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RADIATIVE HEAT PUMPS USING NARROW-BANDGAP SEMICONDUCTORS

P. Berdahl

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Radiative heat pumps using narrow-bandgap semiconductors*

Paul Berdahl

Applied Science Division, Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

Abstract

The Solid State Radiative Heat Pump (SSRHP) concept is introduced. It offers the potential to pump infrared radiation—for heating and cooling—with high second law efficiency. In particular, some of the limitations of Peltier-effect heat pumps can be circumvented. Two approaches for constructing SSRHP devices will be described. In one approach the device is a large-area p-n junction, similar to an IR (light) emitting diode. In the second approach one uses orthogonal electric and magnetic fields to alter equilibrium carrier concentrations of electrons and holes near the crystal surface, altering the IR emission due to electron-hole recombination radiation. This phenomenon is usually termed galvanomagnetic luminescence (GML). Either approach can be used to make radiative heat pumps. Materials suitable for SSRHP devices are narrow-bandgap semiconductors with direct bandgaps in the range of 0.03 - 0.3 eV for room temperature operation. Obvious candidates are InSb, $Hg_{1-x}Cd_xTe$, and $Pb_{1-x}Sn_xTe$. As a first step in the evaluation of InSb, our laboratory has made absolute spectral measurements of its galvanomagnetic luminescence. These and related measurements in Russia and Japan are discussed.

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Introduction

The development of efficient solid state devices for the pumping of heat (i.e., refrigeration and heating) has been a tantalizing if elusive possibility for many years. Potential advantages over conventional refrigeration devices include reliability, silent operation, and design flexibility (especially for small units), as well as better efficiency and cost. The Peltier effect was investigated extensively in the 1950's and early 1960's. In that effect, heat is either released or absorbed as current is passed between the junction of two dissimilar materials, e.g., a semiconductor p-n junction. Unfortunately, high thermodynamic efficiencies were never achieved using the Peltier effect, in part due to irreversible heat conduction along the thermoelectric elements. In contrast, the solid state radiative heat pump concept involves the release or absorption of heat in the form of infrared radiation which then crosses an air gap or other infrared-transparent thermal insulator. Thus, the thermodynamic losses due to ordinary heat conduction can be avoided.

The general concept of the Solid-State Radiative Heat Pump (SSRHP)

The basic idea of the Solid-State Radiative Heat Pump (SSRHP)[1] is that the electron-hole plasma present in narrow-bandgap semiconductors can be used as the working fluid of a radiant heat engine configured as a heat pump. It uses electricity to cause the radiant heat flow. More specifically one produces, by junction injection or other means, an excess or deficit of electrons and holes (compared to thermal equilibrium), and uses this excess or deficit to produce a corresponding excess or deficit of infrared radiation (compared to thermal equilibrium). The band-to-band radiative recombination and generation of electron-hole pairs provides the needed strong coupling between the electron and photon systems, provided that the semiconductor bandgap is of the direct type.

Consider first the equilibrium radiative transfer at temperature $T = T_e$, as shown in Fig. 1. If the SSRHP is not energized by the electric input, then the infrared radiative transfer in the gap is equal in both directions, as required by the second law of thermodynamics. The magnitude of the (canceling) energy fluxes at 300K is 460 Wm^{-2} (46 mW cm^{-2}) if both emitting surfaces behave as blackbodies. If the SSRHP layer is a spectrally selective emitter, as it would be in general, it will emit less radiation than a blackbody. In accordance with Kirchhoff's law, it will also absorb less radiation, so that, on balance it neither heats or cools.*

Now consider perturbations from thermal equilibrium. Some of the equilibrium radiation from the SSRHP narrow-bandgap layer is due to electron-hole recombination. This part of the thermal radiation can be increased or decreased if the concentrations of electrons and holes are increased or decreased by electrical means. Two techniques for modulating these concentrations are (i) carrier injection/extraction through p-n junctions and (ii) galvanomagnetic action, to be discussed more fully below. The use of electric input energy to produce an enhancement or deficit of carrier concentration permits the violation of Kirchhoff's law (which applies only for bodies in

*As an aside, it is interesting that the gap (cavity) contains blackbody radiation under thermal equilibrium conditions even if the emitting surfaces are spectrally selective.

internal thermal equilibrium). Suppose the electron and hole concentrations have been increased. Then the recombination emission is increased. Less obvious, perhaps, is that the presence of an excess electron and hole concentration also results in a comparable reduction in absorption of external radiation by the active layer. (Radiation not absorbed is reflected if the substrate is reflective.) Both of these effects result in a heating of the "external absorber/emitter" shown in Fig. 1. Thus the creation of an excess electron and hole concentration in the SSRHP layer results in a heating such that the temperature T_e becomes greater than T. Correspondingly, if a deficit is created in the carrier concentrations, T_e will fall below T.

P-N Junction SSRHP Devices

A diagram of a hypothetical p-n junction SSRHP device is shown in Fig. 2. In the radiative heating (emission) mode it would operate much like a light emitting diode (LED) which emits with a broad spectrum centered in the thermal infrared, say at 10 μm. The production of the IR radiation occurs under forward d.c. bias because minority carriers injected through the junction recombine with majority carriers (on both sides), producing more IR emission than is normal for thermal equilibrium (zero d.c. bias).* The existence of a heat pumping effect arises from the fact that, for very small forward bias, almost no electrical work is required per electronic charge injected through the junction (this work is qV where q is the electronic charge and V is the voltage). However each charge injected can result in the net emission of one "bandgap photon", e.g., 0.1 eV. The remaining energy necessary for the creation of the photon is thermal energy, associated with the fact that the carriers which happen to have the most kinetic energy are those which surmount the electrostatic barrier at the junction to form the injection current. The ability to convert thermal energy to IR radiated energy is the essential feature of the SSRHP.

To understand operation under reverse bias it is important to keep in mind that, even in thermal equilibrium, two (canceling) electrical currents flow through the junction: the diffusion current and the drift current. The diffusion current is caused by gradients in carrier concentration and is responsible for the minority carrier injection under forward bias just discussed, and the drift current is due to the built-in electrostatic field at the junction. Under reverse bias the diffusion current is reduced and the drift current becomes dominant. The drift current is due to thermally excited minority carriers which diffuse to the junction and fall over the barrier. When the opposing diffusion current is reduced the drift current causes the minority carrier concentrations within a diffusion length of the junction to be reduced compared to their thermal equilibrium values. This deficit of minority carriers leads then to a deficit of IR emission which can in turn be used to radiantly cool a passive external emitter/absorber.

More information on carrier transport in p-n junction devices may be found in standard references.[2,3] Further information concerning the maximum possible radiant heat pumping capacity and the maximum possible efficiency (coefficient of performance, COP) is given in Ref. 4. In brief, the maximum rate of heat pumping per unit of junction area is on the order of σT^4, where

*The external LED emission is reduced, in the usual way, by total internal reflection at the "front" surface. Techniques for dealing with this problem are well known and will not be discussed further here.

σ is the Stefan-Boltzmann constant and T is the absolute temperature. This general rule has the important exception that the limit is raised to $\approx N^2 \sigma T^4$, where N is the IR refractive index, if the dimension d in Fig. 1 can be made small compared to typical thermal wavelengths (e.g., 10 μm at 300K). At small heat pumping rates the COP can approach the Carnot limit imposed on all heat pumps by the first and second laws of thermodynamics.*

The actual COP achievable in a real device will of course be determined by various loss mechanisms. Since the p-n junction SSRHP is similar to a conventional LED, the losses are similar: reflection of radiation, I^2R losses, etc. The most important and fundamental loss mechanism is non-radiative carrier recombination. Not all injected minority carriers recombine to produce photons; some of these carriers can recombine by the Auger mechanism in which the recombination energy appears in the form of an energetic electron or hole. Another mechanism is the Shockley-Read mechanism in which impurity states in the forbidden gap catalyze the recombination of electrons and holes. In any given material, there is a competition between radiative and non-radiative recombination, which can be numerically characterized by η_q, the quantum efficiency for an excess minority carrier (or excess electron-hole pair in intrinsic material) to decay by the emission of a photon. Clearly, the overall efficiency to produce photons is directly proportional to η_q. Also the efficiency to produce a deficit of photons (compared to thermal equilibrium) is also proportional to η_q because the number of carriers which must be extracted by the junction is larger than the number of photons extracted by a factor of η_q^{-1}. The fundamental reason the same parameter, η_q, governs both forward and reverse bias is that the radiative pumping rate is a smooth (analytical) function of the electrical bias current.

Galvanomagnetic Luminescence (GML) SSRHP Devices

The phenomenon of galvanomagnetic luminescence (GML) is the modulation of ordinary thermal emission by the application of mutually orthogonal electric and magnetic fields, parallel to an emitting surface, as depicted in Fig. 3. The electric field causes the drift of carriers in the crystal, with electrons and holes moving in opposite directions. The Lorentz force due to the magnetic field deflects these carriers toward the emitting surface where they accumulate, producing an enhancement in the recombination emission. If the polarity of either electric or magnetic field is changed, charge carriers are transported away from the surface and the radiative emission is suppressed rather than enhanced. The GML technique can be used to make the active SSRHP layer shown in Fig. 1, in place of a p-n junction device.

GML radiative heat pumps are interesting in their own right as devices to provide refrigeration and heat pumping. However, they are important as a materials evaluation tool because they are inherently simpler to make and understand than p-n junction devices. The GML layer can be composed of a pure uniform semiconductor which can be p-type, n-type, or intrinsic. The quantum efficiency η_q to produce photons by excess electron-hole pairs can be evaluated separately in each case by means of GML measurements. (One also requires knowledge of carrier

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*The Carnot COP for a heat pump which is cooling a heat source at temperature T_1 and rejecting heat to a sink at temperature $T_2 > T_1$, is given by $T_1/(T_2-T_1)$. Thus if $T_2 = 300K$ and $T_1 = 273K$, the COP is 10: each joule of electrical input causes the extraction of 10 joules of heat.

concentrations and mobilities.) As an example, one can evaluate p- and n-type material with GML and estimate the performance of a corresponding p-n junction device. In the next section we discuss the first evaluation of η_q by GML,[5] for intrinsic InSb.

Quantitative Spectral Measurements of GML from InSb

The GML theory for InSb is summarized in Ref. 5. Here I give only the result for intrinsic material for the change in the emitted radiant energy flux per unit photon energy:

$$\Delta F(\nu) = \frac{16N}{(N+1)^2}\left(\frac{\pi b(\nu)}{L+\alpha^{-1}(\nu)}\right)\left(\frac{s}{L}+\tau^{-1}\right)^{-1}\left(\frac{\mu_e\,\mu_h\,B}{\mu_e+\mu_h}\right)\left(\frac{j_x}{qn_o}\right). \tag{1}$$

where N is the index of refraction (dispersion is neglected), $b(\nu)$ is the Planck blackbody spectrum per unit solid angle per unit photon energy, $\alpha(\nu)$ is the equilibrium optical absorption coefficient, s is the surface recombination velocity, L is the effective ambipolar diffusion length, τ is the excess carrier lifetime, μ_e and μ_h are electron and hole mobilities, B is the magnetic field (z-direction), q is the electronic change, n_o is the intrinsic carrier concentration, and j_x is the electric current density (x-direction). The photon energy is $h\nu$, where h is Planck's constant. The crystal surface is in the $y=0$ plane, and the emission occurs across this plane in the negative y-direction. The effective diffusion length L is given approximately by

$$L^2 = \left(1+\mu_e\,\mu_h\,B^2\right)^{-1}\left(\frac{2\,\mu_e\,\mu_h}{\mu_e+\mu_h}\right)\frac{kT}{q}\tau\ . \tag{2}$$

In Eqs. (1) and (2), the parameters μ_e, μ_h, n_o are known from transport (Hall) measurements, $\alpha(\nu)$ is known from optical measurements, and the surface recombination velocity s is believed to be small for etched surfaces.[5] Thus there is only one free parameter — the excess carrier lifetime τ — and it can therefore be determined from the experimental measurement of $\Delta F(\nu)$.

The intrinsic InSb samples were etched with either CP-4 or a dilute solution of bromine in methanol, attached to a copper heat sink with double-sided tape, and had electrical leads attached by soldering with indium. The magnetic field was applied continuously, and the electric current was modulated sinusoidally at 2 kHz. The emitted radiation was focused on the entrance slit of a grating monochromator with a liquid nitrogen cooled $Hg_{1-x}Cd_xTe$ photoconductive detector at the output slit. A preamplifier and lock-in amplifier completed the electronics. The optical system was calibrated by replacing the sample by a small heated blackbody source modulated with a mechanical chopper.

The measured data for one sample is shown in Fig. 4. The lifetime is thus determined to be $\tau = 6.0 \pm 1.2$ nsec, with the uncertainty in τ due largely to the 10% probable error in the absolute radiometric calibration. Two discrepancies between the theoretical curve and the data are observable. There is some apparent structure in the measured data near the emission peak. This structure is due to atmospheric water vapor absorption in the optical path. The calibration procedure cannot completely eliminate this absorption because the water vapor concentration varies during the time required for measurement and calibration. The other discrepancy arises because the emission/absorption edge is temperature dependent. (The bandgap of InSb is reduced by about 0.3 meV per ^{o}C temperature increase.) The data used for $\alpha(\nu)$ are for 22^{o}C and the sample is at 33^{o}C. For this reason the data fall above the fitted curve near the emission/absorption edge. Discounting these two discrepancies, the agreement between theory and experiment is excellent.

The radiative carrier lifetime τ_r in intrinsic InSb is well known.[10] (It is calculated from $\alpha(\nu)$ using the van Roosbroeck-Shockley relation.) The quantum efficiency for radiative recombination at 33^{o}C is thus determined to be

$$\eta_q = \tau/\tau_r \approx 1.0\% \quad . \tag{3}$$

Although this value is fairly low, it is large enough to ensure that working SSRHP devices can be constructed and operated to produce a cooling or heat pump effect, using intrinsic InSb. In fact, the experimental data just presented, together with the theoretical interpretation of the data,[5] show that a reversible heat pump effect has already been observed. In the experiment an alternating (2kHz) heating and cooling effect of about 4 Wm^{-2} is obtained from the integral of $\Delta F(\nu)$; see Fig. 4. Work currently underway is intended to demonstrate a continuous cooling effect.

Other GML Measurements

Prior GML measurements give an indication of which materials may be best for SSRHP applications. InSb has been investigated by two groups in Russia[6,7] and one in Japan.[8] These prior measurements were at best roughly calibrated and the spectral resolution was not sufficient to resolve the line shape in pure InSb. Thus it was not possible to determine the carrier lifetimes and the consequent quantum efficiency to produce radiation. Nevertheless these measurements demonstrated that the GML phenomenon existed and clearly established that the radiation which was modulated was band-to-band recombination radiation.

Kessler and Mangelsdorf[10] have made GML measurements on germanium. This is a difficult experiment because the equilibrium emission of "bandgap" photons is quite small due to the large ratio of gap energy to kT. Also, because germanium has an indirect gap, optical emission throughout the entire sample is important. In contrast, for InSb, only the first few microns of the crystal below the surface participate in the emission.

Recently[11] the group at Kiev has observed GML from $Hg_{1-x}Cd_xTe$. Other narrow-bandgap semiconductors with direct gaps, not yet investigated, which should be examined, are the lead salt materials, $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$, and the alloy $InAs_xSb_{1-x}$, which has a minimum energy gap of about 0.1 eV at $x = 0.4$ at room temperature. Further candidate materials for GML observations and potential SSRHP applications may be sought among materials with high thermoelectric power (Seebeck coefficient).

Summary and Conclusions

A new approach for constructing solid-state refrigeration devices, termed solid-state radiative heat pumps, has been presented. Absolute spectral measurements of the galvanomagnetic luminescence (GML) of pure InSb have been used to determine the magnitude of the radiant heat pump effect in this material. Under the experimental conditions, a few watts per square meter of radiant heat transfer were pumped. A theoretical fit to the spectrum gives a value of 6 nsec for the room temperature carrier lifetime and consequently gives an efficiency for excess carriers to produce infrared photons of 1.0%.

Better thermodynamic performance for solid-state radiative heat pumps can be anticipated in the future after the study of GML in various narrow-bandgap materials as a function of doping and temperature.

References

1. P. Berdahl, "Solid-state radiative heat pump," patent pending (1984).
2. S.M. Sze, *Physics of Semiconductor Devices,* John Wiley & Sons, New York (1982).
3. R. Dalven, *Introduction to Applied Solid State Physics,* Plenum Press, New York (1980).
4. P. Berdahl, "Radiant refrigeration by semiconductor diodes," *J. Appl. Phys.,* 1 August (1985).
5. P. Berdahl and L. Shaffer, "Galvanomagnetic luminescence of indium antimonide," submitted to *Appl. Phys. Lett.* (1985). Also Lawrence Berkeley Laboratory report LBL-19478.
6. T.S. Moss, G.J. Burrell and B. Ellis, *Semiconductor Opto-Electronics,* John Wiley, New York (1973).
7. V.I. Ivanov-Omskii, B.T. Kolomiets, and V.A. Smirnov, *Sov. Phys. Doklady 10,* 345-346 (1965) and *Sov. Phys. J.E.T.P. Lett. 3,* 185-187 (1966).
8. S.S. Bolgov, V.K. Malyutenko, and V.I. Pipa, *Sov. Tech. Phys. Lett. 5,* 610-611 (1979), and *Sov. Phys. Semicond. 17,* 134-137 (1983).
9. T. Morimoto and M. Chiba, *Phys. Lett. 85A,* 395-398 (1981), *Phys. Lett. 95A,* 343-344 (1983), and *Jap. J. Appl. Phys. 23,* L821-L823 (1984).
10. F.R. Kessler and J.W. Mangelsdorf, *Phys. Stat. Sol.* (a) *24,* 557-564 (1974) and (b) *105* 525-535 (1981).
11. V.K. Malyutenko, S.S. Bolgov, and E.I. Yablonovsky, in *Third Intn'l Conf. on Infrared Physics,* Zurich, 741-743 (1984).

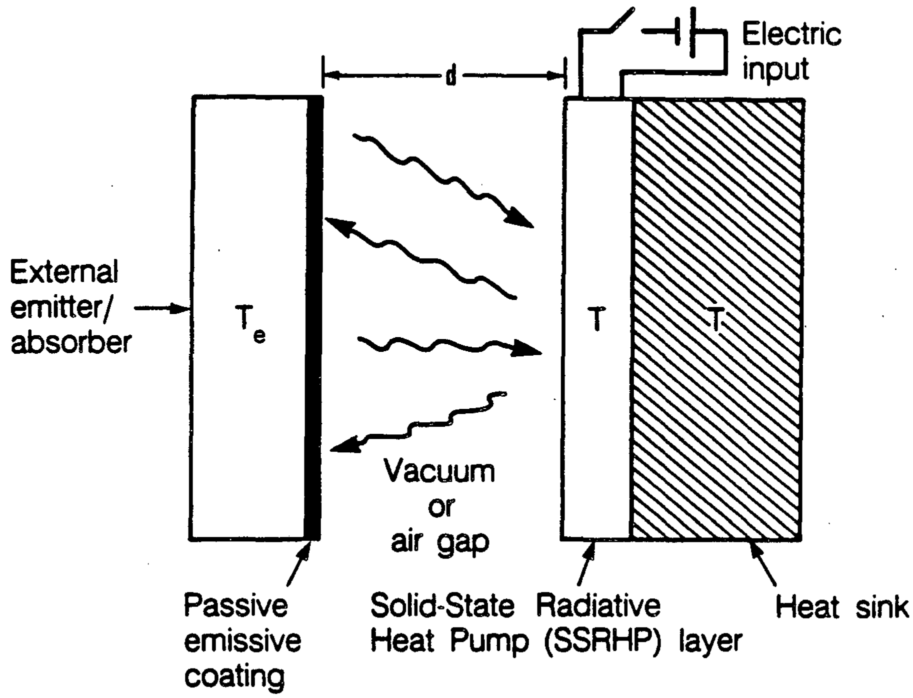

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Fig. 1. Generic configuration for a solid-state radiative heat pump system.

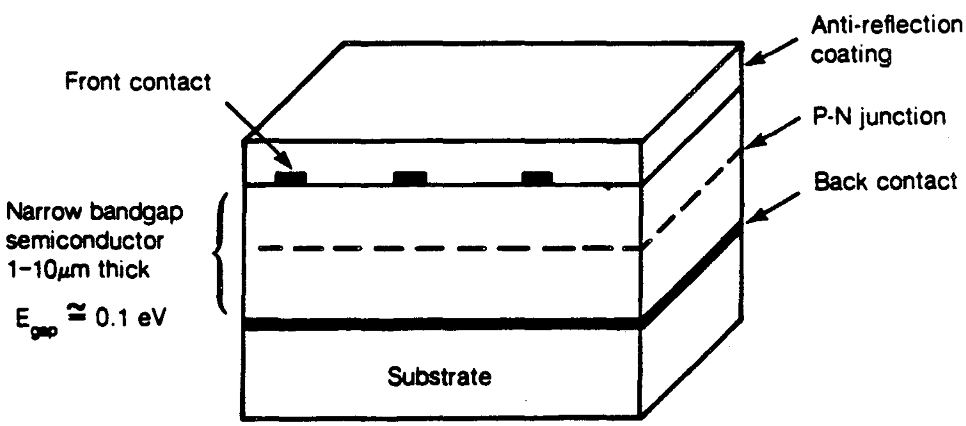

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Fig. 2. Hypothetical p-n junction configuration for the SSRHP active layer.

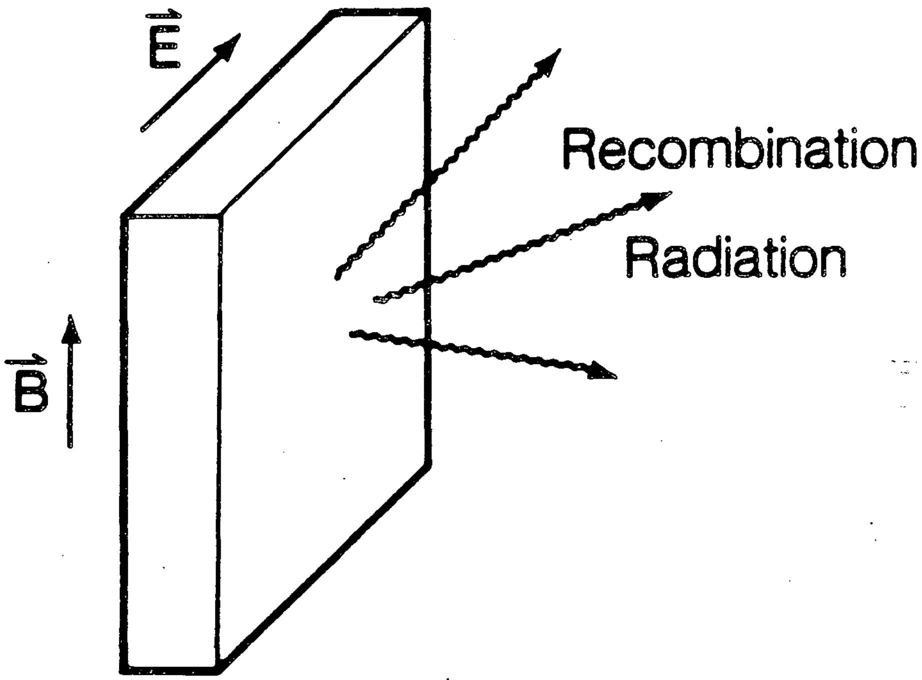

Fig. 3. Geometrical configuration to produce galvanomagnetic luminescence.

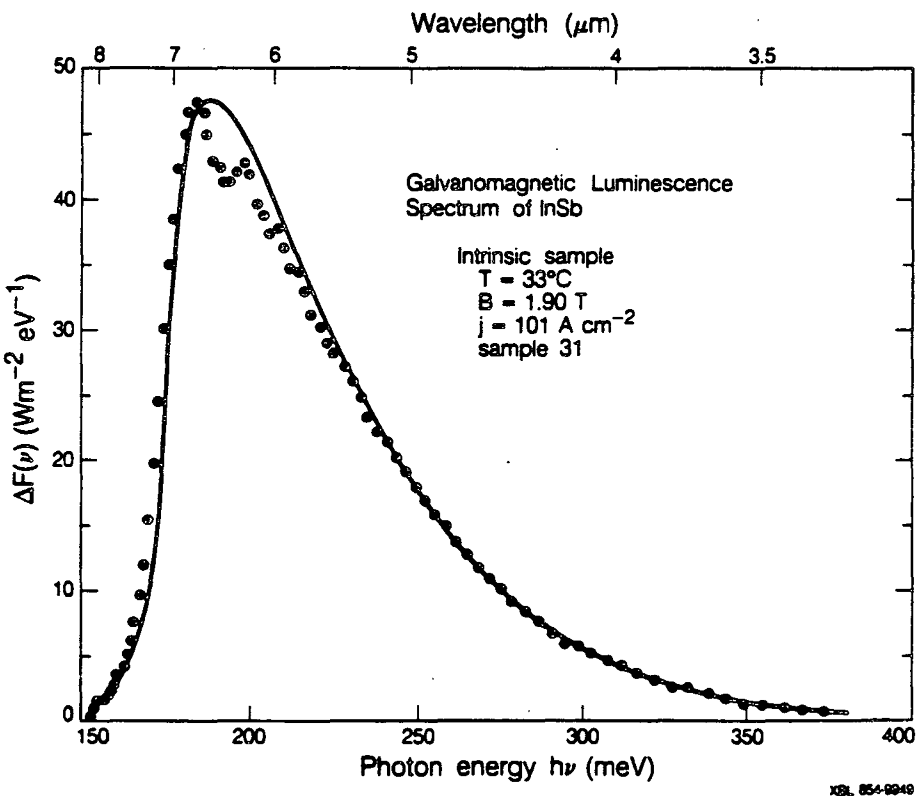

Fig. 4. Spectrum of galvanomagnetic luminescence of intrinsic InSb. $\Delta F(\nu)$ is the change in the equilibrium emission due to the simultaneous presence of electrical current and an orthogonal magnetic field. The solid line is the theoretical curve; the dots are the measured experimental data points.

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