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

Presented at the Fourth International Conference on
Infrared Physics, Zurich, Switzerland,
August 22–26, 1988

State of the Art of Negative Luminescence

P. Berdahl, V. Malyutenko, and T. Morimoto

April 1988

APPLIED SCIENCE DIVISION

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

P. Berdahl,[(a)*] V. Malyutenko,[(b)] and T. Morimoto[(c)]

STATE OF THE ART OF NEGATIVE LUMINESCENCE

(a) Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, USA
(b) Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR, Kiev, USSR
(c) Institute of Atomic Energy, Kyoto University, Uji, Kyoto, Japan

Introduction

Negative Luminescence (NL) is the emission of less radiation than a body emits in thermal equilibrium. A body in complete thermal equilibrium at temperature T must be immersed in blackbody radiation at the same temperature T to be in true thermal equilibrium. If thermal equilibrium is perturbed by some exciting mechanism, then the body may emit either more radiation (positive luminescence, PL) or less radiation (NL) than it does under conditions of thermal equilibrium. If the "environmental" temperature T is equal to zero (that is, the thermal energy kT is small compared to other energies of interest), then there is only positive luminescence and the idea of negative luminescence is irrelevant. However, in the presence of an environment at temperature T, both PL and NL should be measured relative to equilibrium thermal emission at temperature T. After all, it is the *deviation* from the equilibrium radiation flow which represents information presented to an infrared detector and also represents the radiant flow of free energy which is available to perform work in accordance with the second law of thermodynamics.

One example of NL is radiative cooling. The cloudless atmosphere emits less than a full quota of blackbody radiation corresponding to the earth's surface temperature (it is transparent and emits only weakly in the 8-13 μm atmospheric window). Consequently, terrestrial objects exposed to the night sky tend to cool below air temperature due to IR radiative exchange with the atmosphere and space. Count Rumford ascribed this cooling process to "frigorific rays" arriving from space [1]. Another system which can exhibit NL is a system of gas molecules with non-equilibrium populations of excited states, induced, for example, by absorption of laser light [2,3,4]. However, we

* This author was supported by the Assistant Secretary for Conservation and Renewable Energy of the U.S. DOE under contract No. DE-AC03-76SF00098.

are interested here primarily in the negative luminescence phenomenon in semiconductors.

In semiconductors, when the equilibrium carrier concentrations are reduced, either by carrier extraction at reversed-biased diode junctions, or by the magnetoconcentration effect, the normal equilibrium process of light emission due to carrier recombination is suppressed. Therefore, semiconductors exhibit negative luminescence. It is most readily observed when the energy gap, E_g, of the semiconductor is not too large compared to kT; this condition assures that there is some overlap between the blackbody spectrum and the characteristic band-to-band emission spectrum of the semiconductor.

The use of the magnetoconcentration effect to produce luminescence, often termed galvanomagnetic luminescence (GML), is attractive for experimental studies because it is possible to investigate a uniform material with a single free surface. In contrast, reverse-biased diodes are more complex structures. The GML technique uses orthogonal electric and magnetic fields which are each parallel to the emitting surface of the semiconductor. If the Lorentz force is directed toward the free surface, then electrons and holes "pile up" near the surface, causing positive luminescence due to increased radiative recombination. If the polarity of the Lorentz force is reversed, the flux of carriers away from the surface (into the interior of the crystal) causes negative luminescence, due to the absence of carriers which normally combine under equilibrium conditions. For the linear regime in which carrier concentrations are only slightly disturbed from equilibrium conditions, negative luminescence is merely positive luminescence but with opposite sign. For example, it is proportional to applied current density with the same proportionality constant as positive luminescence. When, however, the carrier concentrations differ greatly from equilibrium conditions, various non-linearities become important. For example, radiative recombination is a quadratic function of carrier concentration and Auger recombination is a cubic function of carrier concentration. A most important non-linearity, and an essential qualitative aspect of negative luminescence is that it cannot exceed the magnitude of equilibrium emission, since the *absolute* radiant emission cannot be reduced below zero.

Galvanomagnetic luminescence (GML) measurements and their interpretation

The first published data were obtained for Ge by Bernard and Loudette in 1958 [5,6]. However, the details of the luminescence were obscured by poor signal to noise ratio. In the mid-1960's Ivanov-Omskii, Kolomiets, and Smirnov made pioneering GML measurements on p-type InSb [7,8]. They used 0.1 T to 2 T magnetic fields and microsecond electric field pulses of roughly 10 V/cm and above. These observations showed that Lorentz forces pushing carriers into the crystal produced negative pulses as seen by the detector and showed that for these high current densities (above about 10^3 A/cm^2), the positive luminescence was more intense than the negative luminescence. Also, measured spectra showed clearly that band-to-band recombination was the primary operative mechanism. Finally, they observed that both positive and negative luminescence showed maxima as a function of B. In p-type samples this behavior may be expected due to the fact that the product of B and the minority carrier mobility exceeds unity, which inhibits electron transport. For intrinsic (pure) samples, no corresponding maximum occurs. For a detailed explanation, see Ref. 9.

In 1974 Kessler and Mangelsdorf [10] presented GML measurements on Ge. They observed that the resulting light emission was much more readily observed at elevated temperatures, gaining more than a factor of 1000 by going from 300 to 400 K. This behavior is to be expected, since the overlap between the blackbody and characteristic semiconductor spectra is proportional to $\exp(-E_g/kT)$. In subsequent work [11] these authors extended their measurements to even higher temperatures (450 K) and to fields of 10 T and 20 V/cm. The spectrum of the emission is complex, due to the large carrier diffusion lengths (millimeters as contrasted with micrometers for InSb) and the more complex optical absorption features seen in indirect-bandgap semiconductors.

In 1979 and in 1983, Bolgov, Malyutenko, and Pipa [12,13] extended the measurements of Ivanov-Omskii *et al.*, emphasizing the "negative luminescence" aspects and determining the maximum value of the NL from plots of NL vs. electric field. Results [14] for $Cd_{0.28}Hg_{0.72}Te$ are shown in Fig. 1, which is quite similar to the plots observed for InSb. There is a region of linear PL and NL near E = 0. However, for sufficiently large electric and magnetic fields, the NL saturates when its magnitude is equal to P_o, the equilibrium thermal emission within the appropriate wavelength range. P_o can be computed as the blackbody flux for which the photon energy exceeds E_g, reduced by the reflectance of the semiconductor surface [14]. Fig. 2 shows the comparison of computed values of P_o with measured values inferred from the NL saturation. The good agreement shown confirms the present interpretation and forms the basis by which calibrated radiation sources may eventually be made, utilizing the NL saturation. The high frequency modulation of such sources is limited by carrier lifetimes which are generally much less than a microsecond, so that MHz IR modulation is feasible.

The details of the approach to NL saturation seen in Fig. 1 depend on details of carrier recombination and generation (imprecisely known non-linear functions of concentration), and cannot be computed readily. However, the luminescence in the linear regime for P/P_o near unity can be computed readily and has been discussed in detail by Berdahl [9]. In particular, the spectrum of the radiation agrees with calculations [9,15]. Figure 3, from measurements by Morimoto and Chiba [16], shows the spectrum for intrinsic InSb near room temperature. While the saturation value of NL depends only

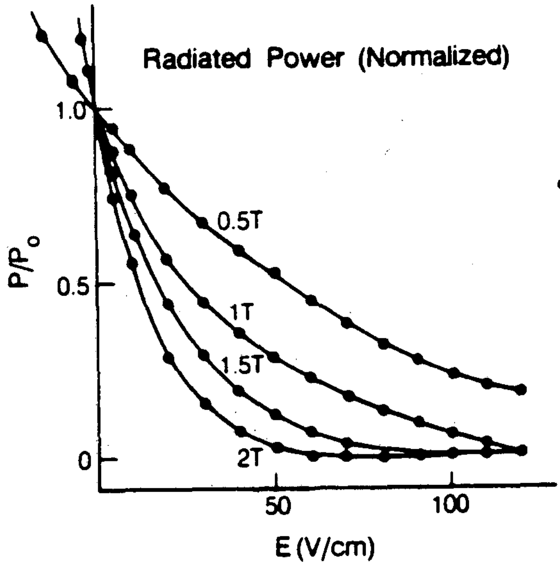

Fig. 1. Positive ($P/P_o > 1$) and negative ($P/P_o < 1$) luminescence for a crystal of $Cd_{0.28}Hg_{0.72}Te$ at 300 K, after [14]. P is the absolute radiated power per unit area, and P_o is the value of P for E = 0.

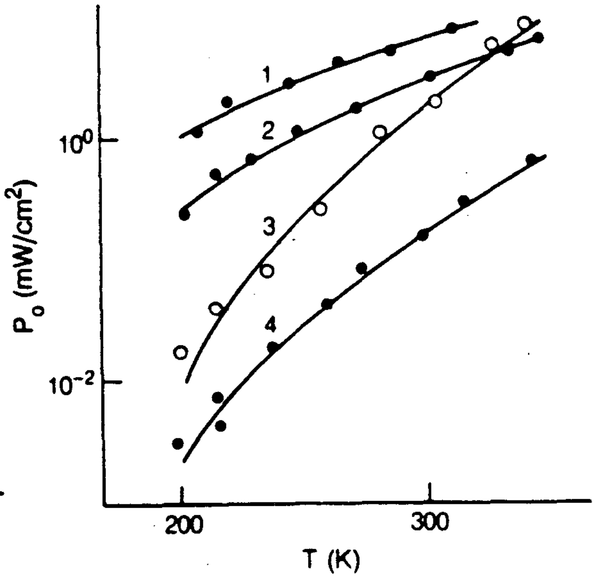

Fig. 2. The temperature dependence of P_o, after [14]. Curves 1,2, and 4 are for $Cd_xHg_{1-x}Te$ with x = 0.18, 0.20, and 0.28, respectively, and curve 3 is for InSb. The lowest curve corresponds to the largest bandgap energy and vice versa. The points are measured values; the curves are calculated.

on the energy gap of the semiconductor, the luminescence in the linear regime is quite sensitive to the quantum efficiency for radiative recombination, as well as carrier mobilities and concentrations. Thus it has been possible to employ measurements of the absolute spectral intensity in the linear regime to determine quantum efficiencies for radiative recombination in intrinsic and p-type InSb. Figure 4 shows data for intrinsic InSb obtained in this way [9]. As a check on the reliability of this novel approach, we note that carrier lifetimes determined from these quantum efficiencies agree well with more conventional measurements[9].

Galvanomagnetic Radiative Cooling Effect

Negative luminescence can in principle be used to produce radiative cooling effects. Recently, such a cooling effect has been demonstrated explicitly with calorimetric measurements [17]. A thin (15 micrometer) layer of InSb in thermal contact with a heat sink was used to produce NL by passing current through it in the presence of a magnetic field. A thin blackened foil, suspended in vacuum with a thermocouple attached, was placed just above

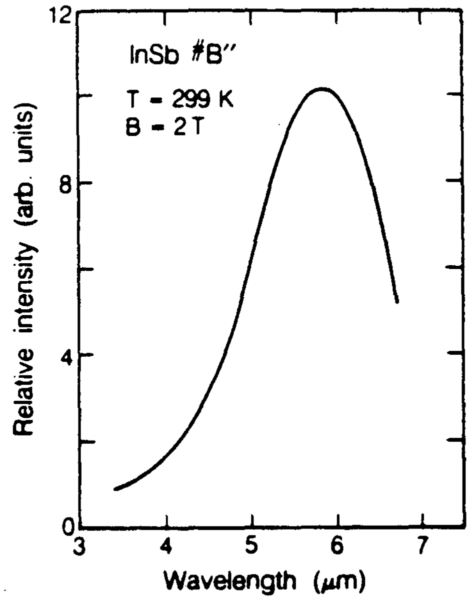

Fig. 3. NL spectrum in the linear regime [16]. The electrical current is 0.1 A in a sample 0.2 mm thick and 3.5 mm wide.

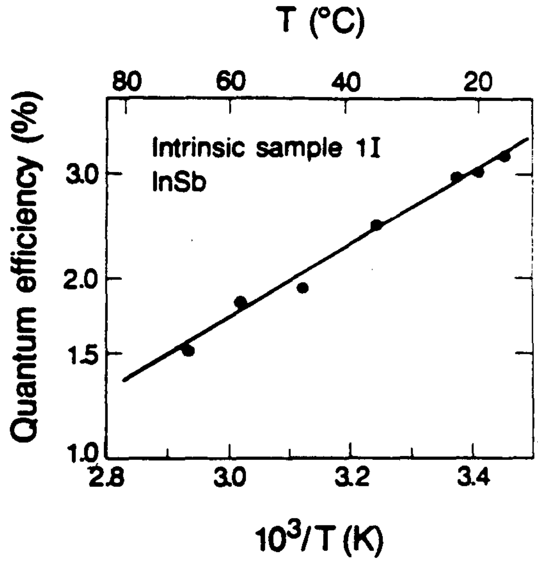

Fig. 4. Quantum efficiency of an intrinsic InSb sample (logarithmic scale), as a function of temperature [9].

the active InSb layer. When the active layer produced negative luminescence, the blackened foil was cooled by exchange of IR radiation. An explicit cooling effect of about 0.03 °C is shown in Fig. 5, at currents of 50 mA. Larger currents caused ohmic heating of the active layer, leading to radiative heating of the foil. (The radiative heating could be reduced by better thermal contact between the active layer and its heat sink.) However, the presence of the cooling effect can still be inferred at higher currents from the difference in the foil temperature caused by inverting the sign of the magnetic field.

The available temperature difference which the galvanomagnetic radiative cooling effect can produce can be increased in several ways. First, as mentioned above, better heat sinking is required. Also, better shielding of the foil to be cooled from extraneous radiation is desired. Finally, it is desired to employ filters or selectively emitting foils to restrict radiative exchange to the wavelength range in which the NL occurs. In principle, temperature differences of hundreds of degrees are achievable. The efficiency of the galvanomagnetic radiative cooling effect can also be improved. This efficiency, or coefficient of performance, is the ratio of cooling effect to input electrical energy. Many factors currently limit attainable efficiency, although one of the most important is the relatively small quantum efficiency for radiative recombination shown in Fig. 4. (There is a correspondingly small probability for radiative carrier generation, which means that many pairs must be electrically extracted from the depletion region per photon-generated pair.)

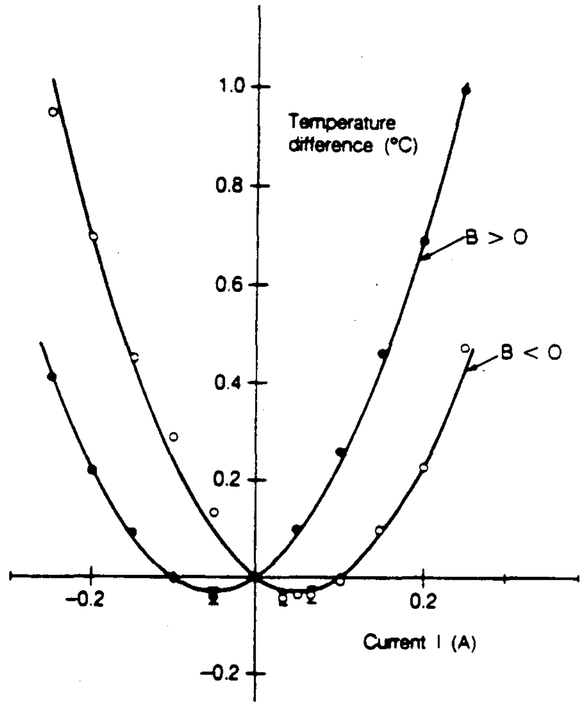

Fig. 5. Measured temperature difference between the blackened foil and the substrate of the active InSb layer, for both polarities of the 1.1 T magnetic field [17].

Future technological applications of NL to produce refrigeration effects seem more likely using reverse-biased diodes rather than the magnetoconcentration effect, since this latter effect requires a magnet. In the case of diodes, a theoretical analysis [18] indicates that, if the quantum efficiency for radiative recombination is unity, the efficiency for cooling can even approach the Carnot limit imposed by the second law of thermodynamics.

Summary

NL phenomena can be used to construct standard IR light sources because the NL intensity saturates when all electron-hole pairs have been removed from the emitting region. If the NL source uses the magnetoconcentration effect, this saturation occurs at large values of E and B. The modulation speed of such a light source should be limited by the recombination lifetime, which is about 20 ns in InSb at room temperature. In the linear regime negative (and positive) luminescence can be used to determine carrier lifetimes and corresponding quantum efficiencies for radiative recombination. Finally, an explicit cooling effect due to NL has been observed in a calorimetric experiment.

References

[1] Count Rumford, *Phil. Trans. of the Royal Soc. of London 94*, 77-182 (1804).

[2] B.I. Stepanov, *Usp. fiz. Nauk 58*, 8 (1956).

[3] B.I. Stepanov and V.P. Gribkovsky, in *Theory of Luminescence*, S. Chomet, editor, King's College, London (1970).

[4] R.K. Huddleston and E. Weitz, *Chem. Phys. Lett. 83* 174 (1981).

[5] M. Bernard and J. Loudette, Academie des Science (Paris) *Comptes Rendus 246*, 1177 (1958).

[6] M. Bernard, *J. Phys. Chem. Solids 8*, 332 (1959).

[7] V.I. Ivanov-Omskii, B.T. Kolomiets, and V.A. Smirnov, *Sov. Phys. Dokl. 10*, 345 (1965).

[8] V.I. Ivanov-Omskii, B.T. Kolomiets, and V.A. Smirnov, *Sov. Phys. JETP Lett. 3*, 185 (1966).

[9] P. Berdahl, *J. Appl. Phys.*, in press (1988).

[10] F.R. Kessler and J.W. Mangelsdorf, *Phys. Status Solidi A 24*, 557 (1974).

[11] F.R. Kessler and J.W. Mangelsdorf, *Phys. Status Solidi B 105,* 525 (1981).

[12] S.S. Bolgov, V.K. Malyutenko, and V.J. Pipa, *Sov. Tech. Phys. Lett 5,* 610 (1979).

[13] S.S. Bolgov, V.K. Malyutenko, and V.I. Pipa, *Sov. Phys. Semi 17*, 134 (1983).

[14] V.K. Malyutenko, S.S. Bolgov, and E.I. Yablonovsky, *Infrared Phys. 25,* 115 (1985).

[15] P. Berdahl and L. Shaffer, *Appl. Phys. Lett. 47,* 1330 (1985); *48,* 1811(E) (1986).

[16] T. Morimoto and M. Chiba, *Jpn. J. Appl. Phys. 23,* L821 (1984). See also T. Morimoto and M. Chiba, *Phys. Lett. A 85,* 395 (1981); *95,* 343 (1983).

[17] P. Berdahl, in *Proc. 18th Int. Conf. on the Physics of Semiconductors,* O. Engstrom, editor, (World Scientific, Singapore), Vol. 2, 1595 (1987).

[18] P. Berdahl, *J. Appl. Phys. 58,* 1369 (1985).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720