changes and those calculated by means of the Clapeyron relation is excellent compared to the comparatively poor agreement[24] for some of the alkali halides. The present discrepancy is ~10%, and is in the usual direction, i.e., the direct determination of Δv yields too high a value, or the latent heat is too low. The consistency of this discrepancy was first pointed out by Clark.[25] The present good agreement can perhaps be ascribed to the fact that the latent heats and volume changes are all based on very recent determinations.[5,22]

[24] C. W. F. T. Pistorius, J. Chem. Phys. **47**, 4870 (1967).
[25] S. P. Clark, Jr., J. Chem. Phys. **31**, 1526 (1959).

ACKNOWLEDGMENTS

The authors would like to thank Mrs. Martha C. Pistorius for writing the computer programs used in fitting the data. Dr. J. C. A. Boeyens was of considerable assistance with the crystallography. We are indebted to Dr. G. Gafner and Dr. E. Rapoport for valuable discussions. J. Erasmus and his staff and G. O'Grady and his staff kept the equipment in good repair, and were responsible for the manufacture of the furnace parts. Calculations were carried out on the IBM System 360 of the National Research Institute for Mathematical Sciences.

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Tuning of PbSe Lasers by Hydrostatic Pressure from 8 to 22 μ

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This paper reports the tuning by hydrostatic pressure of the wavelength of emission of a PbSe laser from 7.5 to 22.3 μ in the infrared. Also discussed are the possibilities for further extension of the emission wavelength, the physical studies thereby rendered possible, the possibility of tunable devices, and the extension of similar ideas and techniques to other semiconductors of the PbSe family.

1. INTRODUCTION

THE results of many experimental[1] and theoretical[2] studies have shown that the face-centered cubic lead chalcogenides PbS, PbSe, and PbTe are semiconductors with small direct energy gaps at the point L of the Brillouin zone, and with large matrix elements for electronic transitions under the influence of electromagnetic radiation. Laser action has been demonstrated in all three of these semiconductors.[3] Separate series of experiments have shown that the pressure coefficients of the energy gaps of all three substances are negative and have about the same vlaue.[4–8] Cal-

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† Research supported by the U. S. Office of Naval Research under Contract No. Nonr 1866(10).
‡ Operated with support from the U. S. Air Force.
[1] Original papers and older references are to be found in the *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964).
[2] The most recent general reference updating the literature at the time of writing (April 1967) is that of D. L. Mitchell and R. F. Wallis, Phys. Rev. **151**, 581 (1966).
[3] J. F. Butler, A. R. Calawa, R. J. Phelan, Jr., A. J. Strauss, and R. H. Rediker, Solid State Commun. **2**, 303 (1964); J. F. Butler, A. R. Calawa, R. J. Phelan, Jr., T. C. Harman, A. J. Strauss, and R. H. Rediker, Appl. Phys. Letters **5**, 75 (1964); J. F. Butler and A. R. Calawa, J. Electrochem. Soc. **112**, 1056 (1965).
[4] The probability of a negative pressure coefficient of the fundamental gap may be inferred from the positive temperature coefficient of between 4 and 5×10^{-4} eV/°K found in all three materials. If this temperature coefficient is regarded as composed of two parts, the first stemming from the increase in volume with increasing temperature, the second from changes in the electron-phonon interaction, and if, following the theory of Fan (Ref. 5) we accept that the second contribution is inherently negative for minimal gaps, we are led to calculate an equivalent *negative* pressure coefficient of at least -15×10^{-6} eV/bar.
In fact, experimental studies of the effect of hydrostatic pressure on the transport (Ref. 6) and optical properties (Ref. 7) have been interpreted to correspond to coefficients of about -9×10^{-6} eV/bar only, implying that, in this case at least, the contribution to the temperature coefficient of the electron-phonon interaction is positive and therefore the effect considered by Fan is not the dominant one (Ref. 8).
[5] H. Y. Fan, Phys. Rev. **82**, 900 (1951).
[6] W. Paul, W. M. DeMeis, and L. X. Finegold, in *Proceedings of the Sixth International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society of London, 1962), p. 712; A. A. Averkin I. G. Dombrovskaya, and B. Ya. Moizes, Fiz. Tverd. Tela **5**, 96 (1963) [English transl.: Soviet Phys.—Solid State **5**, 66 (1963)]; Y. Sato, M. Fujimoto, and A. Kobayashi, J. Phys. Soc. Japan **19**, 24 (1964).
[7] Ya. A. Semenov and A. Yu. Shileika, Fiz. Tverd. Tela **6**, 313 (1964) [English transl.: Soviet Phys.—Solid State **6**, 252 (1964)]; V. Prakash, thesis, Harvard University, 1966 (unpublished) and Technical Report No. HP-13 from the Division of Engineering and Applied Physics, Harvard University (unpublished). This report includes a very extensive historical review on many aspects of the behavior of the lead chalcogenides, with references.
[8] For further brief comment on this difficulty, see Paul *et al.*, Ref. 6, p. 719. For a recent attempt to establish a different theory of electronic band energies in the presence of electron-phonon interaction, which could permit both positive and negative coefficients, see S. C. Yu, thesis, Harvard University, 1964 (unpublished).

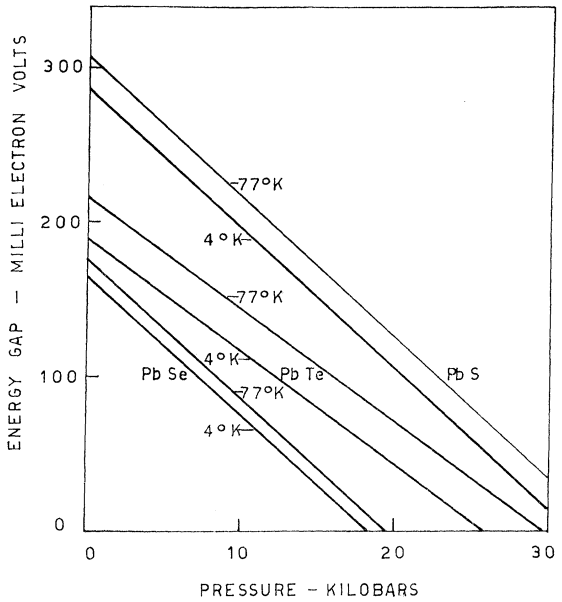

FIG. 1. Variation of the energy gaps of PbS, PbSe, and PbTe with hydrostatic pressures to 25 kbar at 4 and 77°K. The direct observation from the change in the optical absorption edge with pressure extends only to 10 kbar at 300°K and the nearly equal coefficients at higher pressures deduced from transport measurements are quantitatively less reliable because of the difficulties of accurate mobility corrections. Thus all of the variations above 10 kbar must be considered as a (probably very sound) working hypothesis. In constructing these curves we have assumed the following parameters:

PbS: $E_g(4°K)0.286$ eV; $E_g(77°K)0.307$ eV; $(\partial E_g/\partial P)_T=-9.15\times10^{-6}$ eV/bar.

PbSe: $E_g(4°K)0.165$ eV; $E_g(77°K)0.176$ eV; $(\partial E_g/\partial P)_T=-9.1\times10^{-6}$ eV/bar.

PbTe: $E_g(4°K)0.190$ eV; $E_g(77°K)0.217$ eV; $(\partial E_g/\partial P)_T=-7.4\times10^{-6}$ eV/bar.

The 4 and 77°K values at zero pressure are taken from magneto-optical determinations, and the pressure coefficients from the study by Prakash (Ref. 7).

culations[9] of the deformation potentials of the several L-point states show impressive agreement with the experimental results. It is immediately evident that experimentally available hydrostatic pressures may rapidly increase the wavelength of laser emission in the infrared,[10,11] and we have shown in Fig. 1 the deduced

TABLE I. Phase transitions under pressure.

Compound	Approximate pressure of phase change (kg/cm²)
PbS	24 680
PbSe	43 320
PbTe	41 200

and extrapolated variation of the several band gaps at temperatures of 4 and 77°K. The present paper reports the experimental verification of a portion of the curve for PbSe and includes the dependence of the spontaneous emission wavelength and intensity on hydrostatic pressures to 14 kbar, the dependence of the stimulated modes on pressure, and the variation of the refractive index with pressure, as well as some concurrent less complete studies of the laser diode properties at atmospheric pressure.[3]

The construction of the paper will be as follows: In Sec. 2, we shall briefly review the pertinent studies of the properties of the lead salts, especially PbSe. In Sec. 3, we shall discuss the experimental techniques involved, paying particular attention to those which are new. Section 4 will give the experimental results, and an analysis yielding the pressure coefficients of the energy gap. In Sec. 5, we shall summarize our principal findings and discuss the very real possibilities for extension of this study.

2. PROPERTIES OF THE LEAD CHALCOGENIDES, ESPECIALLY PbSe

All of the lead chalcogenides crystallize in the NaCl structure, but all appear to have transitions to the less symmetric SnS orthorhombic ($Pmcn$) structure at high

[9] L. G. Ferreira and G. W. Pratt (unpublished); see L. G. Ferreira, Phys. Rev. **137**, A1601 (1965); S. Rabii, thesis, M.I.T., 1966 (unpublished); and a joint report of the Materials Theory Group (No. 3) and the Semiconductor Laboratory (No. 10) of the Department of Electrical Engineering at the Massachusetts Institute of Technology (unpublished).

[10] Previous studies of the effect of hydrostatic pressure on the frequency and intensity of the spontaneous and stimulated emission, and on the properties of the cavity modes of amplification in GaAs and GaAs-GaP alloys, have been J. Feinleib, S. H. Groves, W. Paul, and R. Zallen, Phys. Rev. **131**, 2070 (1963); G. E. Fenner, J. Appl. Phys. **34**, 2955 (1963); M. J. Stevenson, J. D. Axe, and J. R. Lankard, IBM J. Res. Develop. **7**, 155 (1963); T. A. Fulton, D. B. Fitchen, and G. E. Fenner, Appl. Phys. Letters **4**, 9 (1964); G. E. Fenner, Phys. Rev. **137**, A1000 (1965).

The following three papers examine experimentally the effect of uniaxial stress on the laser emission of GaAs: F. M. Ryan and R. C. Miller, Appl. Phys. Letters **3**, 162 (1963); D. Meyerhofer and R. Braunstein, *ibid.* **3**, 171 (1963); R. C. Miller, F. M. Ryan, and P. R. Emtage, *Radiative Recombination in Semiconductors* (Dunod Cie., Paris, 1964), p. 209.

These measurements, as a group, provided rather precise values of the dependence on strain of energy gaps and refractive indices, and were entirely in agreement with the pattern of behavior expected from previous independent determinations of these quantities for semiconductors of the Germanium family. In particular, it is interesting to note that the energy gap "tuning" of about $+12\times10^{-6}$ eV/bar is actually at a rate greater than reported in the present paper; however, this positive coefficient of energy gaps of about 1.5 eV does not lead to similar spectacular tuning in *wavelength*.

[11] Some measurements of the effect of strain on laser emission of the lead salts have already been reported. The effect of uniaxial stresses has been examined by A. R. Calawa, J. F. Butler, and R. H. Rediker, Bull. Am. Phys. Soc. **10**, 84 (1965). A preliminary account of the present examination, but to lower pressures, was presented by J. M. Besson, J. F. Butler, A. R. Calawa, W. Paul, and R. H. Rediker, Appl. Phys. Letters **7**, 206 (1965). An interesting study of a different nature, but which is based on the same ideas, that of frequency modulating lead-salt diode lasers by acoustic waves, has been conceived and carried out by Pratt and Ripper. See G. W. Pratt and J. E. Ripper, J. Appl. Phys. **36**, 1525 (1965); Bull. Am. Phys. Soc. **10**, 84 (1965); J. E. Ripper, thesis, M.I.T., 1966 (unpublished); and Technical Report No. 5 of the Materials Theory Group of the Department of Electrical Engineering at the Massachusetts Institute of Technology (unpublished).

TABLE II. Properties of PbSe.

$E_g(0°K) = 0.16$ eV[a]; 0.165 ± 0.005 eV[b]
$E_g(77°K) = 0.176 \pm 0.005$ eV[b]
$(\partial E_g/\partial P)_{300°K} = (-8.3 \pm 1) \times 10^{-6}$ eV/bar[c]
$(-9.1 \pm 0.5) \times 10^{-6}$ eV/bar[d]
$(\partial E_g/\partial T)_P = 4.1 \times 10^{-4}$ eV/°K[d]

Electron masses at 4°K:

$m_t^c = 0.040 m_0$; $m_l^c = 0.070 m_0$ (few carriers[e])
$m_t^c = 0.050 m_0$; $m_l^c = 0.085 m_0$ (2×10^{18} cm^{-3} [f])

Hole masses at 4°K:

$m_t^v = 0.034 m_0$; $m_l^v = 0.068 m_0$ (few carriers[e])
$m_t^v = 0.047 m_0$; $m_l^v = 0.094 m_0$ (2×10^{18} cm^{-3} [f])

Refractive index, $n = 5.3$[g]; $P = 1$, $T = 77°K$, $h\nu = 0.165$ eV

$\frac{1}{n}\frac{\Delta n}{\Delta T} = 3 \times 10^{-4}(°K)^{-1}$ between 77 and 300°K[h]

Volume compressibility $= 2.9 \times 10^{-6}$ bar^{-1} [i]
Volume thermal expansion coefficient $= 60 \times 10^{-6}(°K)^{-1}$ [j]
Static dielectric constant $= 280$[k]
Energy of transverse optical phonon at $q = 0$: 44 cm^{-1} [k]

[a] K. F. Cuff, M. R. Ellett, C. D. Kuglin, and L. R. Williams, in *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964), p. 677.
[b] D. L. Mitchell, E. D. Palik, and J. N. Zemel, in *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964), p. 325.
[c] See the first reference under Ref. 6 of text and also Ref. 35.
[d] V. Prakash, thesis, Harvard University, 1966 (unpublished) and Technical Report No. HP-13 from the Division of Engineering and Applied Physics, Harvard University (unpublished).
[e] See Ref. a above.
[f] M. R. Ellett and K. R. Cuff, Bull. Am. Phys. Soc. **8**, 601 (1963).
[g] J. N. Zemel, J. D. Jensen, and R. B. Schoolar, Phys. Rev. **140**, A330 (1965).
[h] J. N. Zemel, J. D. Jensen, and R. B. Schoolar, Phys. Rev. **140**, A330 (1965).
[i] P. W. Bridgman, Phys. Rev. **57**, 237 (1940).
[j] S. S. Sharma, Proc. Indian Acad. Sci. **A34**, 72 (1951).
[k] J. N. Zemel, in *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964), p. 1061.

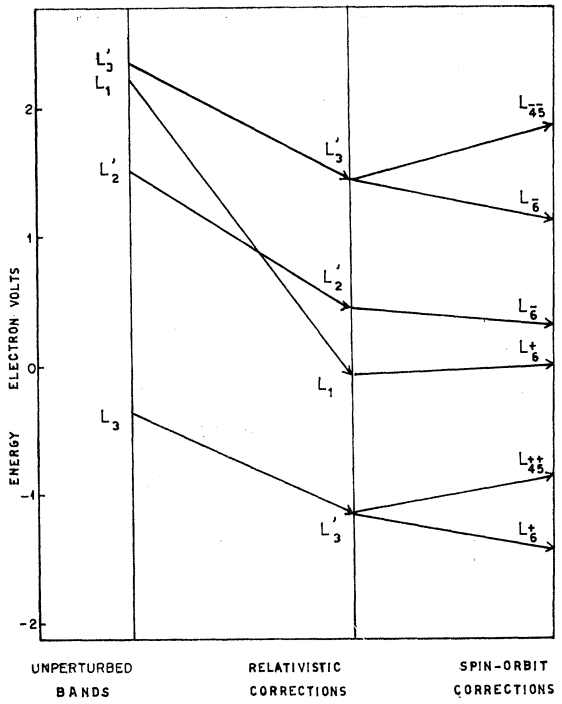

FIG. 2. Variation of the energies of several L-point states in PbSe, as additional terms are included in the Hamiltonian (adapted from Pratt and Ferreira, Ref. 13).

pressures,[12] as indicated in Table I. Clearly the pressures are high enough that in the experimental study to be reported here—on PbSe at 77°K to 15 kbar—there is no danger of transformation.

There have now been several theoretical calculations of the over-all band structure of the lead salts from different standpoints and many experimental results bearing on the bands far from the Fermi level and on the detailed structure near the Fermi level.[1] The consensus appears to be that the fundamental gap in all three compounds occurs between a valence-band maximum of symmetry L_6^+ and a conduction-band minimum of symmetry L_6^-. Figure 2, adapted from a revealing study of Pratt and Ferreira,[13] shows the probable ordering of the states at the L point and the effect of adding into the Hamiltonian the different physical interactions. The great effect of the relativistic correction on S-like states is particularly to be noted. Spin-orbit mixing of the two L_6^+ valence-band states and of the two L_6^- conduction-band states leads to there being a finite matrix element of the momentum between L_6^+ and L_6^- for all directions of k near L. A quantitative discussion of the effect of pressure changes of laser emission wavelength and intensity must entail, *inter alia*, an estimate of the change in spin-orbit mixing caused by relative band displacement.

Some of the properties of PbSe are given in Table II. The band gap of PbSe is the smallest of the three, the departure from systematic ordering not being well understood at the moment of writing. The gaps at 4 and 77°K are rather well established from magneto-optical absorption measurements. The absorption edge itself displays a low-energy exponential tail, a feature shared with the other two compounds,[14] as well as several other solids. We shall not attempt an explanation of this shape here,[14] but shall have to correlate the shape of the emission in an empirical way with the presence of such an absorption tail. The negative pressure coefficient and positive temperature coefficient of the gap are taken from the displacement without much shape change of recognizable features of the absorption edge.

The effective masses for electrons and holes are approximately equal and approximately isotropic. Both bands rapidly become nonparabolic away from their extrema so that the mass values quoted depend on the carrier concentration considered. This clearly affects

[12] P. W. Bridgman, Phys. Rev. **57**, 237 (1940); W. A. Bassett, T. Takahashi, and P. W. Stook, Rev. Sci. Instr. **38**, 37 (1967).
[13] G. W. Pratt and L. G. Ferreira, in *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964), p. 69.
[14] See Prakash, Ref. 7.

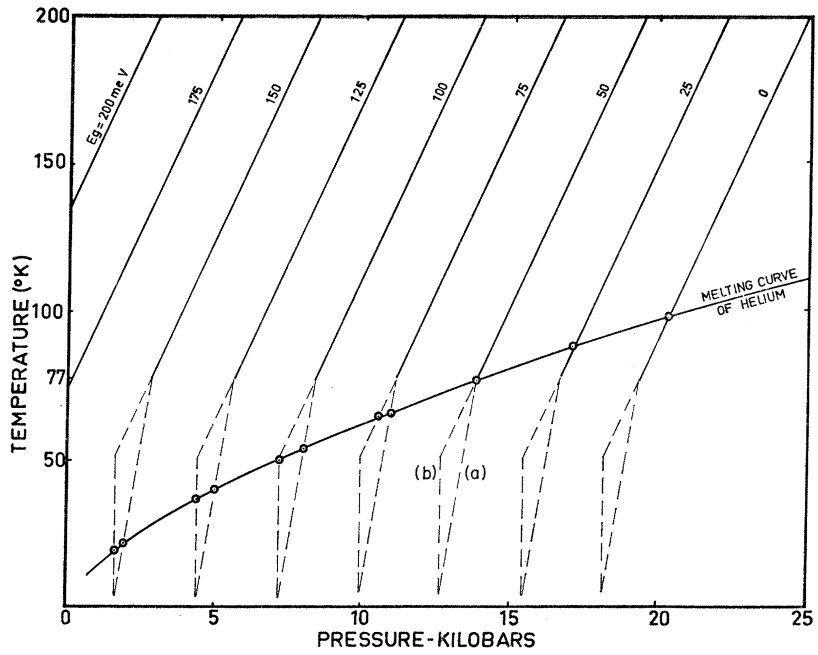

FIG. 3. Variation of the freezing pressure of helium with temperature. Also, lines of equal energy gap, constructed using the values at atmospheric pressure and very low temperature from magneto-optical work, and the pressure and temperature coefficients given in Table II. Of the two dotted lines drawn at low temperature for each curve of equal energy gap, line (a) corresponds to the assumption that the gap is 165 meV at 4°K, 176 meV at 77°K, and has a linear variation at a rate of $+4.1\times10^{-4}$ eV/°K above 77°K, while line (b) corresponds to the assumption that the gap varies linearly at the above rate for temperatures both above and below 77°K, but with an asymptote to the value experimentally determined at 4°K.

the position of Fermi levels and quasi-Fermi levels at all pressures.

Of the other coefficients listed in Table II, we should remark on the very high static dielectric constant, which is probably related to the very low value of the transverse optical phonon energy and to a possible instability of the lattice against distortion into the Bi structure.[15] The refractive index is comparable to that of the Ge family, and is known to decrease considerably with addition of free carriers, rise in temperature, and decrease in hydrostatic pressure.[16]

The several pressure coefficients of the energy gap, the effective masses, and the refractive index are qualitatively self-consistent.

The theoretical studies have been most valuable in suggesting an over-all band structure facilitating interpolation and extrapolation when pressure, temperature, or atomic constituents are changed. Figure 2 shows several L-point extrema close in energy. Although the band gap L_6^+-L_6^- closes with pressure, there is always a possibility of the intervention of one of the other bands which might possess a greater pressure shift and so accelerate the band-gap decrease or otherwise affect the carrier distributions or the interband matrix elements. Not illustrated here but evident in the published band diagrams are valence-band maxima close to the L_6^+ energy but in the (110) direction of k space, which, if their energy is correctly estimated and their pressure coefficients suitably large, might affect the experimental observations at high pressures. In this connection, as one example, it is to be noted that in PbTe,[17] as in the related compounds SnTe [18] and GeTe,[19] there is transport and optical evidence for lower valence-band maxima of undetermined symmetry about 0.1 eV from the maximum L_6^+.

Among the several theoretical calculations we select those of Pratt and his collaborators, who have calculated both the bands and their changes with strain. The calculated and experimental coefficients are in very good agreement for the fundamental gap L_6^+-L_6^-. A summary of some of these coefficients may be found in the thesis of Rabii.[20]

3. EXPERIMENTAL TECHNIQUES

In these experiments, we wished to reach the maximum possible hydrostatic pressure at a temperature low enough to allow laser action, and to measure under these conditions the intensity of emission of long infrared wavelengths. This necessitated some extension of existing techniques, which we shall outline.

[15] M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964).

[16] See Prakash, Ref. 7.

[17] R. S. Allgaier *et al.*, J. Appl. Phys. Suppl. **32**, 2185 (1961); Bull. Am. Phys. Soc. **7**, 544 (1962); **9**, 479 (1964); J. Appl. Phys. **37**, 302 (1966); H. R. Riedl, Phys. Rev. **127**, 162 (1962); Y. Sato, M. Fujimoto, and A. Kobayashi, J. Phys. Soc. Japan **19**, 24 (1964); J. R. Dixon and H. R. Riedl, Phys. Rev. **138**, A873 (1965); A. A. Averkin and P. G. Dermenzhi, Fiz. Tverd. Tela **8**, 103 (1966) [English transl.: Soviet Phys.—Solid State **8**, 79 (1966)].

[18] See R. A. Hein, Phys. Letters **23**, 7 (1966); also, W. Cochran, *ibid.* **13**, 193 (1964); R. A. Hein *et al.*, in *Proceedings of the Tenth International Conference on Low Temperature Physics, 1966* (Moscow, Proizvodstrenno-Izdatel'skii Kombinat, VINITI 1967), p. 604.

[19] N. V. Kolomoets, E. Yu Lev, and L. M. Sysoeva, Fiz. Tverd. Tela **6**, 706 (1964) [English transl.: Soviet Phys.—Solid State **6**, 551 (1964)]; R. A. Hein *et al.*, J. Phys. Soc. Japan Suppl. **21**, 643 (1966), also the commentary.

[20] See Rabii, Ref. 9.

We have seen that the energy gap of PbSe decreases both at low temperatures and high pressures; the laser emission is very much enhanced at 4°K over 77°K, and not obtainable at the time of writing much above 77°K. Thus if one were prepared to leave aside any preference for well-defined hydrostatic pressures, the best conditions for maximum observability and tuning into the far infrared of the radiation would appear to be near 4°K. Taking helium as the most suitable fluid medium at low temperatures, we have sketched in Fig. 3 the variation of its freezing pressure with temperature[21] and lines connecting the pressure-temperature combinations corresponding to a series of decreasing values of the energy gap. In Fig. 4, we have drawn the expected variation of infrared wavelength corresponding to the energy-gap variation with pressure at 4 and 77°K, along with indications of energies where experimental difficulties caused by freezing or poor window transmission (see below) may be anticipated. All things considered, it appears that for the present state of diode development, the longest wavelengths of laser emission will require penetration into the regime of solid helium. However, we have chosen for this study to confine ourselves to the maximum hydrostatic pressure available at 77°K, that is, 14.150 kbar.[22]

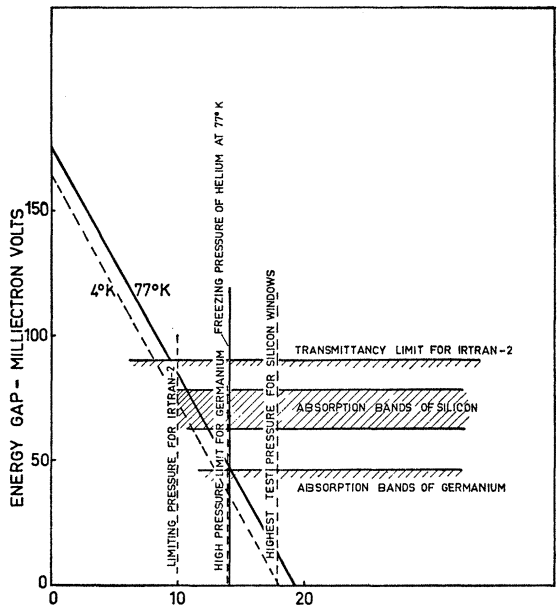

FIG. 4. Expected variation with pressure of the wavelength corresponding to the band gap of PbSe at 4 and 77°K. The freezing pressure of helium at the two temperatures is marked as are the safe pressure limits for windows of Irtran 2, silicon and germanium, and the wavelength ranges of lattice vibration absorption of silicon and germanium.

[21] J. S. Dugdale and F. E. Simon, Proc. Roy Soc. (London) A218, 291 (1953); also Ref. 22.
[22] D. Langer, J. Phys. Chem. Solids 21, 122 (1961).

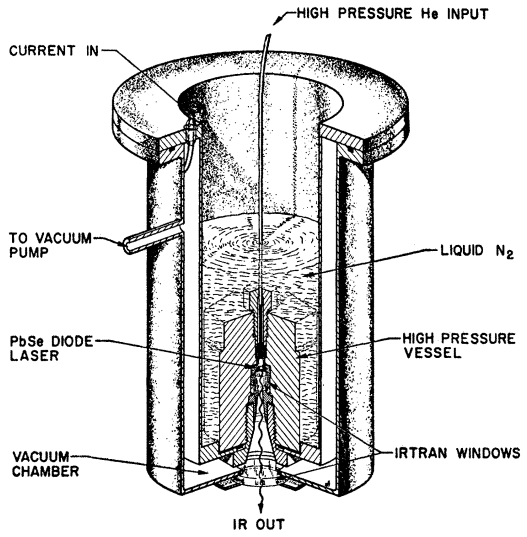

FIG. 5. Schematic diagram of the high-pressure vessel for optical work, mounted in a cryostat for work at 77°K.

The pressure-generating apparatus is standard,[23] so that a known pressure can be delivered by way of $\frac{1}{8}$-in. outside-diameter stainless-steel tubing to a pressure vessel contained in a nitrogen cryostat. Figure 5 shows a schematic diagram of this final state of the pressure apparatus. The diode is mounted on a standard plug for this sort of experiment,[24] with two electrical leads to supply current to the diode and a window both strong enough to withstand the pressure and transparent to infrared wavelengths.

At the beginning of the experiment, the only pressure windows which had been extensively used were made of sapphire which has an infrared cutoff near 5 μ. During the course of the experiment, in collaboration with W. M. DeMeis, windows of Irtran-2,[25] silicon, and germanium were developed.[26] Their characteristics are summarized in Table III.[26] We note here simply that cylinders of pure, polycrystalline germanium, $\frac{1}{2}$-in. in diameter by $\frac{1}{2}$ in. long, placed over an aperture in a polished steel seat of $\frac{1}{8}$-in. diameter, withstood pressures

TABLE III. Optical windows for high-pressure experiments.

Material	Transmission range (μ)	Window diameter × length (in.)	Window seat aperture (in.)	Maximum test pressure (kbar)	Maximum decompression rate (bar/sec)
Irtran 2 (ZnS)	3.5 – 12	$\frac{1}{2}\times\frac{1}{2}$	$\frac{3}{16}$	10	2
Ge	2 – 25; 60 – ∞	$\frac{1}{2}\times\frac{1}{2}$	$\frac{1}{8}$	12	10
Si	1 – 13; 2 – ∞	$\frac{1}{2}\times\frac{1}{2}$	$\frac{1}{8}$	18	10

[23] See, for example, D. Langer and D. M. Warschauer, Rev. Sci. Instr. 32, 32 (1961); and Ref. 24.
[24] See J. Feinleib, S. H. Groves, W. Paul, and R. Zallen, Phys. Rev. 131, 2070 (1963).
[25] Kodak Company, Rochester, N. Y.
[26] W. Paul, J. M. Besson, and W. M. DeMeis (to be published).

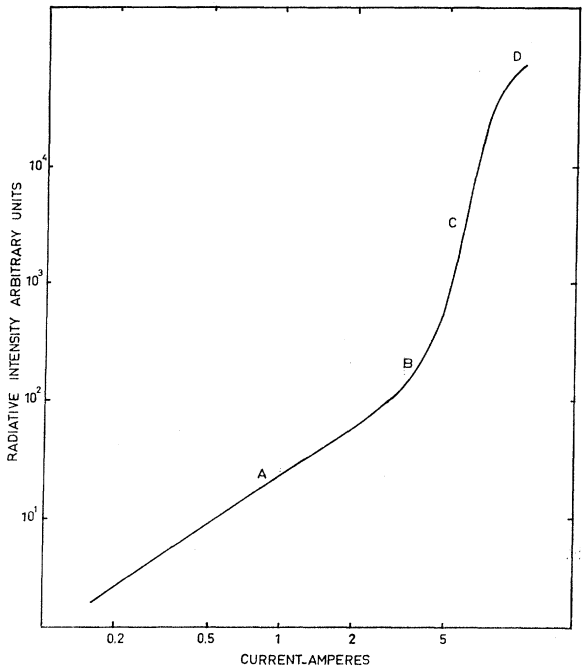

FIG. 6. Total light output of PbSe diode No. 112 at $T = 77°K$ and $P \sim 1$ kbar, as a function of injected current. Current pulses 120 nsec long were used for parts C and D, pulses of 1000 nsec for A and B. If part C can be taken to correspond to unit efficiency of photon production, the external efficiency in the spontaneous regime A is smaller than 10^{-2}. If the small slope of D is due partly to heating of the diode, the deduced external efficiency in the spontaneous regime A must be even smaller than 10^{-2}.

up to 12 kbar, while similar silicon cylinders under the same conditions were unchanged by pressures up to 18 kbar. Both types of window are useful for us, since the wavelengths of their optical absorption caused by lattice vibrations are different (see Fig. 4).

The polished end of the pressure vessel is sealed against the polished stainless-steel flange at the bottom of the cryostat using a $\frac{1}{32}$-in.-thick torus of indium. The window at the bottom of the cryostat is either of Irtran-2 or of KRS-5 depending on the spectral range under examination. The radiation is directed by standard mirror optics into a Perkin-Elmer grating monochromator. The eventual detection utilizes a Raytheon Cu-doped germanium detector. Initial lining-up of the system is accomplished with a visible light source replacing the diode.

The pressure is measured in the main pressure generator at room temperature, using a 100-Ω manganin wire gauge and our standard circuit.[27] The gauge was calibrated against the freezing pressure of mercury at 0°C, taken to be 7566 bar.[28]

The preparation of the diodes has been discribed elsewhere, so that only the essential details need be given here.[3] The starting material is the end product of prolonged heating of the PbSe in Se vapor, which adjusts the stoichiometry to give the required carrier density. The junctions are produced by diffusion at elevated temperatures. The exact nature and distribution of the carrier producing defects and of the scattering and recombination centers is not well understood. Strains may be produced in the diode material either in the process of manufacture or in the fabrication of the diode. Any influence of these strains on transport and recombination may be modified (sometimes reversibly, sometimes not) by the application of hydrostatic pressure. The order of magnitude of the final carrier densities is $3\text{–}6\times10^{17}$ carriers cm^{-3} and of the mobility 3×10^4 cm^2 V^{-1} sec^{-1} at 77°K.

For the time and temperature of the diffusion, the junctions are produced about 100 μ below the surface, deep enough that their properties may be unaffected when current-carrying leads are soldered at the surface. The actual samples are parallelepipeds cleaved on {100} planes to be about 0.15 mm thick and 0.1×0.5 mm on the plane parallel to the function. Ohmic contacts are made to the diode using a gold deposit on the p side and a deposit of In-Sn alloy on the n side. The diode is mounted using an In solder on a much

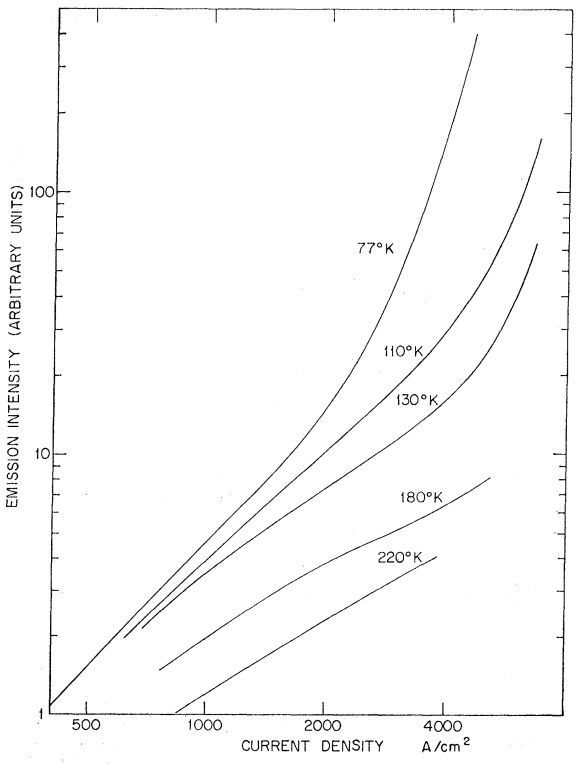

FIG. 7. Total light output of PbSe diode No. 111 at $P \sim 2$ kbar and at several temperatures, as a function of injected current density. The temperatures are estimated to an accuracy of a few degrees only from an equation of state for the helium pressure fluid, maintained at a constant pressure but slowly variable volume and temperature.

[27] D. M. Warschauer and W. Paul, Rev. Sci. Instr. **29**, 675 (1958).

[28] D. N. Newhall, L. H. Abbott, and R. A. Dunn, in *High Pressure Measurement*, edited by A. A. Giardini and E. C. Lloyd (Butterworths Scientific Publications, Washington, D. C., 1963).

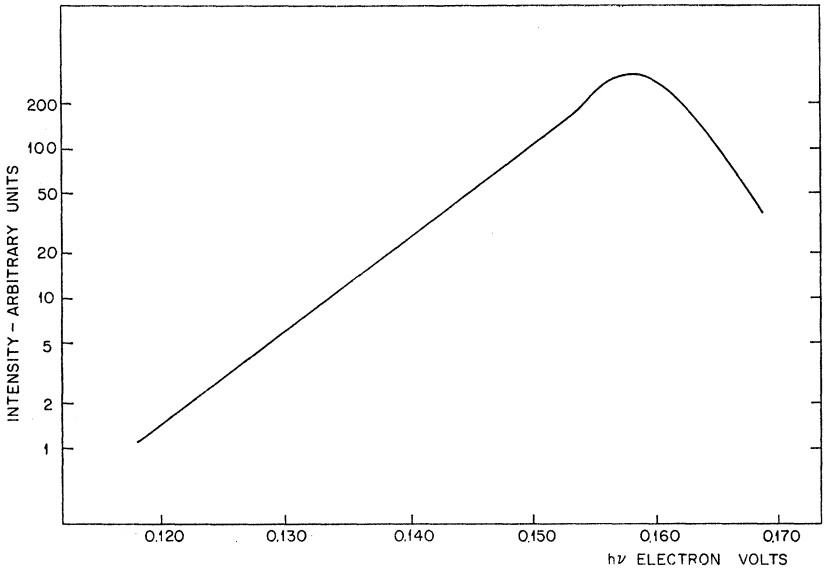

FIG. 8. Spontaneous emission spectrum of PbSe diode No. 111 at $P=1540$ bar and $T=77°K$. The injection current density was 1800 A/cm² and the pulses 8 μsec long.

more massive piece of copper, which acts as heat sink and good electrical contact. The other contact to the sample is a silver wire soldered with indium. This way of soldering and mounting has proved to be satisfactory at 77°K up to 15 kbar. The over-all dimensions of the diode package are less than 4 mm, the smallness being a major consideration in reducing the total volume which has to be subjected to the high pressure.

During the experiments, a certain number of irreversible or temporary phenomena were observed, which were attributed to residual strains in the diode structure rather to any nonhydrostatic external stresses caused by the mounting in the pressure vessel. The latter were judged not to provide nonhydrostatic constraints of any magnitude, drawing on our experiences with GaAs diode lasers under pressure.[10]

4. RESULTS AND ANALYSIS

A. Principal Results

Figure 6 shows the total light output of a representative diode as a function of the injected current, and Fig. 7 the same characteristic for a second at several temperatures. Figures 8 and 9 show the spectral emission at an injected current density below the threshold for laser action, while Fig. 10 illustrates the change in this emission as one passes into the laser regime.

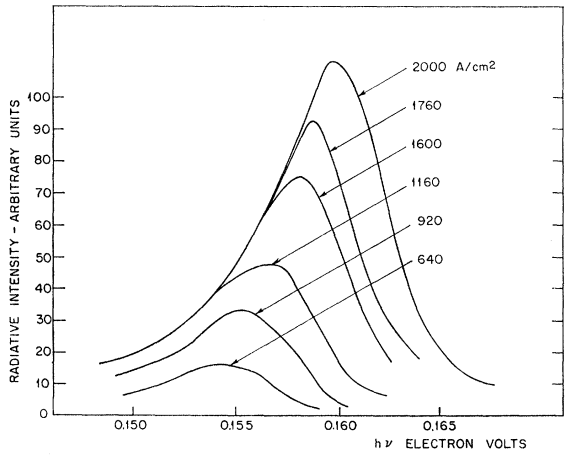

FIG. 9. Spontaneous emission spectrum of PbSe diode No. 111 at $P=1520$ bar and $T=77°K$, as a function of injection current (pulse length 8 μsec) over a spectral region close to the energy gap.

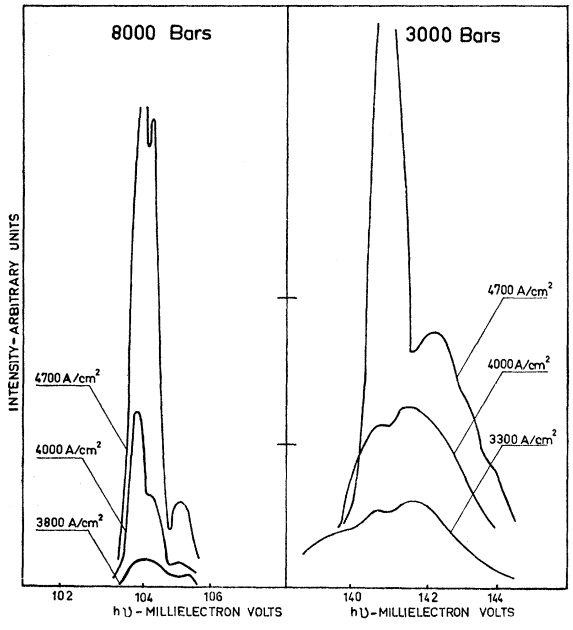

FIG. 10. Stimulated emission of PbSe diode No. 111 at 77°K and at pressures $P\sim3000$ and ~8000 bar, as a function of injection current density. Pulse lengths 600 nsec.

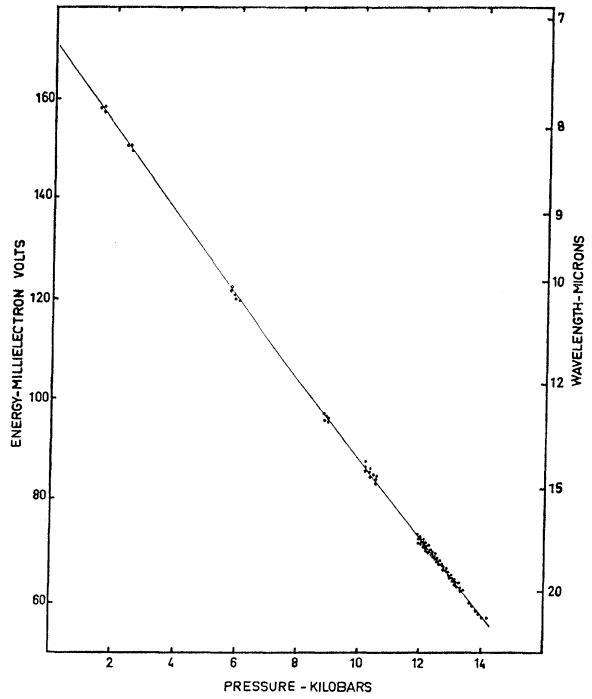

FIG. 11. Energy of the dominant mode of stimulated emission as a function of pressure at 77°K. Measurements on PbSe diode No. 111 at an injection current density of 4800 A/cm.[2]

The laser emission is in the neighborhood of the peak of the spontaneous emission. The wavelength of the principal laser emission at each pressure is plotted versus pressure in Fig. 11. At each pressure it is possible to study the shift of the dominant laser modes for small excursions of pressure. These shifts, and the mode-jumping which also occurs, are illustrated for pressures near 9 kbar in Fig. 12.

B. Analysis and Comment on Results

Although the principal aim of this work was to examine the possibility of "tuning" the laser emission to very long wavelengths, a few preliminary studies were done essentially at atmospheric pressure. These experimental results are presented here for completeness in Secs. 1 and 2 below, but they are not sufficient for the deduction of anything other than broad general conclusions about the nature of the emission.

1. Total Light Output

Since the total light output is being measured, Fig. 6 can be determined using short current pulses of less than 1 μsec, which helps to prevent heating of the diode. Figure 6 was actually determined at a constant pressure of about 2 kbar, which by ensuring good thermal contact also helps to avoid a rise in temperature between the diode and the helium gas in which it is immersed; however, the curve will represent the properties of the diode at atmospheric pressure well enough for our present purposes.

Part A of Fig. 6 shows that the number of emitted photons increases nonlinearly with injected current density at low injection levels. In Part B the emission increases at a stronger rate, while in parts C and D laser action takes place, as is indicated by the appearance of a spectrum of cavity modes. There is a great difference—for these diodes, and our optical setup—between the external efficiency of photon production in the laser regime and that in the regime of stimulated emission. Principally for this reason we chose to carry out our experiments on the shift of the emission with pressure at current levels above the laser threshold.

The decrease in emission with increasing temperature in the spontaneous regime is usual and may be due either to a change with temperature of the proportion of nonradiative recombination or to an increase in absorption by free carriers, or, of course, to a combination of effects. At the highest temperature 220°K, the emitted intensity is about linear in the current, while at 77°K, the variation over the same injection range is almost quadratic. It is again not possible to deduce a unique reason for this behavior from the few studies we have done.

From Fig. 7 we conclude that it is not easy to define a threshold current for laser action in these diodes at temperatures of 77°K and above. Roughly, the thresh-

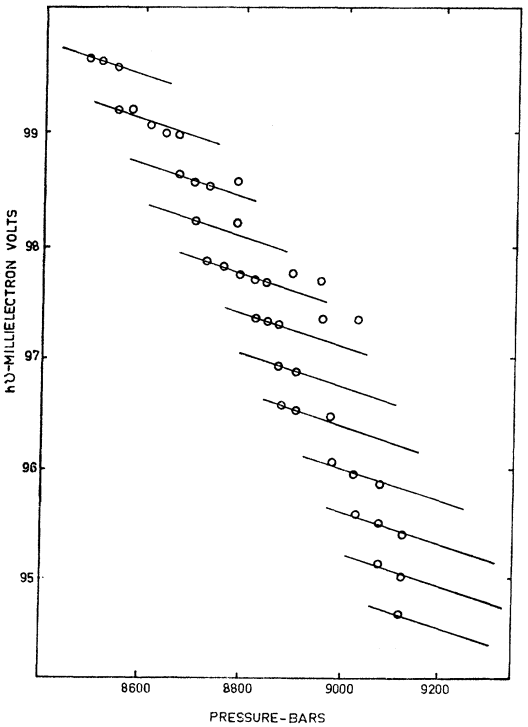

FIG. 12. Energy of the various laser modes seen between 8500 and 9200 bar, as a function of pressure. Measurements on PbSe diode No. 111.

old given by the maximum curvature of $\log I$ versus $\log J$, or by the appearance of line narrowing, increases a little more slowly than the square of the temperature up to 130 °K.

2. *Spontaneous Emission Spectrum*

The first thing to note about Figs. 8 and 9 is the tail to the emission at energies below the energy gap, which has an experimental spectral characteristic independent of injection current level, and an emission intensity independent of injection currents above 1160 A/cm². The second is the displacement of the peak in the emission to higher energies as the injection current density is increased.

Structure, presumably due to impurity effects but no identifiable experimental tail, was noted in the earlier work on electroluminescent PbSe.[29] No tail was reported in the study of photoluminescence of Washwell and Cuff.[30] However, despite the fact that there is less reabsorption of the emitted radiation in photoluminescent samples than in the electroluminescent diodes, the photoluminescent signal intensity is weak enough that any tail at low energies could be lost in the noise. A simple argument may be proposed to show that the exponential tail we observe can be related to the absorption coefficient of the bulk material and consequently is not a result of the excitation by means of a *p-n* junction.

The rate of spontaneous emission may be written[31]

$$r(h\nu)=[n(h\nu)^2/\pi c^2\hbar^3]\alpha \exp[\{(h\nu-\Delta F)/kT\}-1]^{-1}, \quad (1)$$

where n is the index of refraction, $h\nu$ the photon energy, α the absorption coefficient, and ΔF the energy difference between the quasi-Fermi levels of the electrons and holes. This expression gives, for the slope of a curve of the measured spontaneous emission intensity I versus energy,

$$\frac{d\ln I}{dh\nu}=\frac{d\ln r(h\nu)}{dh\nu}=\frac{2}{h\nu}+\frac{d\ln\alpha}{dh\nu}-\frac{1}{kT}, \quad (2)$$

where we have neglected the energy-dependence of $n(h\nu)$ and have supposed $(h\nu-\Delta F)/kT\gg 1$ in the spontaneous emission regime. From Fig. 8, $d\ln I/dh\nu = 0.138$ meV^{-1}, which, for $T=77$°K and $h\nu=140$ meV, leads to

$$\left[\frac{d\ln\alpha}{dh\nu}\right]^{-1}=3.6 \text{ meV}. \quad (3)$$

On the other hand, Prakash[7] finds that the absorption coefficient of PbSe at energies below the gap may be written

$$\alpha=A\exp\{(h\nu-E_g)/E_0\},$$

so that

$$\left[\frac{d\ln\alpha}{dh\nu}\right]^{-1}=E_0.$$

For PbSe with 10^{17} carriers cm^{-3} at 300°K, Prakash obtained $E_0=6.2$ meV. However, in the case of PbS he proposed a theory for the variation of E_0 with temperature of the form

$$E_0(T)\propto\{\tfrac{1}{2}+[\exp(\hbar\omega_{LO}/kT)-1]\}^{1/3}m^{*1/6}\epsilon_\infty^{-1/3}, \quad (4)$$

where $\hbar\omega_{LO}$ is the energy of the zero wave-vector longitudinal optical phonon, m^* the carrier effective mass, and ϵ_∞ the high-frequency dielectric constant. If we adopt the same functional form for $E_0(T)$ in the case of PbSe, if we ignore any temperature dependence of ϵ_∞, and set $m^*(300°\text{K})=0.11m_0$,[32] $m^*(77°\text{K})=0.06m_0$,[33] and $\hbar\omega_{LO}=0.017$ eV,[30] we deduce

$$E_0(77°\text{K})=4 \text{ meV}. \quad (5)$$

The closeness of the values in (3) and (5), despite the extrapolations involved, suggests that the same mechanism is responsible for the same experimental tails both in the absorption coefficient and in the spontaneous emission. One can also give the following qualitative physical argument to explain the independence of the slope of the exponential tail on current injection level, and of the saturation of the emission intensity in the tail as the current injection is increased. Let us adopt the model in which the transitions responsible are between states giving tails to the conduction and valence bands. If the injection current is very low, the carrier distribution in the tails is independent of it. On the other hand, if the injection current is high, the tails will be saturated, and the carrier distribution again independent of current injection. Only in a region between the two, when the quasi-Fermi levels enter the tails, will there be a dependence of carrier distribution (and so emitted radiation as a function of energy) on injection current. However, at low levels of injection the emitted intensity will depend on the injected current, while at high levels the carrier saturation in the tails will imply a similar saturation in the emitted intensity. The displacement of the peak of the emission with injection level may be due, in principle, either to filling of the normal band states or (apparently the case here) to a rise in temperature. If the former, the qualitative arguments on the tail emission are unaffected. If the latter, it might appear at first glance that the tail emission should also be displaced rigidly to higher energies: This change, however, tends to be

[29] J. F. Butler and A. R. Calawa (private communication).
[30] E. R. Washwell and K. F. Cuff, *Radiative Recombination in Semiconductors* (Dunod Cie., Paris, 1964), p. 11.
[31] J. Lasher and F. Stern, Phys. Rev. 133, A553 (1964).
[32] A. K. Walton and T. S. Moss, Proc. Phys. Soc. (London) 81, 503 (1963).
[33] D. L. Mitchell, E. D. Palik, and J. N. Zemel, in *Proceedings of the Seventh International Conference on Semiconductors* (Dunod Cie., Paris, 1964), p. 325.

compensated by the change in shape and state density of the tail at the higher temperatures. Conversely, the behavior of the tail emission as a function of current injection level tells us nothing about the reasons for the displacement of the peak of the emission.

In GaAs, a displacement of the peak of the emission to higher energies as a function of current injection level is explained by filling of the conduction band states of low energy. In PbSe, the positive temperature coefficient of the energy gap would lead to the same direction of displacement if the injected current heats the junction. Comparison of Figs. 6 and 9 shows that the increase of emitted intensity is smaller for Fig. 9 (taken with long current pulses in order to obtain the spectral distribution) than for Fig. 6 (taken with short current pulses, because only the integrated intensity was required). The difference may be attributed to heating of the junction, and the rise in temperature roughly estimated from Fig. 7. This rise in temperature can then be translated into an increase of the energy gap; when this is done it is found that within experimental error the whole displacement observed could be explained by heating, without any appeal to band filling. That this is the correct explanation in this case is confirmed by observations of the spectra at very short pulse lengths but variable pulse heights. This should eliminate heating while affecting the filling of the bands. No shift of the emission peak was found, strongly suggesting that heating is the cause of the shifts seen at longer pulse lengths.

The results and discussion of Secs. 1 and 2 were preliminary to the high-pressure measurements and were necessary for an estimate of the possible conditions for these experiments and for extensions to higher pressures. They were not, however, extensive enough to establish definitively the various processes involved, so that the conclusions drawn from them should be regarded as tentative.

3. *Dominant Laser Emission as a Function of Pressure*

It is necessary to be precise about what is being reported on Fig. 11. The low external intensity of the spontaneous emission gives preference to a measure of the stimulated emission under pressure. What is actually plotted is the energy and pressure at which an observed laser mode reaches its maximum intensity. The pressure range over which a mode is observed is usually less than 100 bar, and the uncertainty in an estimate of the pressure at which the peak emission intensity occurs of the order of 15 bar. The relation of the energy of the dominant mode to the energy gap will be considered below.

At a given pressure, the energy of the dominant laser mode increases slightly as the injection current density or pulse length is increased. Any part of this which were due to a temperature increase would not affect a deduction of the pressure coefficient of the energy gap, provided the temperature rise with injected current density were independent of pressure, and using the reasonable hypothesis that the pressure coefficient of the energy gap is only weakly temperature-dependent, if at all. On the other hand, if the shift is due to band filling, we must make careful corrections to obtain the energy gap from the energy of the laser emission. Clearly, a first step in this correction procedure is to determine all of the laser emission energies versus pressure at a fixed carrier injection density or, what is the nearest thing we can do experimentally, a fixed injection current density and pulse length.

From Fig. 11, we see that the slope of the curve of emission energy versus pressure decreases slightly near the top pressures. We shall now show that the displacement with pressure of the peak of the stimulated emission may be explained in terms of the linear decrease of the energy gap to the top pressure and a simultaneous decrease of the effective masses. Qualitatively, the decrease in the effective masses with pressure means that the quasi-Fermi levels will penetrate deeper into the bands for the same injected carrier density, and this will lead to a displacement of the peak of the emission towards higher energies which compensates to some extent the decrease of the forbidden gap with pressure. To demonstrate this quantitatively and to obtain the pressure coefficients of the gap and masses, we have to make certain working hypotheses: (a) We suppose that the emission is between conduction and valence bands which have equal effective masses constant in momentum $\hbar k$ and energy E. (b) We assume that the dominant laser modes appear near the maximum of the gain curve. (c) We suppose that the density of states effective mass varies linearly with pressure such that at zero pressure $(1/m_{D0})(dm_D/dP)=A$. As a first approximation only, $A=(1/h\nu)(dh\nu/dP)$, where $h\nu$ is the energy of the laser emission. More generally, we can set $A=\gamma^{-1}(1/E_{g0})(dE_g/dP)$, where, for example, γ takes the value 1 if all components of the mass tensor are determined by the energy gap E_{g0} and the value $\frac{3}{2}$ if only two components are so determined. (d) We suppose that the number of injected carriers is constant at all pressures for the same value of the injected current density and pulse length. This is a major assumption which is hard to justify rigorously. The relative independence of the current threshold for laser action on pressure is an argument in its favor. On the other hand, there is no guarantee that the current through the junction is carried in the same proportion by all the possible processes—for example, minority carrier injection, excess current through impurities, band-to-band tunneling—at all pressures. Also, even if the current were carried in the same proportion, the changes in parameters such as mobility, state density, and diffusion length ensure that equal injection current densities do not imply equal excess carrier populations. Without more knowledge of the current transport mechanism in PbSe diodes than we now have, it is

not worthwhile to attempt to deduce the changes in the excess carrier populations as a function of pressure. However, we can certainly examine later the dependence of the energy gap versus pressure curve deduced from Fig. 11 on *assumed* changes with pressure of the injected carrier density.

The calculation proceeds as follows. First we calculate the energetic distance of the quasi-Fermi level F from the extremum of a band, as a function of pressure, with A and the injected carrier density n_i as parameters. The appropriate formula is

$$n_i = 2(2\pi m_D kT^{3/2}/h^2)\mathfrak{F}_{1/2}(F/kT), \qquad (6)$$

where $\mathfrak{F}_{1/2}$ is the Fermi integral of order $\frac{1}{2}$, and m_D is the density of states effective mass, which varies with coefficient A as previously defined. We have used $m_{D0}=0.17$ times the free-electron mass, estimated from a value for the conductivity mass[33] of $0.06m_0$ and for the ratio of the ellipsoidal mass components[33] of 1.6. The value of conductivity mass used was confirmed independently from an analysis of curves of reflectivity versus wavelength and represents an average mass for a carrier density of 10^{18} cm^{-3}; however, it is a reasonable approximation to use it here since we have ignored nonparabolicity in the bands.

Using the deduced dependence of $F(P,n_i,A)$ we next calculate the energy $h\nu_{\max}$ of the maximum of the gain curve, which is where the stimulated emission will occur. We use the model of Lasher and Stern, which assumes that the presence of impurities in the junction eliminates any momentum selection rule on the band-to-band transitions, so that the rate of stimulated emission is given by

$$g = C\int_0^{h\nu-E_g} E^{1/2}(h\nu-E_g-E)^{1/2}\{[1+\exp(E-F)/kT]^{-1} - [1+\exp(E-F-h\nu+E_g)/kT]^{-1}\}dE. \qquad (7)$$

We then choose the best values for $E_g(P)$, $m_D(P)$, and n_i in order to fit the experimental variation of Fig. 11. For the following reasonable values of these parameters, we obtain a very good agreement between experiment and calculation, shown in Fig. 13:

(a) $2\times10^{17} < n_i < 2.8\times10^{17}$,

(b) $0.165\text{ eV} < E_g(0) < 0.170\text{ eV}$,

(c) $-9.2-0.2\times10^{-6} < (dE_g/dP)_{77^\circ\text{K}} < -9.2+0.2\times10^{-6}$ (eV bar^{-1}),

(d) $A=(1/m_{D0})(dm_D/dP)_{77^\circ\text{K}} = -34\times10^{-6}$ bar^{-1}.

Figure 13 also shows the sensitivity of the fitted curve to variations of n_i, and $\gamma=(1/A)(1/E_{g0})(dE_g/dP)$.

The values for $E_g(0)$ agree reasonably well with the values at 77°K given in the literature.[33] The Bernard-Duraffourg condition,[34] $E_g+2F \gtrsim h\nu$, obliges us to take $n_i \gtrsim 1.6\times10^{17}$, otherwise the quasi-Fermi levels would be in the forbidden gap; this limit also fits our selected injected carrier density. The pressure coefficient of the energy gap is also in good agreement with the literature values shown in Table II. The pressure coefficient is insensitive to the choice of γ and n_i. In particular, on Fig. 13 is shown the variation for two values of n_i differing by 40%. It seems clear that a continuous change with pressure of n_i would also very little affect the coefficient of the variation of E_g with P deduced here. The fit of experiment and calculation is not very sensitive to the value of γ chosen, but we find our best choice is $\gamma=1.6$. For comparison, Averkin, Ilisavsky, and Regel find $\gamma=1.5$.[35] These results agree with the notion that only two components of the effective mass tensor are proportional to the fundamental gap, but in view of the known mixing of the L-point states in PbSe, this might just be a fortuitous averaging effect, and should be treated with caution.

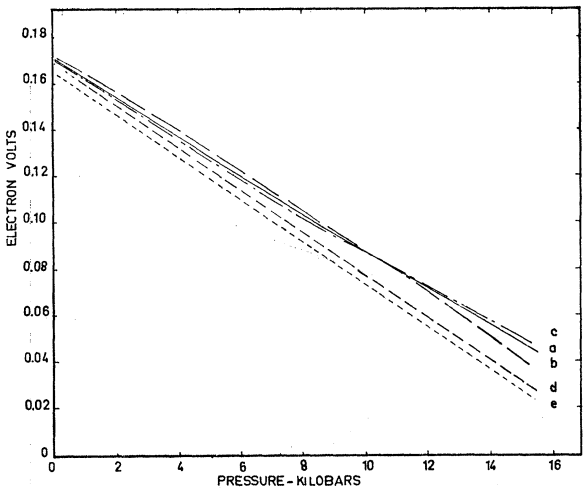

FIG. 13. Fit between the experimental variation of the emission peak (Fig. 11) and that calculated for different values of the injected current density (n_i), and of the pressure change of the effective mass (A or γ). Also shown is the deduced variation of the energy gap, for two assumed values of the injected carrier density. The curves are for the following conditions: (a) experimental curve almost coincident with $h\nu(P)$ calculated for $n_i=2\times10^{17}$ and $n_i=2.8\times10^{17}$, $\gamma=1.6$, (b) $h\nu(P)$ for $n_i=5\times10^{17}$, $\gamma=1.6$, (c) $h\nu(P)$ for $n_i=2\times10^{17}$, $\gamma=1.3$, (d) $E_g(P)$ for $n_i=2\times10^{17}$, $\gamma=1.6$, (e) $E_g(P)$ for $n_i=2.8\times10^{17}$, $\gamma=1.6$.

4. *Changes in Cavity Modes with Pressure*

The shift with pressure of a dominant cavity mode of a definite order depends only on the change of the optical dimensions of the cavity; the overall shift of the band gap and so of the spontaneous emission only helps to determine at what pressures the gain in this mode will be superior to the gain in others. From curves such as those of Fig. 12, we construct the variation of the slope $[\partial(h\nu)(\text{single-mode})/\partial P]_{77^\circ\text{K}}$ as a function of pressure,

[34] M. G. A. Bernard and G. Buraffourg, Phys. Status Solidi **1**, 699 (1962).

[35] A. A. Averkin U. V. Ilisavsky, and A. R. Regel, in *Proceedings of the Sixth International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 690.

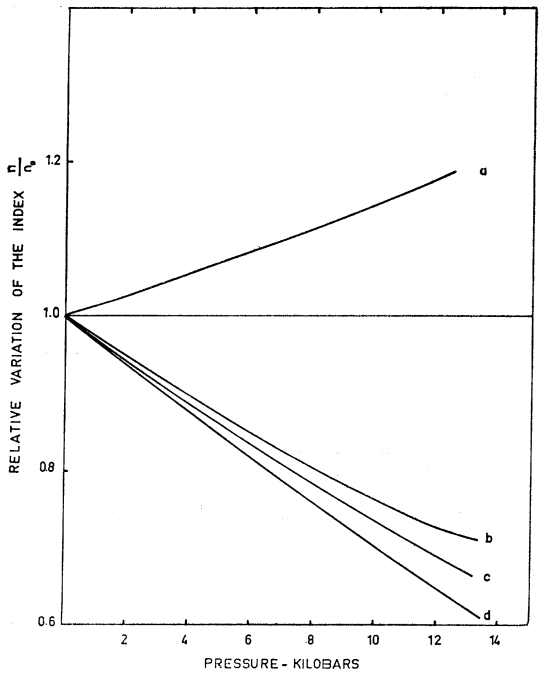

FIG. 14. Variation with pressure of the refractive index at the energy of the principal laser emission, i.e., near the energy of the maximum of the gain curve. Curve a is the experimental variation of the index. Curves b, c, and d are computed contributions from Eq. (12) of the part of the shift due to the band edge, for three slightly different assumptions about the energy of E_g.

shown in Table IV. Although the variation is not very well determined, it is clear that the slope goes through a minimum as a function of pressure; it is also clear that the magnitude of the shift is very much smaller than the pressure coefficient of the energy gap. It is also possible to observe at least two modes of a single cavity at the same time (a cavity which does not necessarily correspond to the length of the diode) and so to measure the change of the spacing of successive modes with pressure. This is also given in Table IV.

From the formula governing the appearance of modes, $2nl\nu/c=m$, where m is an integer, n the refractive index, l the length of the cavity, and ν the mode frequency, we can write

$$\frac{dn}{dP}=-\frac{n}{\nu}\frac{d\nu}{dP}-\frac{n}{l}\frac{dl}{dP}, \tag{8}$$

whose resolution for n gives us the change in the refractive index with pressure at the (changing) energy of laser emission; that is to say, we get the refractive index at about the energy of the peak of the gain curve. In order to obtain the rate of change of the index at a fixed frequency, one has to use the formula

$$\frac{dn}{dP}=-\left(\frac{n+\nu(dn/d\nu)}{\nu}\right)\frac{d\nu}{dP}-\frac{n}{l}\frac{dl}{dP}, \tag{9}$$

TABLE IV. Separation in wavelength of successive modes of the cavity and slope of the variation of individual modes with small pressure increments around a few selected pressure values. Diode PbSe #111—$T=77$°K.

Pressure kbar	0.4	2	3.6	6	8.4	9.1	12.1
Wavelength separation of successive modes mμ	···	20	23	31	45	48	80
Pressure coefficient of the energy of individual modes of the cavity 10^{-6} eV/bar	2.5	2.0	1.9	1.2	1.3	1.4	2

which one can resolve, for the quantity $n+\nu(dn/d\nu)$ is given by the mode spacing

$$\nu_{m+1}-\nu_m=[2l\{n+\nu(dn/d\nu)\}]^{-1}. \tag{10}$$

We show in Fig. 14 the variation of the n at the (changing) energy of laser emission (curve a), noting immediately that the change is a big one. One is tempted to try to analyze this change into a part related to the shift of the fundamental absorption edge to lower energies with pressure, and a part related to the changes of all other mechanisms producing dispersion at energies near the gap. This second part would be expected to be linear; first, because the main transitions causing high absorption and a large contribution to the index are much higher in energy, and second, because the contributions of free carriers and lattice vibrations are also small near the wavelengths of the experiment. One might try to calculate the contribution of the first part, the shift of the fundamental edge, starting from the contribution Δn to the index, given by an absorption edge which is exponential below the gap energy E_g, and which varies as $(h\nu-E_g)^{1/2}$ just above the edge. However, at energies just above the gap (which is where we measure the index, since the laser emission occurs there), the main contribution should come from the direct band-to-band transitions and thus be given by

$$\Delta n_g=Am^{*3/2}(h\nu+E_g)^{1/2}/h\nu, \tag{11}$$

where m^* is a reduced mass for the valence and conduction bands. We saw earlier that $(1/m^*)(dm^*/dP)\approx\frac{2}{3}(1/E_g)(dE_g/dP)$, so that it becomes clear that, under pressure, the effects of changing mass and frequency of measurement in Eq. (11) will oppose each other, the net effect being a *decrease* of Δn_g with pressure. We have included in Fig. 14 the variation $\Delta n_g(P)/\Delta n_g(0)$ computed using Eq. (11) and Fig. 13. The nonlinear experimental variation of Δn and the nonlinear computed variation of Δn_g are qualitatively self-consistent, if we suppose that the contribution of the other transitions to Δn is dominant and positive. It seems unlikely that a more exact evaluation from the Kramers-

Kronig integral of the change in Δn_g would alter this conclusion. However, we are more inclined to think that the use of the single expression (11) is an error here, and that the large change in n is somehow directly related to effects near the band gap. The quoted form of the dependence of α on energy is what is found experimentally, except that the dependence on mass is not explicitly demonstrated. Perhaps it is significant that we have never been able to identify, in pressure experiments, changes in the slope of absorption curves due to mass changes. Because of this uncertainty that the calculated $\Delta n_g(P)/\Delta n_g(0)$ is correct, it has not seemed worthwhile to proceed further with the separation of the observed change in n into its two components.

If we use Eq. (9) to obtain dn/dP at fixed energy, we discover from the mode spacing that $dn/d\nu$ is quite small, $[n+\nu(dn/d\nu)]$ is little different from n, and $(1/n)(dn/dP)$ near zero pressure has the value $(13.5\pm1)10^{-6}$ bar^{-1}. For the reasons cited above, we again cannot divide this into a part due to the shift of the fundamental edge and a part due to other transitions. Also, there have been no independent experimental measurements of dn/dP, say from measurements on interference fringes under pressure. We can however make a qualitative comparison with the results of Prakash[7] on PbS. He found, for energies close to the gap energy, $(1/n)(dn/dP)(300°\text{K})\approx 7\times10^{-6}$ bar^{-1}. The value for PbSe is two times larger, but this does not seem unreasonable.

C. Other Observations

The spontaneous emission intensity decreased under pressure for all values of the injection current density below threshold. The decrease was less the closer the current was to threshold. As an example, it was about a factor of 5 for one diode between 1 and 8 kbar at a current density of 3000 A/cm^2, when the lasing threshold was just over 4000 A/cm^2.

The threshold current for laser action was little affected by pressure. The emitted laser intensity just above threshold was on the average not much changed by the pressure. Depending on the diode and the actual injection current for that diode, the laser intensity could increase or decrease; the increases seem to be correlated with monomode operation of the diode and the decreases with operation in several modes simultaneously. We found no certain evidence for a decrease in the efficiency of stimulated radiative recombination of the material itself.

5. CONCLUSIONS

We have shown that the emission wavelength of PbSe diodes may be changed from about 7 μ at atmospheric pressure to 22.5 μ at the freezing pressure of helium at 77° K, 14 150 bar, without recognizable decrease in the laser efficiency. In this section, we shall consider the possibility of further extending the emission wavelength, the opportunities for physical studies and device application that would afford, and the extension of this technique to other members of the PbSe family.

A. Extension to Higher Pressures

If we assume that we exclude, for reasons of laser efficiency, operating temperatures above 77°K, further extension of the pressure range implies the use of solid pressure media. Maintenance of hydrostatic pressure (which is not absolutely essential for all purposes here) is probably best achieved by creating a high hydrostatic pressure at elevated temperature and then cooling the assembly through the freezing point of the pressure fluid. We have verified that the diodes used in the present study survive undamaged in solid helium. Raising the pressure in a soft solid, although not inconceivable, is probably less satisfactory if quantitatively interpretable results are sought. Assuming that the high pressure can be produced, it is very likely that windows of pure silicon and germanium of somewhat reduced aperture will both withstand the pressure and be transparent through the infrared. We have established that PbSe diodes continue to have diode characteristics at room temperature to at least 29 kbar. Since the energy gap predicted at this pressure and temperature is almost exactly zero, it seems that the diode characteristic would also be good at 77°K and pressures beyond 14 kbar.

B. Physical Studies

We have shown in the previous section that we cannot detect a departure of the variation of the energy gap with pressure from linearity to pressures of 14 kbar. When the decrease in the lattice constant is large there is no reason, in principle, why the shift in the energy gap should be linear with pressure. In the case of the L_6^+ and L_6^- states, which appear to determine the extrema of the valence and conduction bands at all pressures, the likely change in the gap would seem to be a monotonic (not necessarily linear) decrease to zero, followed by a monotonic increase at still higher pressures, with the symmetry of the valence and conduction band extrema inverted from that shown in Fig. 2 for atmospheric pressure.[36] The possibility of examining the changing band structure under such novel conditions, through a study of luminescence or by other optical or transport experiments, is one of the attractions of an extension of the work described here.

It should be added that it seems unlikely that the phase transition which occurs at 43 kbar at room temperature is caused by the electronic contribution to the free energy. In our picture the minimum energy gap is zero and occurs near 29 kbar at room temperature so that by 43 kbar the number of carriers will be smaller

[36] We are grateful to Dr. John Dimmock for correction and clarification of an early version of the manuscript.

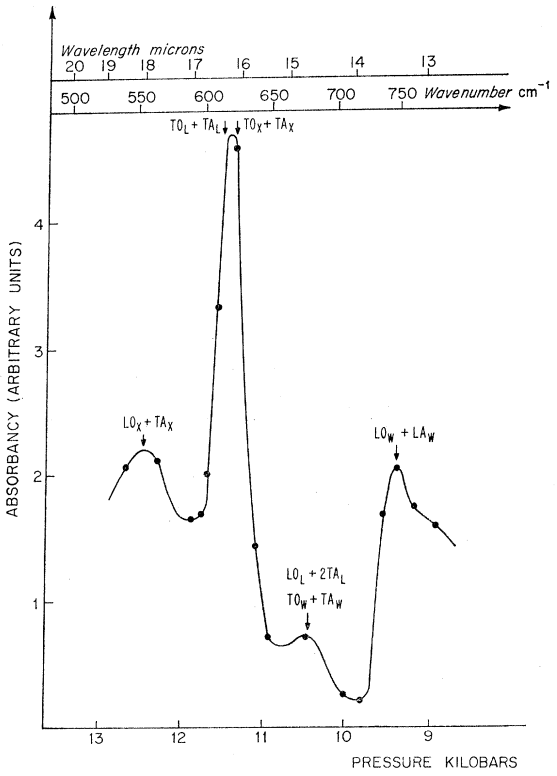

FIG. 15. Absorbance of the silicon pressure windows at 77°K. Curve taken by measuring the intensity of laser emission as a function of pressure, without using conventional dispersion methods. The labels identify combinations of lattice vibration frequencies believed responsible for the absorption.

than at 29 kbar; furthermore the analogous transition in PbS, which has a larger gap at zero pressure and the same pressure coefficient, occurs at considerably lower pressure (see Table I). Thus we do not expect that, at 77°K, a lattice distortion will occur in the pressure range where the energy gap is extremely small.

The laser emission wavelength, if observed, will decrease less fast than that corresponding to the energy gap, under conditions of constant number of injected carriers, because of the decrease of effective mass with pressure and the resultant increase in band filling. However, if the critical injection density for laser action can be reduced—the Bernard-Duraffourg conditions will be more easily satisfied as the gap decreases, but other recombination processes may intervene, see below—the departure of the laser wavelength from that corresponding to the gap may not be great.

As the gap becomes of the order of single-phonon energies, we expect to find some change in the proportion of recombination by the three processes (1) with emission of photons, (2) with emission of phonons in a single or multiphonon transition, (3) by the Auger effect, the excess energy going to a third carrier. The third process becomes increasingly important as the energy gap becomes smaller, as may be judged from the standard treatments of the effect. It is easy to show that, when the energy gap becomes smaller than the energy of the smallest zero wave-vector phonon, the conditions for simultaneous conservation of energy and momentum in conduction-band to valence-band transitions involving single long-wavelength phonons are easily satisfied, and that these wavelengths can be of the same order of magnitude as the dimensions of the diode cavity. If the phonon emission becomes a very important process there remains the difficulty of its demonstration, other than by the absence or decrease of radiative emission. The possibility arises of the energy of recombination entering a few simple, dominant cavity modes of vibration, and the practical question of their transmittal into a neighboring medium. At somewhat larger values of the band gap, energy and momentum conservation could be satisfied by simultaneous two-phonon emission where the wavelengths are comparable with atomic dimensions. Whether under these conditions of increased probability of phonon emission and Auger excitation, laser effects will remain possible cannot be predicted. Whether laser emission continues or not, any spontaneous recombination radiation will be strongly absorbed at the wavelengths of the lattice vibrations (between 40 and 80 μ for the two-phonon processes and between 80 and 250 μ for the single-phonon process). Thus there are rich possibilities for fundamental studies of the mechanism of recombination as the energy gap decreases into the critical range of phonon energies.

C. Device Applications

Since laser action is maintained to at least 22.5 μ it is clear that—even allowing for the difficulties of the present assembly—a tunable source of energy of considerable power and undoubted monochromaticity already exists. An interesting byproduct of our present study has been the spectrum of laser radiation transmitted through the Si pressure windows and measured without a monochromator. The peaks in the deduced absorbance shown in Fig. 15 correspond exactly with certain combinations of lattice vibration frequencies, as first established using conventional monochromator methods by Balkanski, Nazarewicz, and DaSilva.[37] It would appear that at even longer wavelengths, where powerful sources are harder to find, and provided the laser efficiency remains, the present system might sometimes be useful.

The tuning of the energy gap by pressure could also provide a photocell of variable wavelength sensitivity. Despite the fact that photocells of germanium and silicon doped with impurities having energy levels at different distances from the nearest band now provide very sensitive detectors over very wide ranges of the infrared, it might for some applications be useful to have

[37] M. Balkanski, W. Nazarewicz, and E. DaSilva, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 347.

an intrinsic material of proved high sensitivity in one region of the spectrum whose range of maximum sensitivity could be varied continuously. A first step in the direction of such development was already taken in 1959 by Prakash and Paul,[38] who tuned the wavelength of sensitivity of a commercial PbS photocell to longer wavelengths at the rate expected from the variation of the energy gap with hydrostatic pressure.

D. Other Members of the Chalcogenide Family

The other members of this family we wish to consider briefly are PbS and PbTe, and the chalcogenides of Sn and Ge. The band structures of PbS and PbTe near the fundamental gap are almost certainly of the same form as that of PbSe, and the gap pressure coefficients are about the same also. However, the energy gaps at atmospheric pressure are larger so that higher pressures would be needed to reach very long wavelengths.

Some of the compounds of Sn and Ge are noncubic, but the distortion is small enough that this does not affect our present general argument.[39] The replacement of Pb by Sn or Ge affects the energy of the state L_6^+ most. In this state, the wave function concentrates charge near the cation nucleus more than for the other L-point states, and this (see Fig. 2) leads to a very large relativistic correction to the energy when the cation is heavy. The correction is sufficiently smaller when Pb is replaced by Sn or Ge so that the L_6^+ state rises in energy above the L_6^- conduction-band state, which leads to semiconductivity in all of the cubic Sn or Ge compounds but with a band structure near the Fermi level inverted from that of Fig. 2. It is immediately evident that, in the very probable event that the deformation potentials remain approximately the same for the states in the inverted structure, experiments to determine the band-gap variation with pressure would give direct confirmation of the present hypotheses. At the time of writing these have not been reported.

What has been reported is the variation of the optical band gap in alloys of PbTe with SnTe [40] and of PbSe with SnSe.[41] It is found that the band gap decreases with alloying starting from either of the pure components, and that the temperature coefficient of the band gap changes sign between the end components. It should be remarked that, although this change of sign of the band gap temperature coefficient has been quoted as an integral part of the argument for band inversion,[40,41] such a change is contrary to the prediction of a negative coefficient by the presently accepted theory for the effect of temperature on band gaps.[5,8] The positive temperature coefficient of the band gap in the lead chalcogenides is thus "anomalous," but the observed change of sign in the alloys, while confirming the need for a new theory,[8,42] localizes the problem to a consideration of the properties of electronic states in which the charge is very differently distributed about two atoms of a lattice which because of their different masses may have very different vibrational amplitudes.

In the context of the present study, the decrease of the band gap in the alloys suggests immediately that, in the likely event that the deformation potentials remain relatively unchanged, alloys at the lead-rich end of the series will have smaller band gaps at atmospheric pressure than PbSe, but the same large negative pressure coefficient. The difficulties of experimentation at pressures beyond 15 kbar are thus circumvented, although the problem of quantitative interpretation of an alloy rather than a pure material appears. This however does not seem to be a serious drawback. The results so far reported have been for Sn alloys but the same arguments are clearly applicable to even lighter group IV elements such as Ge.

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[38] V. Prakash and W. Paul, (unpublished).

[39] The papers of Pratt and his group provide the quantitative data underpinning the qualitative description given here.

[40] J. O. Dimmock, I. Melngailis, and A. J. Strauss, Phys. Rev. Letters **16**, 1193 (1966).

[41] A. J. Strauss (private communication).

[42] A. Bienenstock and F. Molea, Bull. Am. Phys. Soc. **11**, 232 (1966).