

tering, and were found in reasonable agreement with the assumed cross section for He-He scattering. If the liquid were indeed at the temperature determined by beam measurements and had its usual vapor pressure of 7 Torr, the apparatus would have been overloaded with He. The liquid results do not depend significantly on bath temperature, on changes in the arrangement of heat exchangers and inlet pipe geometry, or on the level of vibration as qualitatively altered by operating a number of extra mechanical pumps. Adequate time to attain equilibrium was allowed.

The data indicate that the Maxwell-Boltzmann distribution is valid for helium gas down to 0.6°K and indirectly confirm the validity of the Massey-Mohr scattering theory in the low-energy limit. The evaporating liquid velocities are similarly distributed in the usual modified Maxwellian way, but are characterized by a velocity that would be associated with a gas warmer by  $1.0 \pm 0.1^\circ\text{K}$  than the actual source temperature.

It is perhaps premature to try to attribute this result to the well-known quantum properties of He II, but it is interesting that the energy excess per atom is in agreement with that predicted by Toda<sup>5</sup> for the formation of eight-atom microcrystallites ( $1.05^\circ\text{K}$  per atom).

Further development of these techniques will be necessary before beams emitted from liquids can be observed over a wider range of temperatures and with other gases. We feel that the classical molecular-beam method as exemplified by this first experiment can serve as a useful tool in the study of the microscopic properties of liquid helium. Meyer *et al.*<sup>6</sup> have observed the velocities of atoms evaporated by heat pulses from films of <sup>3</sup>He and <sup>4</sup>He within a small sealed cavity, and found several anomalous effects. No comparison with our results seems immediately apparent.

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\*Present address: Bell Telephone Laboratories, Crawford Hill Laboratory, Holmdel, New Jersey.

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## BAND STRUCTURE AND LASER ACTION IN $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$

J. O. Dimmock, I. Melngailis, and A. J. Strauss

Lincoln Laboratory,\* Massachusetts Institute of Technology, Lexington, Massachusetts

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This Letter reports the observation of spontaneous and coherent emission in the vicinity of  $15 \mu$  from  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  alloys at  $12^\circ\text{K}$  optically excited by radiation from a GaAs-diode laser. A model of the band structure of the alloy system is proposed to explain the composition dependence of the band gap and the change in sign of the temperature coefficient of the band gap between PbTe and SnTe.

In the photoluminescence experiments a small crystal sample and the GaAs laser pump were mounted on a copper heat sink which was in contact with liquid helium.<sup>1</sup> The Fabry-Perot cavity was formed by two parallel faces of the sample which were perpendicular to the surface irradiated by the GaAs laser beam. Current pulses of a few microseconds duration

were applied to the GaAs diode at the rate of 3000/sec.

Figure 1 shows the emission spectra of a  $\text{Pb}_{0.81}\text{Sn}_{0.19}\text{Te}$  laser at  $12^\circ\text{K}$ , below and above threshold. The sample was a vapor-grown *n*-type crystal ( $n = 1.7 \times 10^{17} \text{ cm}^{-3}$  at  $77^\circ\text{K}$ ) with the as-grown shape of a parallelepiped  $550 \mu$  long in the direction of laser emission. The onset of coherent emission, which was evidenced by an abrupt increase in emission intensity as well as by the appearance of mode structure, occurred at a GaAs-diode current of 3.7 A, which corresponds to approximately 1.5 W of  $0.84\text{-}\mu$  radiation. A single cavity mode at  $15.9 \mu$  was excited at currents between 3.7 and 8 A, and multimode operation was observed at higher currents. The mode spacing corresponds

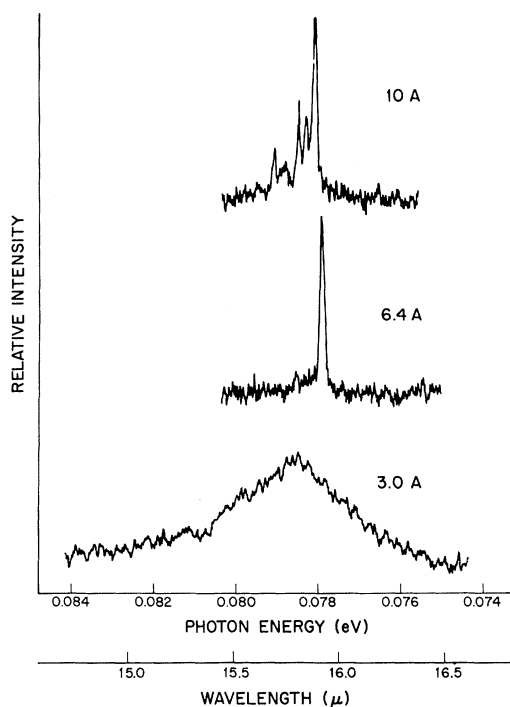


FIG. 1. Emission spectra of optically excited  $\text{Pb}_{0.81}\text{Sn}_{0.19}\text{Te}$  at about  $12^\circ\text{K}$ , obtained below threshold at a GaAs-diode current of 3 A and above threshold at 6.4 and 10 A. The spectra above threshold show resolution-limited mode structure.

to a value of approximately 6.5 for the quantity  $[n_0 - \lambda_0 dn/d\lambda]$ . Coherent emission was also obtained from a  $\text{Pb}_{0.83}\text{Sn}_{0.17}\text{Te}$ -alloy sample at  $14.9 \mu$ .

The luminescence data of Fig. 1 give an energy gap of 0.078 eV for  $\text{Pb}_{0.81}\text{Sn}_{0.19}\text{Te}$  at  $12^\circ\text{K}$ , compared to 0.186 eV obtained in PbTe from luminescence measurements at this temperature.<sup>2</sup> A decrease of the energy gap with increase in Sn concentration has also been observed in Pb-rich  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  alloys at  $300^\circ\text{K}$  by means of optical-absorption measurements.<sup>3,4</sup> However, recent tunneling experiments<sup>5</sup> have indicated that SnTe is a semiconductor with an energy gap at  $4.2^\circ\text{K}$  of approximately 0.3 eV, i.e., larger than the energy gap of either PbTe or  $\text{Pb}_{0.81}\text{Sn}_{0.19}\text{Te}$  at low temperatures. Furthermore, inspection of the tunneling data at  $300^\circ\text{K}$  indicates that the band gap in SnTe at this temperature is approximately 0.18 eV, i.e., smaller than the gap in SnTe at low temperatures. This decrease in the energy gap with increasing temperature is opposite to the temperature dependence of the energy gap in PbTe. These results lead us to propose a band-

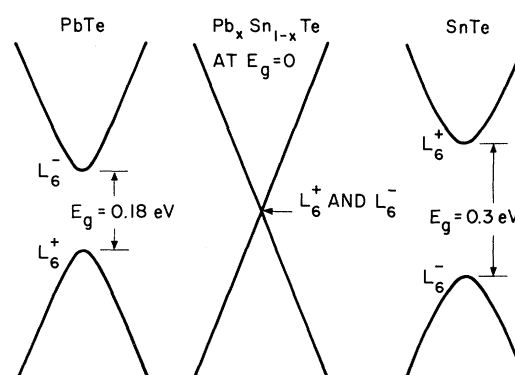


FIG. 2. Schematic representation of the valence and conduction bands at  $12^\circ\text{K}$  for PbTe, for the composition at which the energy gap is zero, and for SnTe.

structure model for the  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  alloys in which the valence and conduction bands of SnTe are inverted from those of PbTe.

The valence- and conduction-band edges in PbTe occur at the  $L$  point in the Brillouin zone. It is believed that the valence-band edge is an  $L_6^+$  state and the conduction-band edge is an  $L_6^-$  state.<sup>6</sup> According to our proposed band model, with increasing Sn composition the energy gap initially decreases as the  $L_6^+$  and  $L_6^-$  states approach each other, goes to zero at some intermediate composition where the two states become degenerate, and then increases, with the  $L_6^+$  state now forming the conduction-band edge and the  $L_6^-$  state forming the valence-band edge. Since the  $L_6^+$  and  $L_6^-$  states each have only a two-fold spin degeneracy, their crossover does not result in a semimetal but in a semiconductor with the valence and conduction bands interchanged. Figure 2 shows schematically the proposed valence and conduction bands for PbTe, for the composition at which the energy gap is zero, and for SnTe.

In Fig. 3, we have plotted the energy gap as determined by the luminescence data at low temperatures and by the optical-absorption data at  $300^\circ\text{K}$ . The gap energies determined from the tunneling experiments in SnTe are also plotted but as negative values to conform with the proposed inverted-band model. A dashed curve has been drawn through the low-temperature data to indicate roughly the gap variation with composition, and a parallel curve has been drawn through the room-temperature data. The extrapolations indicate that at  $12^\circ\text{K}$  the energy gap passes through zero at  $1-x \approx 0.35$  whereas at  $300^\circ\text{K}$  this occurs at  $1-x \approx 0.62$ .

The change in energy gap with composition for the  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  alloy series can be understood qualitatively in terms of the difference between the relativistic effects in Pb and Sn. Conklin, Johnson, and Pratt<sup>6</sup> have calculated the band structure of PbTe and have shown that relativistic corrections are extremely important in determining the positions of the energy bands. An estimate of the difference in these corrections for the conduction and valence bands of PbTe and SnTe can be obtained from the calculated band functions of PbTe and the difference in the relativistic effects for the valence states of atomic Pb and Sn. The band calculations indicate that about 36% of the valence-band  $L_6^+$  state comes from a Pb  $s$  state and 31% of the conduction-band  $L_6^-$  state comes from a Pb  $p$  state. The difference between the relativistic shifts of the valence states of Pb and Sn is 2.75 eV for the  $s$  states (6s for Pb vs 5s for Sn) and 0.73 eV for the  $p$  states.<sup>7</sup> Using these values, we estimate an upward shift of the  $L_6^+$  state by 0.99 eV and of the  $L_6^-$  state by 0.23 eV in going from PbTe to SnTe. This corresponds to a relative shift of 0.76 eV and indicates that the bands should cross at some intermediate value of composition. The data and interpretation indicated in Fig. 3 call for a shift of only about 0.5 eV. Relativistic effects, therefore, more than account for the change in energy gap required by the model. On the basis of the difference between the relativistic shifts in Pb and Sn, similar variations in band structure with compositions can be expected in the  $\text{Pb}_x\text{Sn}_{1-x}\text{Se}$  and  $\text{Pb}_x\text{Sn}_{1-x}\text{S}$  alloys

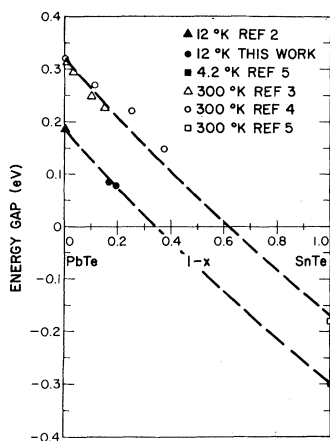


FIG. 3. Energy gap of  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  as a function of mole fraction of SnTe,  $1-x$ . The data points are obtained from luminescence at 12°K, optical absorption at 300°K, and tunneling in SnTe at 4.2° and 300°K.

with rocksalt structure.

Due to the energy-band crossover, the temperature dependence of the energy gap for SnTe and the Sn-rich alloys is of opposite sign and, as can be seen from the data in Fig. 3, about equal in magnitude to that of PbTe and the Pb-rich alloys. This should be true for the pressure dependence of the energy gap as well. For alloys on the Sn-rich side of  $\text{Pb}_{0.65}\text{Sn}_{0.35}\text{Te}$  it should be possible to close the energy gap by increasing the temperature. For alloys on the Pb-rich side it should be possible to close the energy gap by increasing the pressure. The energy gap in SnTe should close at about 470°C whereas at 12°K the energy gap in PbTe should close at about 25 kbar.<sup>8</sup> For the alloy  $\text{Pb}_{0.81}\text{Sn}_{0.19}\text{Te}$ , the energy gap at 12°K should close at about 10 kbar assuming that the pressure coefficient is the same as in PbTe. The possibility of arbitrarily reducing the energy gap by changing the composition or by varying pressure or temperature is especially attractive for use in long-wavelength infrared detection as well as for tunable long-wavelength lasers. Unfortunately, many of the interesting transport phenomena associated with small energy gap and small effective masses may be obscured in the  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  alloys because at present they can be grown only with very high carrier concentrations. However, it should be interesting to observe the luminescence as the gap energy approaches the vicinity of the optical-phonon energies. This occurs at 0.0135 eV or 92  $\mu$  (longitudinal) or 0.0039 eV or 320  $\mu$  (transverse) in PbTe.<sup>9</sup> One would expect the luminescence to be quenched in the vicinity of these energies due to the possibility of nonradiative interband transitions via optical phonons. On the other hand, this may result in the generation of unusually high optical-phonon densities. If quenching does occur, it would also be interesting to see if the luminescence resumes at longer wavelengths and if so at what wavelength it finally ceases.

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<sup>1</sup>For details of the experimental arrangements, see

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## CRITICAL CURRENTS AND SURFACE SUPERCONDUCTIVITY

J. G. Park

Department of Physics, Imperial College, London, England

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In a certain range of magnetic field, metals for which the Ginzburg-Landau parameter  $\kappa$  is greater than 0.417 are superconducting only in regions close to the surface—we suppose the field to be directed everywhere parallel to the surface. Superconductors with  $\kappa > 0.417$  include both type-2 superconductors ( $\kappa > 0.707$ ) for which this range of field extends from the upper critical field of the mixed state ( $H_{C2}$ ) up to the nucleation field for surface superconductivity ( $H_{C3}$ ), and the class of type-1 superconductor—we shall call them type-1-2 superconductors—for which the range of field runs from the thermodynamic critical field ( $H_C$ ) up to  $H_{C3}$  ( $0.417 < \kappa < 0.707$ ). The three critical fields are related through  $\kappa$ :  $H_{C2} = \sqrt{2} \kappa H_C$ ,  $H_{C3} = 1.695 H_{C2}$ .<sup>1</sup> In a cylindrical sample whose axis is parallel to the field, the surface superconducting layer forms a hollow cylindrical sheath. Persistent currents induced by the magnetic field as it is changed, inevitably, from one value to another during the measurement of magnetization, at constant temperature, can be expected to flow in this sheath, just as they do in a superconducting tube, and to produce hysteresis effects in the magnetization curve: A hysteretic tail is observed in the magnetization curves of type-1-2<sup>2,3</sup> and type-2 superconductors<sup>4</sup>; hysteresis due to surface currents is also found in the mixed state of type-2 superconductors.<sup>5</sup> This type of hysteresis can be distinguished from hysteresis caused in other ways by the form of the minor hysteresis loops and its sensitivity to surface condition. It is brought about because the component of magnetization  $I$  pro-

duced by the induced surface currents is diamagnetic when the field is increasing and paramagnetic when it is decreasing. Let us call  $|I|$  the surface current magnetization  $M$ . See Fig. 1(a).

Fink and Barnes<sup>6</sup> have recently pointed out that we must expect  $M$  for a cylinder in a field parallel to its length to depend on the radius of the cylinder ( $R$ ) and they have described a method of calculating it. Fink has applied the results of that paper to the calculation of the real and imaginary part of the ac susceptibility.<sup>7</sup> We have also calculated  $M$ , in the same limit ( $R \gg \lambda/\kappa$ , where  $\lambda$  is the penetration depth), but by a different method which avoids some of the approximations made by Fink and Barnes; our results are in general rather smaller than theirs, particularly for low values of  $\kappa$  when the reduced field  $h$  is small ( $h = H_0/H_{C2}$  where  $H_0$  is the applied field). In this Letter we describe our calculation of  $M$  and also our calculation, by a similar method, of the critical current of a foil carrying a current.

We assume the Ginzburg-Landau equations and the expression for the free energy from whose minimization they may be derived, to describe the behavior of our material. Suppose the surface of the material to be the plane  $x = 0$  and the surface current  $\vec{j} = (0, j, 0)$  to be everywhere normal to the field  $H = (0, 0, H(x))$ . We choose a vector potential  $\vec{A} = (0, A, 0)$  and write the order parameter  $\psi$  in the form

$$\psi/\psi_0 = f(x)e^{iky},$$

where  $\psi_0$  is the order parameter in zero field,