Solid State Research 1968

Prepared under Electronic Systems Division Contract AF 19(628)-5167 by

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Lexington, Massachusetts
The work reported in this document was performed at Lincoln Laboratory, a center for research operated by Massachusetts Institute of Technology, with the support of the U.S. Air Force under Contract AF 19(628)-5167.

This report may be reproduced to satisfy needs of U.S. Government agencies.

This document has been approved for public release and sale; its distribution is unlimited.

Non-Lincoln Recipients

PLEASE DO NOT RETURN

Permission is given to destroy this document when it is no longer needed.
This report covers in detail the solid state research work at Lincoln Laboratory for the period 1 February through 30 April 1968. The topics covered are Solid State Device Research, Optical Techniques and Devices, Materials Research, and Physics of Solids.

Accepted for the Air Force
Franklin C. Hudson
Chief, Lincoln Laboratory Office
INTRODUCTION

1. SOLID STATE DEVICE RESEARCH

Photovoltaic detectors with long-wavelength cutoffs up to 20 μ at 77°K and up to 30 μ at 12°K have been produced from annealed Bridgman-grown and vapor-grown Pb₁₋ₓSnₓTe crystals in the 0 < x < 0.25 composition range. Responsivities as high as 190 V/W, detectivities of nearly 10¹⁰ cm/W s·c⁰¹², and external quantum efficiencies up to 37 percent have been obtained at wavelengths up to 12 μ in diodes operated at 77°K. Detectivities at 12°K were generally about an order of magnitude higher than at 77°K.

Photoconductivity at wavelengths up to 15 μ has been observed at 77°K in Bridgman-grown and subsequently annealed crystals of Pb₁₋ₓSnₓTe which had carrier concentrations as low as 2 × 10¹⁵ cm⁻³ and 77°K mobilities of about 3 × 10⁴ cm²/V sec. Detectivity values between 10⁸ and 10⁹ cm/W sec¹² at 77°K and 10¹⁰ cm/W sec¹² at 4.2°K were measured. Photoconductive lifetimes of about 10⁻⁸ and 10⁻⁶ sec were obtained at the two respective temperatures.

Diode lasers with low thresholds and emission wavelengths up to 28.1 μ have been fabricated from vapor-grown single crystals of Pb₁₋ₓSnₓTe containing Bi as the dominant donor impurity. For x > 0.2, 77°K threshold current densities were less than 1500 A cm⁻². With pulse bias, a peak power output of 0.1 W and an external quantum efficiency ηₓ of 0.08 were observed in a Pb₀.₈Sn₀.₂Te diode at 12°K, and a peak power of 0.03 W with ηₓ = 0.01 was measured at 77°K. With CW operation at 12°K, 5 × 10⁻³ W with ηₓ = 0.03 was obtained.

Extrinsic far-infrared photoconductivity has been observed at 4, 2°K in high-purity n-type epitaxial layers of GaAs grown on Cr-doped semi-insulating GaAs substrates. Responsivities as high as 5 × 10⁴ and 4 × 10⁴ V/W have been measured at 195 and 337 μ, respectively. At 902 μ, the responsivity dropped to 9 × 10² V/W. Measurements of the noise in the detection system at 300 Hz in a 1-Hz bandwidth yield an NEP of 1.2 × 10⁻¹¹ W at 195 μ, 1.4 × 10⁻¹² W at 337 μ, and 6 × 10⁻¹¹ W at 902 μ. The time constant of the detector has been determined to be shorter than 1 μsec using a Ge avalanche modulator to chop the incident radiation. A time constant of about 5 nsec was measured using impact ionization in the GaAs.

We have found that proton radiation damage can be used to convert both p- and n-type GaAs into high-resistivity material, and have used this technique to isolate p-n junctions on a diffused GaAs substrate and also to prevent edge breakdown in Au-GaAs Schottky barriers. This technique of creating high-resistivity material should be useful for the fabrication of structures in which thin high-resistivity layers are required.

The photovoltaic response of InSb-MOS detectors to modulated 3.9-μ radiation from an InAs diode emitter has been measured at 77°K following irradiation with short wavelength light in the energy range between 1 and 5 eV. Effects are observed due to trapping and detrapping of electronic charge at oxide states and/or at oxide-InSb interface states; however, the precise model for this trapping has not yet been determined.
II. OPTICAL TECHNIQUES AND DEVICES

The 100-W CO\textsubscript{2} laser amplifier has been operated in the sealed-off mode and yields an output of 88 W compared with 114 W using a flowing gas mixture. The output beam pattern is a close reproduction of the input TEM\textsubscript{00} mode.

The 1.5-meter stable CO\textsubscript{2} oscillator has been used to drive the above amplifier. An output power of 10 to 15 W is obtained, and the frequency stability should be comparable to that of previous smaller versions once the output window heating is eliminated by the use of lower-loss materials.

An attempt has been made to observe thermal blooming of a 10.6-\mu CO\textsubscript{2} laser beam in an absorbing gas. Substantial blooming does occur, but difficulty has been encountered in making quantitative measurements due to the asymmetry caused by convection in our horizontal gas cell and to the lack of a good image detector at the 10-\mu wavelength.

Optical heterodyning at 10.6 \mu \text{m} between a current-tunable, single-mode Pb\textsubscript{0.88}Sn\textsubscript{0.12}Te diode laser and a stable, single-frequency CO\textsubscript{2} gas laser has produced a controllable beat frequency in a Ge:Cu detector from under 50 to 1300 MHz. From these measurements, we have determined the cutoff frequency of a Ge:Cu detector considered for application in the laser radar system, and have obtained a direct indication of the linewidth of emission from the semiconductor p-n junction laser.

III. MATERIALS RESEARCH

A theoretical analysis of the forced convection method of vapor crystal growth has shown that the growth velocity is proportional to the first power of the available concentration of condensing vapor and to the square root of the carrier gas velocity. These results are supported by experimental data reported previously on the growth of iodine and camphor crystals. The condition required for stability of the growth interface has been formulated in terms of a relationship between the temperatures at the interface, at the edge of the diffusion boundary layer adjacent to the interface, and at the solid source.

Optical transmission measurements have been made at room temperature on single crystals of Cd\textsubscript{1-x}Mg\textsubscript{x}Te alloys with 0 \leq x \leq 0.46. The energy gap evaluated from the data increases linearly with increasing x, from 1.50 eV for CdTe to 2.23 eV for x = 0.46.

Photoluminescence spectra due to oxygen in ZnTe\textsubscript{1-x}Se\textsubscript{x}, ZnTe\textsubscript{1-x}S\textsubscript{x}, and Zn\textsubscript{1-x}Cd\textsubscript{x}Te alloys have been measured at 4.2°K. As expected for the isoelectronic trap model of the oxygen center, the trapping energy decreases with increasing ZnSe and ZnS content, but is essentially independent of CdTe content.

The pressure-composition phase diagram for the Ba\textsubscript{1-x}Sr\textsubscript{x}RuO\textsubscript{3} system at 1000°C has been determined by x-ray diffraction measurements on powdered samples. Four different structures, with different proportions of cubic and hexagonal close packing, are observed. The addition of strontium and the application of pressure both favor structures with more cubic and less hexagonal close packing.

A method has been developed for evaluating absolute atomic form factors in solids by analysis of integrated intensity data obtained in x-ray diffraction measurements. Application of this method to data for nickel suggests a transfer of 0.3 electron from the outer levels (4s) to the first inner levels (3d), but this should be considered as a qualitative result.
IV. PHYSICS OF SOLIDS

The optical investigation of the band structure of nickel has now been extended to nickel-copper alloys. Reflection measurements, from 0.2 to 11 eV, in several alloys seem to indicate that below 4 eV the alloys behave according to a "localized states" or to a "minimum polarity" model.

The study of the effect of stress on the impurity spectrum of bismuth-doped silicon has now been completed. All measured relative intensities and transition energies as a function of stress are in agreement with predictions of a strain Hamiltonian derived from effective mass and deformation potential theory.

Two sets of interband transitions, analogous to those in HgTe, have now been observed in the magnetoreflection of gray tin. One of the lowest energy transitions does not fit into the Landau level scheme; it is suggested that this line may arise from transitions between impurity states associated with the Landau levels.

Investigation of the "extra" transitions in the interband magnetoreflection and magneto-electroreflection of lnSb, caused by the warping and linear-k splitting of the valence band, has been concluded. The warping obtained is in good agreement with the cyclotron resonance results of Bagguley, et al.; the linear-k splitting is one-third the value deduced from cyclotron resonance by Robinson, but is in agreement with the theoretical estimate of Kane.

A technique has been developed for determining the Debye temperature, $\Theta_D$, of crystals by means of thermal modulation of x-ray diffraction. This new method, which has been tested on NaCl, gives results in good agreement with other techniques, and, aside from holding promise of surpassing the accuracy of existing DC methods, has the additional advantage of yielding $\Theta_D$ from measurements at a single temperature.

Substantial amplification, greater than 25 dB/cm, of 9-GHz longitudinal ultrasonic waves has been obtained in n-InSb on application of a pulsed electric field. Theoretical calculations of this effect are in reasonable qualitative agreement with the experiment.

Measurements of the magnetic properties of the high-pressure (orthorhombic) phase of MnAs have been extended to 11 kbars. The variation with temperature of the magnetic moment has been studied as a function of magnetic field and throughout the pressure range.

A study of the properties of the one-dimensional, two-sublattice model of a spiral magnetic structure has been completed. For a range of parameters, a ferrimagnetic conical spiral structure is the ground state. The spin wave spectrum for this case has been investigated.

The well-known spherical model of a ferromagnet has been shown to be thermodynamically identical to a system of infinite-dimensional spins interacting through a Heisenberg Hamiltonian.

It is known that for the Ising model, the onset of magnetic order is characterized by the collapse of the eigenvalue spectrum of a certain linear operator. It has been demonstrated that the same mathematical phenomenon characterizes the onset of ordering in a set of $\nu$-dimensional spins interacting via a Heisenberg Hamiltonian.
Introduction

A new form of temperature-dependent Hartree-Fock theory is being investigated, based on a variational principle for the free energy. The one-electron orbitals used to construct single determinant wave functions must satisfy an equation which is more general than the usual Hartree-Fock equations. This new formulation eliminates some of the paradoxical results of ordinary temperature-dependent Hartree-Fock theory.

Using high-resolution Brillouin scattering techniques, the velocity and attenuation of 28-GHz longitudinal phonons propagating along the x-axis of a-quartz have been measured in the temperature range 300° to 600°K. Although the velocity variation with temperature agrees with the earlier ultrasonic measurements, the hypersonic attenuation agrees with theoretical extrapolations of ultrasonic data only in order of magnitude.

For the first time, light scattering has been observed from screened single-particle electron and also hole excitations. Scattering from electron excitations was found in GaAs, InP, AlSb, and CdTe, and from hole excitations in p-type GaAs doped with cadmium, zinc, and magnesium.

The study of thermal defocusing of a laser beam has now been extended to steady state (and approach to steady state) conditions. Competing conduction and convection processes have been investigated in a number of new experiments.

Methods of achieving single-mode operation of a high-power pulsed ruby laser have been explored. In the best arrangement, a single transverse mode and less than six longitudinal modes are obtained.
CONTENTS

Abstract iii
Introduction v
Organization xi
Reports by Authors Engaged in Solid State Research xii

I. SOLID STATE DEVICE RESEARCH
A. Photovoltaic Detectors of Pb$_{1-x}$Sn$_x$Te 1
B. Photoconductivity in Single-Crystal Pb$_{1-x}$Sn$_x$Te 2
C. Long Wavelength Infrared Pb$_{1-x}$Sn$_x$Te Diode Lasers 5
D. Far-Infrared Photoconductivity in High-Purity Epitaxial GaAs 7
E. Isolation of Junction Devices in GaAs Using Proton Radiation Damage 10
F. Short Wavelength Response Characteristics of InSb-MOS Photovoltaic Detectors 11

II. OPTICAL TECHNIQUES AND DEVICES 13
A. 100-Watt CO$_2$ Amplifier 13
B. Stable Laser Oscillator, Design and Testing 15
C. Thermal Blooming 15
D. Optical Heterodyne Detection at 10.6 μm of the Beat Frequency Between a Tunable Pb$_{0.88}$Sn$_{0.12}$Te Diode Laser and a CO$_2$ Gas Laser 16

III. MATERIALS RESEARCH 19
A. Boundary Layer Analysis of Forced Convection Crystal Growth 19
B. Optical Transmission of Cd$_{1-x}$Mg$_x$Te Alloys 22
C. Photoluminescence Due to Oxygen in ZnTe Alloys 25
D. Composition- and Pressure-Induced Structural Changes in the Ba$_{1-x}$Sr$_x$RuO$_3$ System 28
E. Determination of Experimental Form Factors on an Absolute Scale from Relative X-Ray Intensities 30

IV. PHYSICS OF SOLIDS 35
A. Electronic Band Structure 35
B. Magnetism 46
C. Laser Scattering and Nonlinear Effects 55
ORGANIZATION

SOLID STATE DIVISION

A. L. McWhorter, Head
P. E. Tannenwald, Associate Head
M. J. Hudson, Assistant
F. P. Warekois

SOLID STATE THEORY

H. J. Zeiger, Leader
M. M. Litvak, Assistant Leader

Argyres, P. N.*
Chinn, S. R.†
Dresselhaus, G. F.
Hamilton, D. C.
Hanus, J. G. C.
Kaplan, T. A.
Kelley, P. L.
Kleiner, W. H.
Landon, S. N.
Larson, D. M.
Palm, R. J.†
Stanley, H. E.

OPTICS AND INFRARED

R. H. Kingston, Leader
R. J. Keyes, Assistant Leader

Bates, D. H.
Bostick, H. A.
Carbone, R. J.
Freed, C.
Gilmartin, T. J.
Hinkley, E. D.
Longaker, P. R.

McPhie, J. M.
Quist, T. M.
Ross, A. H. M.
Sullivan, F. M.
Swezey, L. W.
Zimmerman, M. D.

ELECTRONIC MATERIALS

J. B. Goodenough, Leader
A. J. Strauss, Associate Leader

Anderson, C. H., Jr.
Andrews, H. L.†
Arcott, R. J.
Baraus, M. D.
Batson, D. A.
Brebrick, R. F., Jr.
Button, M. J.
Capes, R. N.
Delaney, E. J.
England, R. E.
Fahy, R. E.
Ferretti, A.
Finn, M. C.
Iseler, G. W.
Kafalas, J. A.
Kasper, H. M.
LaFleur, W. J.
Lavine, M. C.†
Longo, J. M.
Mastromattei, E. L.
O'Connor, J. R.
Owens, E. B.
Plonko, M. C.
Racah, P. M.
Reed, T. B.
Roddy, J. T.
Scarlen, I. H.
Smith, F. T. J.
Steininger, J. M.
Wheatley, G. E.

SOLID STATE PHYSICS

J. G. Mavroides, Leader
G. B. Wright, Assistant Leader

Brandt, R. C.
Burke, J. W.
Carman, R. L.†
Crooker, P. P.
Dresselhaus, M. S.†
Dwight, K. Jr.
Feinleib, J.
Feldman, B.
Fulton, M. J.
Groses, S. H.
Henrich, V. E.
Johnson, F. J.
Kernan, W. C.
Kolesar, D. F.
Krag, W. E.
Menegailis, J.
Menyuk, N.
Murphy, H. C.
Nill, K. W.
Parker, C. D.
Perry, F. H.
Pine, A. S.
Scouler, W. J.
Stickler, J. J.†
Strahm, N. D.†
Tichovolsky, E. J.†
Waldman, J.†
Weber, R.

APPLIED PHYSICS

J. O. Dimmock, Leader
T. C. Harman, Assistant Leader
L. Melgailis, Assistant Leader

Brueck, S. R. J.†
Butler, J. F.
Calawa, A. R.
Carter, F. R.
Canwell, F. H.
Clough, T. F.
Donaldson, P. L.
Donnelly, J. P.
Donne, G. A.
Foyt, A. G.
Hewitt, C. E.
Lindley, W. T.
Moore, A.†
Murphy, R. A.†
Oliver, M. R.†
Paladino, A. E.
Phelan, R. J., Jr.
Stillman, G. F.
Ward, J. E. R., III
Wolfe, C. M.
Youtz, P.

* Leave of Absence
† Research Assistant
‡ Part Time
REPORTS BY AUTHORS
ENGAGED IN SOLID STATE RESEARCH

15 February through 15 May 1968

PUBLISHED REPORTS

<table>
<thead>
<tr>
<th>JA No.</th>
<th>Title</th>
<th>Authors</th>
<th>Journal Articles*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3108</td>
<td>Magnetic Properties of La$_0.5$Sr$_0.5$CoO$_3$ Near Its Curie Temperature</td>
<td>N. Menyuk, P. M. Raccah, K. Dwight</td>
<td>Phys. Rev. 166, 510 (1968)</td>
</tr>
<tr>
<td>3119</td>
<td>Tellurium Vapor Pressure and Optical Density at 370-615°C</td>
<td>R. F. Brebrick</td>
<td>J. Phys. Chem. 72, 1032 (1968)</td>
</tr>
<tr>
<td>3137</td>
<td>Metallurgical and Electronic Properties of Pb$_{1-x}$Sn$<em>x$Te, Pb$</em>{1-x}$Sn$_x$Se, and Other IV-VI Alloys</td>
<td>A. J. Strauss</td>
<td>Trans. Met. Soc. AIME 242, 354 (1968)</td>
</tr>
</tbody>
</table>

*Reprints available.
†Author not at Lincoln Laboratory.
Reports

JA No.

3187 Isotope Effect in Superconducting Rhenium  E. Maxwell*  M. Strongin*  T. B. Reed  Phys. Rev. 166, 457 (1968)


3230 Linear-k Valence Band Splitting in InSb  C. R. Pidgeon*  S. H. Groves  Phys. Rev. Letters 20, 1003 (1968)


MS No.


* Author not at Lincoln Laboratory.
Reports

MS No.

1958 Resistivity and Magnetic Order in Ti$_2$O$_3$  
L. L. Van Zandt  
J. M. Honig  
J. B. Goodenough  
J. Appl. Phys. 39, 594 (1968)

1959 Band Structure of Nickel and Low-Energy Optical Transitions  
J. Hanus  
J. Feinleib  
W. J. Scouler  
J. Appl. Phys. 39, 1272 (1968)

1961 Observation of Ferri- and Antiferromagnetic Resonance in Insulating Magnetic Spiral Structures  
J. J. Stickler  
H. J. Zeiger  
J. Appl. Phys. 39, 1021 (1968)

UNPUBLISHED REPORTS

Journal Articles

JA No.

3186 Light Scattering from Single-Particle Electron Excitations in Semiconductors  
A. Mooradian  
Accepted by Phys. Rev. Letters

3192 Spin-Orbit-Coupling Effects in Transition-Metal Compounds  
J. B. Goodenough  
Accepted by Phys. Rev.

3206 Partial Pressure of Se$_2$(g) in Selenium Vapor  
R. F. Brebrick  
Accepted by J. Chem. Phys.

3218 Band Model for Transition-Metal Chalcogenides Having Layer Structures with Occupied Trigonal-Bipyramidal Sites  
J. B. Goodenough  
Accepted by Materials Res. Bull.

3219 The Tuning of PbSe Lasers by Hydrostatic Pressure from 8 to 22 Microns  
J. M. Besson*  
A. R. Calawa  
W. Paul*  
Accepted by Phys. Rev.

3220 Type Conversion and p-n Junctions in n-CdTe Produced by Ion Implantation  
J. P. Donnelly  
A. G. Foyt  
E. D. Hinkley  
W. T. Lindley  
J. O. Dimmock  
Accepted by Appl. Phys. Letters

3223 Upper and Lower Bounds for the Intermediate Coupling Polaron Ground State Energy  
D. M. Larsen  
Accepted by Phys. Rev.

3225 Tri-Arc Furnace for Czochralski Growth with a Cold Crucible  
T. B. Reed  
E. R. Pollard  
Accepted by J. Cryst. Growth

3239 Copper-Doped Germanium Detectors  
T. M. Quist  
Accepted by Proc. IEEE

* Author not at Lincoln Laboratory.
### JA No.

<table>
<thead>
<tr>
<th>JA No.</th>
<th>Title</th>
<th>Authors</th>
<th>Accepted by</th>
</tr>
</thead>
</table>

### Meeting Speeches*

<table>
<thead>
<tr>
<th>MS No.</th>
<th>Title</th>
<th>Author(s)</th>
<th>Location/Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1719F</td>
<td>Interstellar OH Maser Emission</td>
<td>M. M. Litvak</td>
<td>Seminar, M.I.T., 10 May 1968</td>
</tr>
<tr>
<td>1882D</td>
<td>Raman Scattering from Elementary Excitations</td>
<td>A. Mooradian</td>
<td>Seminar, M.I.T., 5 April 1968</td>
</tr>
<tr>
<td>1882E</td>
<td>Raman Scattering from Plasmons and Phonons</td>
<td>G. B. Wright</td>
<td>Seminar, Southern Illinois University, 26 February 1968</td>
</tr>
<tr>
<td>2141B</td>
<td>Zero Gap Semiconductors</td>
<td>S. H. Groves</td>
<td>Seminar, Lowell Technological Institute, 3 April 1968</td>
</tr>
<tr>
<td>2161</td>
<td>Spark Source Mass Spectroscopy, Recent Developments and Present Capabilities</td>
<td>E. B. Owens</td>
<td>American Chemical Society, San Francisco, 1 April 1968</td>
</tr>
<tr>
<td>2165</td>
<td>Polymorphism in Ag₂Te at High Pressures and Temperatures</td>
<td>M. D. Banus, M. C. Finn</td>
<td></td>
</tr>
<tr>
<td>2179</td>
<td>Si-Te System: Partial Pressures and Thermodynamic Properties from Optical Density of the Vapor Phase</td>
<td>R. F. Brebrick</td>
<td></td>
</tr>
<tr>
<td>2166</td>
<td>Electronic Raman Scattering from Impurities in Semiconductors</td>
<td>G. B. Wright, A. Mooradian</td>
<td></td>
</tr>
<tr>
<td>2174</td>
<td>The Two Phonon Infrared and Raman Spectrum of CdTe</td>
<td>A. Mooradian, G. B. Wright</td>
<td>American Physical Society, Berkeley, California, 18 – 21 March 1968</td>
</tr>
<tr>
<td>2183A</td>
<td>Interband Magnetoreflection of Gray Tin</td>
<td>S. H. Groves, C. R. Pidgeon, A. W. Ewald, R. J. Wagner</td>
<td></td>
</tr>
</tbody>
</table>

* Titles of Meeting Speeches are listed for information only. No copies are available for distribution.
† Author not at Lincoln Laboratory.
Reports

MS No.

2184  Exciton Structure in the Magneto-absorption Spectrum of Germanium  E. J. Johnson

2188A  Electoreflection Study of Inversion Asymmetry and Warping Induced Interband Magneto-Optical Transitions in InSb  C. R. Pidgeon*  S. H. Groves

2189  Microwave Acoustic Amplification and Noise Emission from n-InSb  K. W. Nill

2191  Type Conversion and p-n Junctions in n-CdTe Produced by Ion Implantation  J. P. Donnelly  A. G. Fayt  E. D. Hinkley  W. T. Lindley  J. O. Dinnick

2193  Optical Transmission of Cd$_{1-x}$Mg$_x$Te Alloys  A. J. Strauss

2197  Photoluminescence Due to Oxygen in ZnTe$_{1-x}$Se$_x$ and Zn$_{1-x}$Cd$_x$Te Alloys  G. W. Iseler  A. J. Strauss

2198  Determination of Experimental Form Factors on an Absolute Scale from Relative X-Ray Intensities  P. M. Raccah

2202  Electronic Energy Bands in Cu and Ni  G. F. Dresselhaus  J. Hanus

2203  Electronic Energy Bands and Optical Properties of Cu and Ni  J. Hanus  G. F. Dresselhaus

2204  Plasma Waves and Fermi Liquid Effects in Alkali Metals  D. C. Hamilton  A. L. McWhorter

2205  Effect of Orbital Overlap on Charge Densities in Crystals  T. A. Kaplan  J. Hanus  W. H. Kleiner  P. M. Raccah  H. E. Stanley


* Author not at Lincoln Laboratory.
<table>
<thead>
<tr>
<th>MS No.</th>
<th>Title</th>
<th>Authors</th>
<th>Conference/Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>2211</td>
<td>Optical Properties of Ni-Cu Alloys at 300 and 77°K from 2-11 eV</td>
<td>W. J. Scouler, J. Feinleib, J. Hanus</td>
<td>American Chemical Society, Bayside, New York, 5 April 1968</td>
</tr>
<tr>
<td>2264A</td>
<td>The d-Electrons in Thiospinels</td>
<td>J. B. Goodenough</td>
<td>American Physical Society, Boston, 26 – 28 February 1968</td>
</tr>
<tr>
<td>2212</td>
<td>The Present Position of Solids Mass Spectroscopy in Trace Analysis</td>
<td>E. B. Owens</td>
<td>Colloquium, Brandeis University, 5 March 1968</td>
</tr>
<tr>
<td>2251</td>
<td>Homogeneity Range of Bi₂Te₃ from Optical Density of the Vapor</td>
<td>R. F. Brebrick</td>
<td>Seminar, United Aircraft, East Hartford, Connecticut, 7 March 1968</td>
</tr>
<tr>
<td>2264</td>
<td>Band Structure and Magnetic Interactions in Transition-Metal Chalcogenide Spinels</td>
<td>J. B. Goodenough</td>
<td>Seminar, Naval Research Laboratory, Washington, D.C., 19 March 1968</td>
</tr>
<tr>
<td>2266</td>
<td>Raman Scattering from Plasmons in Semiconductors</td>
<td>A. L. McWhorter</td>
<td>American Physical Society, Boston, 26 – 28 February 1968</td>
</tr>
<tr>
<td>2267</td>
<td>Growth, Properties and Band Structure of Pb₁₋ₓSnₓTe and Pb₁₋ₓSnₓSe</td>
<td>T. C. Harman</td>
<td>Conference on Semimetals and Narrow Gap Semiconductors, University of Durham, England, 2 – 4 April 1968</td>
</tr>
<tr>
<td>2277</td>
<td>Electronic Structure of Transition Metals</td>
<td>J. Hanus</td>
<td>Seminar, United Aircraft, East Hartford, Connecticut, 7 March 1968</td>
</tr>
<tr>
<td>2278</td>
<td>CO₂ Laser Radar</td>
<td>R. H. Kingston</td>
<td>Seminar, Naval Research Laboratory, Washington, D.C., 19 March 1968</td>
</tr>
<tr>
<td>MS No.</td>
<td>Title</td>
<td>Author</td>
<td>Location/Date</td>
</tr>
<tr>
<td>-------</td>
<td>----------------------------------------------------------------------</td>
<td>-----------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>2284</td>
<td>Crystal Growth Research at the M. I. T. Lincoln Laboratory</td>
<td>T. B. Reed</td>
<td>Seminar, Texas Instruments, Incorporated, Attleboro, Massachusetts, 21 March 1968</td>
</tr>
<tr>
<td>2285</td>
<td>Recent Results in the Statistical Mechanics of Magnetism</td>
<td>H. E. Stanley</td>
<td>Seminar, University of California, 22 March 1968</td>
</tr>
<tr>
<td>2296</td>
<td>Hydrodynamic Modes and Propagation of Intense Light Beams in Liquids and Gases</td>
<td>P. L. Kelley</td>
<td>Seminar, Harvard University, 10 April 1968</td>
</tr>
<tr>
<td>2299</td>
<td>Exact Solution for a Linear Chain of Isotropically Interacting Classical Spins of Arbitrary Dimensionality</td>
<td>H. E. Stanley</td>
<td>19th Statistical Mechanics Meeting, Yeshiva University, 10 April 1968</td>
</tr>
<tr>
<td>2305</td>
<td>Fermi Liquid Effects on Plasma Wave Propagation in Metals</td>
<td>A. L. McWhorter</td>
<td>Seminar, M.I.T., 12 April 1968</td>
</tr>
<tr>
<td>2324</td>
<td>Polaron s in Indium Antimonide</td>
<td>D. M. Larsen</td>
<td>Seminar, Northeastern University, 7 May 1968</td>
</tr>
</tbody>
</table>
I. SOLID STATE DEVICE RESEARCH

A. PHOTOVOLTAIC DETECTORS OF Pb$_{1-x}$Sn$_x$Te

Photovoltaic detectors with significantly improved sensitivity have been fabricated from vapor-grown Pb$_{1-x}$Sn$_x$Te with compositions between $x = 0.17$ and 0.20, for which the cutoff wavelength at 77°C falls in the 8- to 14-µ atmospheric window. The detectivity has been improved by increasing both the quantum efficiency and the zero-bias impedance of the diodes. Most diodes were produced by a combined operation of vapor-growth, annealing, and diffusion which was performed in an evacuated ampoule by varying the temperature. The samples were then cleaved, contacts were made by gold-plating, and leads were attached with a Ga-In alloy. The junctions were 5 to 40 µ deep. In most cases, the deeper junctions had higher zero-bias impedances. This seems to correlate with the absence of metallic inclusions from the bulk of vapor-grown crystals, as opposed to regions near the surface where high densities of inclusions have been detected by etching. In order to remove damaged layers from the cleaved faces and to reduce the junction depth, the diodes were stream-etched with an electrolytic solution consisting of 20 g KOH, 45 ml H$_2$O, 35 ml glycerin, and 20 ml of ethanol.

<table>
<thead>
<tr>
<th>Area (mm$^2$)</th>
<th>Temperature (°K)</th>
<th>Cutoff Wavelength (µ)</th>
<th>Incremental Resistance (ohms)</th>
<th>Efficiency</th>
<th>Peak Responsivity (V/W)</th>
<th>Peak Detectivity (cm/W sec$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>77</td>
<td>9.5</td>
<td>180</td>
<td>0.14</td>
<td>190</td>
<td>$5.3 \times 10^9$</td>
</tr>
<tr>
<td>0.25</td>
<td>77</td>
<td>11</td>
<td>16</td>
<td>0.17</td>
<td>27</td>
<td>$4 \times 10^9$</td>
</tr>
<tr>
<td>0.2</td>
<td>77</td>
<td>10</td>
<td>10</td>
<td>0.33</td>
<td>26</td>
<td>$3.5 \times 10^9$</td>
</tr>
<tr>
<td>0.1</td>
<td>77</td>
<td>12</td>
<td>16</td>
<td>0.37</td>
<td>70</td>
<td>$7.5 \times 10^9$</td>
</tr>
<tr>
<td>0.17</td>
<td>77</td>
<td>10</td>
<td>25</td>
<td>0.32</td>
<td>64</td>
<td>$8 \times 10^9$</td>
</tr>
<tr>
<td>0.18</td>
<td>77</td>
<td>12</td>
<td>10</td>
<td>0.19</td>
<td>18</td>
<td>$3.7 \times 10^9$</td>
</tr>
</tbody>
</table>

*After antireflection coating with Se.

Table I-1 gives representative values of responsivity, detectivity, and efficiency that have been obtained. In the case of the last detector in the Table, an antireflection coating of Se (1/4 wavelength thickness at 10 µ) was applied by means of evaporation. This apparently eliminates
the reflection loss over most of the 8- to 14-μ wavelength range, thereby producing an increase
by about a factor-of-two in the quantum efficiency. A. R. Calawa T. C. Harman
I. Melngailis P. Youtz

B. PHOTOCONDUCTIVITY IN SINGLE-CRYSTAL $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$

Photoconductivity at wavelengths up to 15 μ has been observed at 77°K in Bridgman-grown and
subsequently annealed crystals of $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$. The annealing parameters and the resulting car-
rier concentrations and mobilities of the crystals used for photoconductors are shown in Table I-2.
The two compositions, $x = 0.17$ and $0.20$, are of particular interest for detectors because for the
0.17 alloy the photoconductivity at 77°K peaks very close to 10.6 μ, whereas for the 0.20 alloy
the peak is at 14 μ, i.e., detectors of this composition cover the 8- to 14-μ atmospheric window.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>$x$</th>
<th>Sample Temperature (°C)</th>
<th>Annealing Time (days)</th>
<th>Sample Thickness (mm)</th>
<th>Hall Carrier Concentration at 77°K $\left(\text{cm}^{-3}\right)$</th>
<th>Hall Carrier Mobility at 77°K $\left(\text{cm}^2/\text{V sec}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>66168C</td>
<td>0.17</td>
<td>500</td>
<td>22</td>
<td>0.29</td>
<td>$2.3 \times 10^{15}$ P</td>
<td>$3.1 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>661613E2</td>
<td>0.17</td>
<td>650</td>
<td>4</td>
<td>0.27</td>
<td>$5.8 \times 10^{15}$ P</td>
<td>$2.6 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6741</td>
<td>0.20</td>
<td>600</td>
<td>8</td>
<td>0.25</td>
<td>$7.5 \times 10^{15}$ N</td>
<td>$3.2 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673R</td>
<td>0.17</td>
<td>600</td>
<td>5</td>
<td>0.06</td>
<td>$2.6 \times 10^{16}$ N</td>
<td>$2.9 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Contacts to the photoconductors were made by gold-plating and then cold-bonding leads to
the gold layer using indium. The samples were then etched both to reduce their thickness and
to lower the surface recombination velocity. The etch cons-
isted of 10 parts potassium hydroxide, 1 part hydrogen
peroxide, and 10 parts ethylene glycol.

In order to insure uniform cooling and to avoid the
danger of thermal stresses, the samples were immersed
directly in the liquid coolant in preference to mounting them
on a heatsink. To insure that photoconductivity rather than
slow thermal effects (bolometer effect or thermoelectric
effect) are observed, the response speed was measured by
using a GaAs diode laser. Figure 1-1 shows the response
at 77°K. The 15-nsec response time corresponds to the
effective carrier lifetime. In addition to photoconductivity,
a photovoltaic effect is observed at the gold contacts, presumably due to the presence of a Schottky barrier. This can be eliminated by focusing the light spot on regions removed from the contacts.

Figure 1-2 shows the response spectra of two photoconductors at 77°K—one for a 0.17 and one for a 0.20 alloy. The response peaks are at 10 and 14 μ, respectively. Near the bandgap, there is a small peak as the radiation begins to penetrate into the bulk where the lifetime of carriers is longer than near the surface. The fact that the peak is small indicates that the surface recombination velocity is not very high. This means that the effective lifetime obtained from the pulse measurements provides an approximate measure of the bulk lifetime. Figure 1-3 shows the spectrum of a Pb_{0.83}Sn_{0.17}Te photoconductor at 4.2°K.

Measurements of noise indicate that for some types of contacts there is a considerable current noise with a 1/f type of frequency dependence. So far, we have found that gold-plated contacts produce the least noise. For the photoconductors used at bias currents up to the point where there was evidence of heating, the measured noise was within 50 percent of the Johnson noise calculated for the resistance of the photoconductor at liquid nitrogen temperature. The generation-recombination noise was estimated to be about one order of magnitude smaller than the Johnson noise for the samples used. Hence, Johnson noise appears to be the basic noise limitation at present.

The properties of a number of photoconductors are shown in Table 1-3. At the 900-Hz frequency, the noise in the first sample was about 50 percent higher than the Johnson noise for the 42-ohm resistance at 77°K. At 3000 Hz, the measured noise exceeded the Johnson noise by only 25 percent. The detectivity is given for 11 μ and 900 Hz. The peak D_A at high frequencies, which is limited by thermal noise, is about \(4.5 \times 10^8\) cm/W sec \(1/2\).

At 4.2°K, the sensitivity is greatly improved because the lifetime at 4.2° is much longer than at 77°K. Lifetime measurements obtained by observing directly the decay of the photocurrent following a GaAs diode laser pulse are shown in Table 1-4 for a number
### TABLE 1-3
PROPERTIES OF Pb$_{1-x}$Sn$_x$Te PHOTOCONDUCTORS

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Crystal No.</th>
<th>Dimensions</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>$T$ (°K)</th>
<th>$R$ (ohms)</th>
<th>$I_o$ (mA)</th>
<th>$i_v$(λ) $P$ (V/W)</th>
<th>$\lambda$ $P$ ($\mu$)</th>
<th>$D^*(\lambda$, 900, 1) $(cm/W sec^{1/2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>94A</td>
<td>66-16</td>
<td>4.0</td>
<td>2.0</td>
<td>0.05</td>
<td>77</td>
<td>42</td>
<td>10</td>
<td>0.7</td>
<td>10</td>
<td>3 x 10^8</td>
<td>1.7 x 10^{10}</td>
</tr>
<tr>
<td>94B</td>
<td>66-16</td>
<td>4.0</td>
<td>2.0</td>
<td>0.03</td>
<td>4.2</td>
<td>52</td>
<td>4</td>
<td>80</td>
<td>14</td>
<td>1.5 x 10^8</td>
<td>1 x 10^8</td>
</tr>
<tr>
<td>97A</td>
<td>67-4</td>
<td>1.5</td>
<td>1.0</td>
<td>0.05</td>
<td>77</td>
<td>13</td>
<td>30</td>
<td>0.6</td>
<td>14</td>
<td>0.7 x 10^-6</td>
<td>0.7 x 10^-6</td>
</tr>
</tbody>
</table>

### TABLE 1-4
LIFETIME MEASUREMENTS IN Pb$_{1-x}$Sn$_x$Te PHOTOCONDUCTORS

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$\tau_{eff}$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 94B</td>
</tr>
<tr>
<td>300</td>
<td>4 x 10^-8</td>
</tr>
<tr>
<td>198</td>
<td>3 x 10^-8</td>
</tr>
<tr>
<td>77</td>
<td>1.5 x 10^-8</td>
</tr>
<tr>
<td>4.2</td>
<td>1.2 x 10^-6</td>
</tr>
</tbody>
</table>
of temperatures. For the crystals for which both responsivity and lifetime measurements were available, the lifetime calculated from the responsivity was in good agreement with the measured lifetime.

The direct radiative recombination lifetime at 77°K is estimated to be of the order of $10^{-5}$ sec in Pb$_{1-x}$Sn$_x$Te with an energy gap of 0.1 eV and with a carrier concentration of the order of $10^{15}$ cm$^{-3}$; hence, additional recombination mechanisms which reduce the lifetime must be predominant in these crystals.

I. Melngailis
T. C. Harman

C. LONG WAVELENGTH INFRARED Pb$_{1-x}$Sn$_x$Te DIODE LASERS

The long wavelength limit for semiconductor lasers has been extended to 28 μ using Pb$_{1-x}$Sn$_x$Te diode lasers with x up to 0.27. The p-n junctions were diffused into the vapor-grown single crystals in a special fused silica ampoule which remained sealed throughout the entire growth and diffusion-annealing processes. Pb$_{1-x}$Sn$_x$Te diode lasers have previously been fabricated by a different method for x ≤ 0.17 (see Ref. 1). The previous maximum wavelength for semiconductor lasers was 22.5 μ, observed in a pressure-tuned PbSe laser, while the long wavelength limit for unstressed semiconductor lasers was 18.8 μ, obtained with Pb$_{1-y}$Sn$_y$Se (Ref. 3). Threshold current densities in the present lasers were observed to be dependent on diode surface conditions and could be reduced to 50 percent or less of their original values by etching.

A schematic diagram of the special growth and diffusion-annealing ampoule is shown in Fig.1-4(a). The fused silica ampoule consists of a tubular section about 1.8 cm i.d. and 14 cm long, tapered to a point at the bottom, and with three indentations about 4 cm from the tip. The evacuated (10$^{-7}$ torr) ampoule is suspended in a vertical tubular furnace, which has the temperature profile depicted in Fig.1-4(b). The temperature difference between the source material and vapor-grown crystals was about 1°C. The vapor source, which is a two-phased coarse powder obtained from a quenched ingot of composition (Pb-Sn)$_{0.51}$Te$_{0.49}$, is contained in the inner quartz tube which has a 1.0 cm i.d. and is 6.5 cm long. The crystals usually grow on the walls of the ampoule in the conical tip region. After a growing time of approximately 20 hours, the tube is air-cooled. Crystals with (100) surfaces 1 mm$^2$ or larger in area and of composition up to x = 0.27 have been obtained by this method. The rapidly cooled, as-grown crystals have bulk interior carrier concentrations which are given approximately by the

![Fig. 1-4. (a) Schematic diagram of special vapor growth and diffusion-annealing ampoule (there are three indentations in outer quartz tube which are spaced 120° apart). (b) Section of furnace temperature profile (overall length of vertically positioned furnace is 60 cm).](https://example.com/fig1-4)
Section I

TABLE 1-5
ANNEALING PARAMETERS AND OPERATING CHARACTERISTICS
OF Pb$_{1-x}$Sn$_x$Te DIODE LASERS

<table>
<thead>
<tr>
<th>x</th>
<th>Annealing Time (days)</th>
<th>Annealing Temperature (°C)</th>
<th>Emission Wavelength (µ)</th>
<th>Minimum Threshold Current Density (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>12°C</td>
<td>77°C</td>
</tr>
<tr>
<td>0.15</td>
<td>None</td>
<td>None</td>
<td>11.7</td>
<td>9.5</td>
</tr>
<tr>
<td>0.17</td>
<td>2</td>
<td>450</td>
<td>13.0</td>
<td>9.9</td>
</tr>
<tr>
<td>0.19</td>
<td>3</td>
<td>450</td>
<td>14.5</td>
<td>11.0</td>
</tr>
<tr>
<td>0.20</td>
<td>3</td>
<td>450</td>
<td>15.1</td>
<td>11.2</td>
</tr>
<tr>
<td>0.21</td>
<td>2</td>
<td>450</td>
<td>16.8</td>
<td>12.0</td>
</tr>
<tr>
<td>0.22</td>
<td>7</td>
<td>450</td>
<td>17.2</td>
<td>-</td>
</tr>
<tr>
<td>0.24</td>
<td>14</td>
<td>400</td>
<td>20.0</td>
<td>-</td>
</tr>
<tr>
<td>0.25†</td>
<td>3</td>
<td>450</td>
<td>22.4</td>
<td>14.9</td>
</tr>
<tr>
<td>0.27</td>
<td>See text</td>
<td>See text</td>
<td>28.0</td>
<td>-</td>
</tr>
</tbody>
</table>

† The quenched ingot used for the vapor growth source was doped with $4 \times 10^{19}$ Bi atoms/cm$^3$.

points on the metal-saturated solidus lines in Ref. 4 corresponding to the growth temperature of about 825°C. N-type layers of thickness $\geq 25 \mu$ were diffused by isothermally annealing the crystals in a horizontal furnace in the unopened growth ampoule and thus in the presence of the remaining source ingot. This method of preparing junctions utilizes the property that, at least for values of x up to x = 0.27, metal-saturated crystals change from p- to n-type conductivity as the temperature is decreased. From isothermal metal-saturation experiments, type conversion temperatures of 580°, 525°, and 425°C are estimated for x = 0.17, 0.20, and 0.27, respectively. For x < 0.27, annealing parameters for junction formation are given in Table 1-5. For x = 0.27, the annealing schedule for preparing junctions was 4 hours at 700°C, 6 days at 650°C, 7 days at 450°C, and 21 days at 400°C, giving an n-region approximately 30 µ deep. Annealing studies indicate the surface electron concentration of annealed undoped Pb$_{0.73}$Sn$_{0.27}$Te to be $\leq 10^{15}$ cm$^{-3}$. From the annealing schedules followed in the present experiments, we expect that the hole concentration in the p-type substrate is less than the surface n-type carrier density for a distance beyond the n-p junction essentially equal to the junction depth. Hence, p-n junction phenomena in these diodes may occur in a region of relatively low carrier concentration.

After annealing, laser structures in the shape of rectangular parallelepipeds were obtained by cleaving perpendicular and parallel to natural (100) faces. To reduce planarity and reflectivity of the longer pair of sides perpendicular to the p-n junction plane, these were subjected to a chemical etch consisting of equal volumes of a saturated water solution of Na$_2$S$_2$O$_3$ and a 15 wt. percent water solution of NaOH (Ref. 5). This leaves the smaller end faces to define the Fabry-Perot cavity. Linear dimensions of the lasers were typically a few hundred microns.
Electrical contacts to the entire top and bottom surfaces were made with electroplated Au followed by electroplated In. The laser structures were mounted in low-inductance packages and leads were attached by room-temperature bonding methods.

It has been found consistently that a final fabrication step consisting of the removal by an electrolytic etch of approximately 10\(^\mu\) of material from the four exposed laser sides reduces the threshold currents by at least 50 percent. This may be due to the removal of a damaged layer at the cleaved faces which exhibits a high rate of nonradiative recombination. Etching studies have shown that such damage exists to a depth of at least several microns. This layer would decrease the effective quantum efficiency for recombination of injected carriers and, by locally reducing the density of injected carriers at a given current level, would produce a region of electromagnetic loss near each end face of the laser cavity. The width of the lossy region would equal approximately the width of the damaged layer plus a diffusion length for bulk minority carriers. Measurements of photoconductivity in Pb\(_{1-x}\)Sn\(_x\)Te at 4.2°K indicate that some crystals of low carrier concentration have carrier diffusion lengths greater than 100\(\mu\), so that even a narrow high recombination rate region could be quite important. The volt-ampere characteristics of the diode lasers exhibit a marked increase in zero-bias impedance after the electrolytic etch, which is evidence of the removal of a region with a high recombination rate. In diodes with areas of 2 \(\times\) 10\(^{-3}\) cm\(^2\), etching has resulted in an increase of zero-bias impedance to as high as 2 \(\times\) 10\(^4\) ohms for \(x = 0.20\) at 12°K, and 2 \(\times\) 10\(^3\) ohms for \(x = 0.15\) at 77°K, from typical pre-etch values of 5 ohms at both temperatures.

Several lasers were fabricated at each of a number of compositions, and were evaluated at 77° and 12°K. The experimental arrangement for measuring spectra has been described elsewhere. Emission wavelengths and minimum threshold current densities at each composition are listed in Table 1-5. In every case, laser action was evidenced by a spectrum with a well-defined mode structure exhibiting the mode spacing expected for the Fabry-Perot cavity. The emission at 28\(\mu\) by the Pb\(_{0.73}\)Sn\(_{0.27}\)Te laser sets a new long wavelength limit for semiconductor lasers. No consistent variation of threshold current with the Pb:Sn ratio is apparent at either 12° or 77°K. Power measurements were performed on a Pb\(_{0.80}\)Sn\(_{0.20}\)Te laser using a calibrated thermopile positioned to intercept nearly all the radiation emitted from one laser end face. With pulse bias, a peak power output of 0.1 W at 15 A, corresponding to an external quantum efficiency \(\eta_x = 0.08\), was observed at 12°K, and a peak power of 0.03 W at 25 A, giving \(\eta_x = 0.01\), was measured at 77°K. With CW operation at 12°K, 5 \(\times\) 10\(^{-3}\) W at 2 A, corresponding to \(\eta_x = 0.03\), was observed.

The observation of laser action up to \(x = 0.27\) indicates that the bandgap in the Pb\(_{1-x}\)Sn\(_x\)Te alloy system is probably direct to at least this composition. The variation of the bandgap with composition as determined by the wavelength of the laser emission is consistent with the variation proposed previously.\(^7\)

J.F. Butler
T.C. Harman

D. FAR-INFRARED PHOTOCONDUCTIVITY IN HIGH-PURITY EPITAXIAL GaAs

With the development of vapor and liquid phase epitaxial techniques, it has become possible to prepare high-purity layers of GaAs. The electrical behavior of this material at temperatures
between 300° and 4°K is dominated by shallow donor impurities with ionization energies of about 0.005 eV in the purest material. We report here the observation of extrinsic photoconductivity involving these shallow impurity levels. The high responsivities and short response times observed indicate that high-purity GaAs has considerable potential as a sensitive and fast far-infrared detector.

The results reported here were obtained with vapor phase epitaxial GaAs which was grown on <111> oriented Cr-doped semi-insulating GaAs substrates using an AsCl₃-Ga-H₂ flow system. The epitaxial layer was 40 μ thick, and the results of Hall effect measurements gave the net donor concentration, \( N_D - N_A \), as \( 6.8 \times 10^{14} \text{ cm}^{-3} \) and a Hall mobility at 77°K of 75,000 cm²/V sec. The net carrier concentration at 4.2°K was \( 1.4 \times 10^{14} \text{ cm}^{-3} \), and the corresponding mobility was 2500 cm²/V sec. The behavior of the resistivity and Hall constant below about 8°K indicated effects of some impurity banding. Ohmic contacts were formed by alloying pure Sn with the GaAs at 300°C in a reducing atmosphere on two opposite edges of the 0.2 x 0.2 cm photoconductive samples. The 4.2° dark resistance of these samples was greater than 3 megohms.

![Figure 1-5](image)

**Fig. 1-5.** Voltage-current characteristic and variation of photoconductive responsivity at 337 μ and noise voltage (\( f = 300 \text{ Hz}, \Delta f = 1 \text{ Hz} \)) with sample current.

Figure 1-5 shows the V-I characteristic of a photoconductive sample at 4.2°K. Similar behavior was observed in the other samples, and the characteristics are identical in the reverse direction, as expected for ohmic contacts. This behavior is ohmic for low currents and voltages, but as the electric field is increased above about 1 V/cm, the V-I characteristic becomes distinctly nonlinear, with the current increasing rapidly with increasing field. At a critical field strength of about 5 V/cm, the electric field decreases to a lower sustaining value which remains
constant with increasing current. Such behavior, as first observed in compensated Ge (see Ref. 12), is due to impact ionization of electrons from the compensated shallow impurity levels or from an impurity band; it has previously been reported in GaAs (Ref. 13).

The photoconductivity was examined at wavelengths of 195 and 337 μ using the emission from a DCN and HCN laser, respectively, and at 902 μ using the output of a carcinotron. The power level of the sources at 902 and 337 μ was 130 μW, and at 195 μ was 90 μW. The sample was mounted in a detector dewar similar to that used for submillimeter InSb detectors,14 in which the sample was suspended at the open end of a silver-plated stainless-steel light pipe about 1 meter long and was immersed in liquid He. Two black polyethylene filters, one of which was cold, were mounted in the light pipe to exclude radiation shorter than about 40 μ. A copper cone and 90° bend were mounted at the top of the light pipe to collect the radiation from the source after it traversed a short air path. The photoconductive responsivity measured at 337 μ is shown in Fig. 1-5 as a function of sample current. The signal increases linearly with current, as expected, until the field reaches the value where impact ionization begins to occur. The responsivities at the other two wavelengths show the same variation with current. The peak responsivities are 5 x 10^3 V/W at 195 μ, 4 x 10^4 V/W at 337 μ, and 9 x 10^2 V/W at 902 μ.

The sample noise was measured at 300 Hz (the chopping frequency used for the photoconductive measurements) with a low-noise, high-impedance preamplifier and a wave analyzer. The results of these measurements are also shown in Fig. 1-5. For electric fields below 0.5 V/cm, the noise is dominated by the Johnson noise of the sample and the load resistor (at 4.2°K) in parallel plus a component due to the amplifier. However, at larger electric fields in the nonlinear region of the V-I characteristic, the total noise increases rapidly and becomes dominated by G-R noise. These noise measurements can be combined with the responsivities to calculate an NEP_λ = V_N^2 / R_λ, where V_N is the rms noise voltage, and R_λ is the responsivity at the wavelength λ. The peak values of NEP_λ are 1.2 x 10^{-11} W at 195 μ, 1.4 x 10^{-12} W at 337 μ, and 6 x 10^{-11} W at 902 μ.

The photoconductive time constant was determined to be shorter than 1 μsec by using the free carrier absorption induced by impact ionization in uncompensated Ge at 4.2°K to chop the incident radiation. A time constant of about 5 nsec for the lifetime of the carriers resulting from impact ionization of the shallow impurity levels in GaAs at low electric fields was measured using a method similar to that described by Koenig.15

There are three possible mechanisms which must be considered in the operation of a detector of this type. The first is the heating of the sample by the incident radiation, or the bolometric effect. However, since this effect is inherently slow, the high responsivities and short time constants observed indicate that this effect is not predominant. The second mechanism is the photoionization of the shallow impurity levels by the incident radiation. There should be a definite long-wavelength threshold for this effect corresponding to the ionization energy of the impurity state. For highest purity material, this should occur at about 250 μ corresponding to a donor level of ~0.005 eV, but for material with higher donor concentrations the threshold could occur at wavelengths longer than 400 μ corresponding to a donor ionization energy ≤0.003 eV (see Ref. 10). Although this threshold has not yet been located precisely, the fact that the photoconductive responsivity at 902 μ is much lower than that at 337 μ indicates that the threshold is
Section I

probably between these two wavelengths and that impurity level photoionization is likely to be the process responsible for the signal at the two shorter wavelengths. The last mechanism, which is probably responsible for the response at 902 μ, is the free carrier hot electron effect as observed in InSb (see Ref. 16). The coupling between the electrons and the crystal lattice is very weak at low temperatures in these materials so that, even at very low electric fields, the average energy of the photo-excited carriers can be appreciably greater than the thermal equilibrium value. Since the mobility is limited by ionized impurity scattering at low temperatures, the mobility of the hot electrons is increased and the sample resistance decreases. The response due to this mechanism should be most important at long wavelengths.

G. E. Stillman  C. D. Parker
C. M. Wolfe  P. E. Tannenwald
I. Melngailis  J. O. Dimmock

E. ISOLATION OF JUNCTION DEVICES IN GaAs USING PROTON RADIATION DAMAGE

We have found that proton radiation damage can be used to convert both p- and n-type GaAs into high-resistivity material, and have used this technique to isolate p-n junctions on a diffused GaAs substrate, to isolate islands of n-type material in an epitaxial layer deposited on semi-insulating GaAs, and also to prevent edge breakdown in Au-GaAs Schottky barriers.

The ion generator used in these experiments is a modified 400-keV Van de Graaff generator designed to accelerate positive ions. The protons are generated by RF excitation, accelerated to 400 keV, and magnetically analyzed. The samples are mounted on a tantalum sample holder, with part of each sample shielded from the ion beam with a molybdenum mask.

The p-n junction devices were formed on a slice of n-type GaAs with n = 2 x 10^{16} /cm^3. Following the diffusion of a Zn-doped p-type layer into the top surface, an array of 0.003-inch gold circles on 0.005-inch centers was plated onto the sample using 0.15-μ pyrolytic SiO_2 as a plating mask. These gold contacts were sufficiently thick (3 μ) that the proton beam could not penetrate them. However, the 1500-Å SiO_2 layer between the contacts, which was left on the sample to reduce sputtering effects, was sufficiently thin so that it had only a slight effect on the proton beam. Consequently, only that part of the sample between the contacts was bombarded. Each sample was then irradiated at room temperature with a proton beam of current density 0.1 μA/cm^2, starting with an energy of 400 keV and subsequently decreasing the beam energy in steps of 20 keV, finishing at 60 keV. At each energy, the sample was exposed for 20 sec, to give a total dose of about 10^{14} protons/cm^2. Before irradiation, the current-voltage characteristics between the contacts were linear with a resistance of about 500 ohms. Following irradiation, these same contacts gave back-to-back diode characteristics, with a leakage current less than 0.1 μA and a breakdown voltage of about 40 V, typical of the substrate. Between a gold contact on the p-layer and an ohmic contact on the substrate, normal diode characteristics were observed.

The islands of n-type material were prepared on a sample which had a 3-μ thick epitaxial layer of n-type material (n ~ 10^{16} /cc) which was deposited on a chromium-doped semi-insulating substrate. The sample was plated with an array of gold-tin contacts which were alloyed. Additional gold was plated to provide a thickness of 3 μ. The sample was then irradiated at 400 keV for 20 sec. Before irradiation, the contact-contact resistance was about 60 ohms; subsequently,
the leakage currents were less than 0.1 $\mu$A at 100 V between these same contacts, indicating that the leakage resistance between the islands was in excess of $10^9$ ohms.

The Schottky barrier diodes were prepared in a manner similar to the p-n junction devices, except that no p-type layer was diffused into the substrate, and irradiation was done only at 400 keV. Following irradiation, the original 3-$\mu$m thick gold contacts were removed and slightly larger semitransparent gold contacts were plated on the same areas. Current-voltage measurements on these devices showed that the reverse breakdown voltage following irradiation had increased substantially compared with the original diode, while the forward characteristic was unchanged. Visual observation of the light emitted from these diodes in reverse bias breakdown indicated that edge breakdown which was present in the original diodes had been suppressed, and that the higher voltage breakdown in the irradiated diodes occurred away from the edge.

We have also done some experiments in which the sample was bombarded before the gold contacts were applied, in order to determine the doping profile of the irradiated regions. These experiments were done by bombarding samples of n-type GaAs with proton beams of intensity 0.1 $\times$A for 20 sec at various energy levels. After bombardment, each sample was plated with gold contacts, and capacity-voltage measurements were done in order to determine the doping profile. The initial results of these experiments are that the damaged region has high resistance (doping levels $\sim 10^{15}$/cc or less) from the surface of the crystal until the protons approach the end of their range. Near the end of the range, there is evidence of a change in the character of the radiation damage, with an indication that shallow donors are created in this region. The depth of the high-resistance region is about 4 $\mu$m at 400 keV.

This technique of creating high-resistivity material is simple and quite easy to use. We feel that it should be a useful tool for the fabrication of other structures in which thin high-resistivity layers are required.

A. G. Foyt J. P. Donnelly
W. T. Lindley C. M. Wolfe

F. SHORT WAVELENGTH RESPONSE CHARACTERISTICS OF InSb-MOS PHOTOVOLTAIC DETECTORS

We have continued to study the effects of short wavelength light on the characteristics of InSb-MOS detectors. The photovoltaic response to modulated 3.9-$\mu$m radiation from an InAs diode emitter has been measured at 77°K. In our model of the MOS structure, this radiation acts as a probe of the InSb depletion region, and has no effect on the state of the structure. For n-type InSb, the depletion layer, in turn, gives an indication of the charge state of the oxide. The surface of the oxide is illuminated with short wavelength radiation from a monochromator, and the change in the response to the 3.9-$\mu$m radiation is measured. At 77°K, there is no response to the InAs radiation so long as the constant irradiation has a wavelength corresponding to photon energies $< 1.3$ eV or $> 4.8$ eV. In equilibrium for photon energies $> 1.3$ eV and $< 4.8$ eV, the response to the 3.9-$\mu$m radiation is relatively constant, independent of the intensity of the constant irradiation, but the time to reach the final value depends linearly on the intensity of the irradiating light, and very strongly on the photon energy.

At liquid nitrogen temperatures, once a response to the 3.9-$\mu$m radiation is created by short wavelength irradiation, the response remains for at least several hours, even if the irradiating light is cut off. In fact, the response remains even if the MOS structure is warmed to room
temperature and then cooled again. However, we find that if the sample is warmed to room
temperature and then irradiated with short wavelength photons before it is cooled for the next
measurement, the response to the 3.9-μ radiation is eliminated. The best wavelength for
"killing" the response seems to occur at the peak of the oxide response shown in Fig.1-4 of
Solid State Research Report (1968:1). These effects are undoubtedly due to trapping and detrapping
of electronic charge at oxide states and/or at oxide-InSb interface states; however, the precise model for this trapping has not yet been determined.

W. E. Krag
R. J. Phelan, Jr.
J. O. Dimmock

REFERENCES

5. M. C. Finn, private communication.
8. I. Melngailis and T. C. Harman (to be published).

42
II. OPTICAL TECHNIQUES AND DEVICES

A. 100-WATT CO₂ AMPLIFIER

Further measurements have been taken of gain, beam size, and frequency pulling on the 9-meter 100-W CO₂ amplifier. Details of the device are given in the previous Solid State Research Report.¹

Gain measurements were made with a sealed-off gas mixture of CO₂, N₂, He, and H₂ in the amplifier and, although not optimized, the gain was within 30 percent of that obtained with a flowing gas mixture. This probably indicates that under the appropriate conditions the amplifier gain would be the same for flowing or sealed-off gas mixtures. Detailed gain measurements for each tube show that the power gain was fairly well approximated by a solution to the gain equation assuming a constant gain with radial position and the power gain only a function of amplifier length L. The homogeneous saturation equation is

\[ \frac{dP}{dz} = \alpha_0 \frac{P}{1 + \frac{P}{P_s}} \]

and, when solved under the restrictions above, yields (when integrated) the gain equation

\[ \ln G + \frac{P_{in}}{P_s} \ln \left( \frac{P}{P_{in}} \right) (G - 1) = \alpha_o L \]

where

- G = P/P_{in}, the gain at L within the amplifier,
- P_{in} = the input power,
- P_s = saturation power = W_o S, the beam cross section is S, and
- \( \alpha_o = \text{cm}^{-1} \), the small signal gain parameter.

Figure II-1 shows the theoretical gain curves as a function of the ratio of tube input power to saturation power of the amplifier. The parameters of these curves were determined from the experimental data and, over the region shown, represent the data fairly well. The power output measured for 2- and 10-W input was 56 and 88 W in the sealed-off condition, which would be 73 and 114 W for a flowing gas mixture. The small signal gain for the 20-mm bore tube is 9.3, the 25-mm bore tube is 8, and the 30-mm bore tube is 4.2.

The beam profile as shown in Fig. II-2 is taken at the output of the 9-meter amplifier. The solid curve is Gaussian and closely approximates the measured laser beam radial distribution of the TEM₀₀ mode at the amplifier output when the amplifier is in the off condition; but, with amplification, this approximation becomes inaccurate with increasing beam radius, presumably because saturation effects are less at the larger radii, resulting in a larger gain and higher relative power at larger distances from the tube center.

Section II

Fig. II-1. CO₂ amplifier tube gain as function of ratio of input power to saturation power.

Fig. II-2. Beam profile of laser and amplifier output compared with Gaussian beam shape.
The output of the laser has been monitored with a monochromator which will resolve a frequency difference of 10 GHz at 10 μm. The laser output within this resolution limitation is not shifted with the amplifier on or off, and independent of a static or flowing gas fill condition existing in the amplifier tubes.

R. J. Carbone

B. STABLE LASER OSCILLATOR, DESIGN AND TESTING

The extensive testing of the 1 m cavity stable oscillator has been completed. Since its completion over a month ago, this laser was successfully utilized as a single-frequency driver for the 100-W amplifier described in Sec. II-A above.

Two potential problems arose during tests of this 10- to 15-W oscillator. At first, in spite of the 100-MHz cavity mode spacing, this laser would only oscillate in the 00° to 02° vibrational band of CO₂ during several weeks of continuous testing. Although systematic variations of pressure and excitation current have been tried over more than a 2:1 range, the output would at most shift to some other strong P- or R-branch rotational transition within the 00° to 02° vibrational band. Subsequently, this behavior was attributed to slightly higher reflectivities in the 9- to 10-μm wavelength region on several output mirrors used in these tests. After changing to mirrors with reflectivities carefully maximized at 06 μm, 00° to 0° vibrational band operation was immediately obtained.

The second potentially very troublesome problem was located when it was noticed that the output mirror holder's temperature increased appreciably with some of the mirrors tried during the testing of the 1 m oscillator. Subsequently, it was determined that most of the IRTRAN IV substrates tested had an absorption appreciably greater than that specified by the manufacturer. Because of the unexpected absorption losses in the output mirror and the high output power of the 1 m oscillator, the output may shift several rotational transitions before reaching a final equilibrium temperature. Although this settling time is very much longer than found with previous lower power tubes, essentially single-transition, single-frequency operation will ultimately occur.

The absorption problem found with IRTRAN IV will be hopefully overcome by the future use of GaAs substrates. All three GaAs substrates tested so far yielded consistent data which were well below the absorption losses of the best IRTRAN IV tested.

Extensive modifications of the laser processing station were carried out. The resulting versatility in the choice of gas fill enabled us to double to 3 W the single-frequency output power of the older 50-cm cavity (20-cm discharge length) stable lasers. Assembly of the completely redesigned versions of the stable lasers was begun, and testing should commence within a month.

C. Freed

C. THERMAL BLOOMING

From elementary considerations, one would expect lens-like effects when a light beam deposits heat in a fluid. Assuming the refractive index change is proportional to the density change, analytic expressions for the steady-state focal length \( f \) (negative) and the time development \( f(t) \) of the focal length of an absorbing medium can be obtained using a simplified model. The validity of this model has been experimentally confirmed in liquid cells. \( ^3 \)
Section II

A cell has been constructed to attempt the measurement of these thermal blooming effects in gases. Because of the relatively high power available, a CO₂ gas laser has been used as the source and pure CO₂ gas at about one atmosphere as the absorber. When necessary, the absorption can be enhanced by the addition of a few torrs of ethylene. Although the blooming in a 2-meter cell with 5-W input in a 1-cm beam is quite substantial \((f \approx -2m)\), all attempts at quantitative measurements of the time development have been unsuccessful. The dynamic range and sensitivity of the temperature-sensitive phosphor⁴ are inadequate with the laser power now available to us (the beam is visible with appropriate mounting of the phosphor, but the time response under these conditions is poor). An attempt was made to measure the output beam diameter by scanning it across a photoconductive detector, but the lack of cylindrical symmetry due to convection and the shape changes as steady state is approached make interpretation of the results difficult. The cell is now mounted horizontally, and the characteristic time for convection effects is comparable to that for thermal diffusion, causing the above problems.

Several possible changes are under consideration, such as using a wavelength where better image detectors are available, using higher power at 10.6\(\mu\)m, or using the 10.6 beam only for heat deposition and using a low-power visible beam for measurements.

A. H. M. Ross

D. OPTICAL HETERODYNE DETECTION AT 10.6 \(\mu\)m OF THE BEAT FREQUENCY BETWEEN A TUNABLE \(\text{Pb}_{0.88}\text{Sn}_{0.12}\) Te DIODE LASER AND A CO₂ GAS LASER

We have used a current-tunable \(\text{Pb}_{0.88}\text{Sn}_{0.12}\) Te diode laser to achieve optical heterodyning with a CO₂ gas laser. The beat frequency was continuously controllable from under 50 to 1300 MHz, the high-frequency limit of our Ge:Cu detector. These experiments have yielded the first direct measurement of the linewidth of the emission from a semiconductor p-n junction laser, displayed on a spectrum analyzer as a frequency spread of the heterodyne signal. Preliminary indications are that the linewidth is less than 100 kHz, with power supply ripple in the diode laser circuit presently precluding a more accurate determination. (The linewidth of the CO₂ laser emission is less than a few hundred hertz.)⁵

The diode used for the heterodyne experiments was cleaved into a rectangular parallelepiped 1.3 mm long, 0.5 mm wide, and 0.2 mm thick from vapor-grown \(\text{Pb}_{1-x}\text{Sn}_x\) Te material tailored to produce spontaneous emission at 10.6\(\mu\)m, for which \(x = 0.12\). Ohmic contacts were applied and the diode was attached to the cold "finger" of a liquid helium dewar. A single-pass grating spectrometer was used to measure the wavelength of the laser emission as a function of diode current; curves similar to those of magnetic-field tuning⁶ were obtained.

The diode laser line is tunable through six modes from 943.6 to 946.7 cm⁻¹ for direct currents from 675 to 1800 mA. (At 1000 mA, the output power is approximately 100\(\mu\)W.) Within each mode, continuous control is achieved over approximately 0.2 cm⁻¹ (6 GHz). The overall tuning range encompasses two adjacent CO₂ rotational transitions: \(P_{18}\) at 945.93 cm⁻¹, and \(P_{20}\) at 944.15 cm⁻¹. Only the \(P_{20}\) transition is close enough to one of the diode laser modes to produce a beat frequency within the limits of our detector. The CO₂ laser, which was especially constructed for highly stable, single-frequency operation,⁵ was tuned to the \(P_{20}\) transition; the
Pb_{0.88}Sn_{0.12}Te diode current was adjusted to produce laser emission in the proper mode. Both beams were directed collinearly onto the Ge:Cu detector, and under these conditions the heterodyne IF detector current is given by

$$i_{IF} = \frac{2qG\eta}{\hbar\nu} (P_1 P_2)^{1/2} \sin[2\pi f_{IF} t]$$

(1)

where the beat frequency $f_{IF} = c(\lambda_{diode} - 1,4), P_1$ and $P_2$ are the absorbed powers, $G$ is the detector gain, and $\eta$ is its efficiency. Polarization and nonalignment terms are neglected.

Figure II-3(a) is an oscillograph of the 100-MHz beat signal produced between the P\textsubscript{20} laser line and the diode laser line emitted at 1135 mA. The sinusoidal variation, in accordance with Eq. (1), is a clear indication of heterodyne operation. The dispersion of a 1250-MHz beat frequency (diode current of 1045 mA), occurring just below the detector cutoff frequency, is shown in Fig. II-3(b). It is evident from the width of the spectrum that the diode laser linewidth is 100 kHz or less. The 1-sec exposure of Fig. II-3(c) represents 100 sweeps of the spectrum analyzer and illustrates the fluctuations in the beat frequency caused by the 100-\mu A rms ripple in the diode laser current. With a better power supply in conjunction with storage batteries, we hope to reduce the ripple in the diode current.

Figure II-4 shows the range over which the beat frequency was continuously tunable, and the dependence of the beat frequency on diode current. The tuning rate of 12.8 MHz/mA agrees well with that predicted from the grating spectrometer data.

E. D. Hinkley  
T. C. Harman  
C. Freed

REFERENCES

2. N. M. Kroll and P. L. Kelley, private communication.
Fig. 11-3. Beat frequency signal between Pb0.88Sn0.12Te diode laser line and P20 line of CO2 laser. (a) $f_{j} = 100$ MHz, $I_d = 1135$ mA; (b) $f_{j} = 1250$ MHz, $I_d = 1045$ mA, single scan; (c) multiple (100) scan, illustrating effect of power supply ripple of 100-µA rms in diode circuit.

Fig. 11-4. Tuning range of beat frequency and dependence on diode current. Frequency values were measured with spectrum analyzer.
A. BOUNDARY LAYER ANALYSIS OF FORCED CONVECTION CRYSTAL GROWTH

We have found that forced convection can be used to increase the rate of crystal growth from the vapor phase and to control the morphology of the growing interface. The relationship between growth rate and carrier gas velocity has now been derived theoretically by analyzing the properties of the diffusion boundary layer at the interface. In addition, the condition required for interface stability has been formulated in terms of the temperatures at the interface, at the edge of the boundary layer, and at the solid source.

![Diagram of apparatus for measuring crystal growth velocity as function of carrier gas velocity and temperatures](image)

The apparatus used to study forced convection crystal growth is shown in Fig. III-1. An inert carrier gas, passing through a packed bed of polycrystalline material, is saturated with vapor at the source temperature \( T_s \). The concentration \( C_S \) of the vapor is related to the saturation vapor pressure \( p_S \) by the ideal gas law \( C = \frac{p}{RT} \). The saturated gas is then heated to a higher temperature \( T_0 \). Finally, it passes over the growing crystal interface at a lower temperature \( T_i \), where condensation reduces the vapor pressure to \( p_i \) (the saturation pressure at \( T_i \)), and correspondingly reduces the concentration to \( C_i \). If it is assumed that the temperature and concentration changes occur in a boundary layer of thickness \( \delta \) adjacent to the interface, forced convection may be regarded as placing a virtual vapor source (at temperature \( T_s \)) and a virtual heat source (at temperature \( T_0 \)) at a distance \( \delta \) from the interface.

If diffusion through the boundary layer is the rate-limiting step in crystal growth, the growth rate given by the material balance at the interface is

\[
v = \frac{MD(C_S - C_i)}{\rho \delta}
\]
where $M$ is the molecular weight of the condensing vapor, $D$ is its diffusion coefficient in the carrier gas, and $\rho$ is the density of the crystal. For forced convection, the thickness of the boundary layer is

$$\delta = B(D/V)^{1/2}$$

(2)

where $V$ is the carrier gas velocity, and $B$ is a geometric constant. Substituting Eq. (2) into Eq. (1) gives

$$v = \frac{M(C_s - C_i)(DV)^{1/2}}{\rho B}$$

(3)

Thus, the crystal growth velocity is proportional to the first power of the available vapor concentration $(C_s - C_i)$, and to the square root of the carrier gas velocity.

Data previously reported for the growth velocity of iodine crystals as a function of the temperature gradient at the interface can be used to test Eq. (3). These data, which were obtained with the apparatus of Fig. III-1 for two different helium carrier gas velocities, have been replotted in Fig. III-2 as a function of the available vapor concentration. In agreement with Eq. (3), it is seen that $v$ is proportional to $(C_s - C_i)$ for a given value of $V$. The straight lines shown in Fig. III-2 were calculated from Eq. (3) by using the measured values of $(C_s - C_i)$ and $V$, the published values of $M$ and $\rho$, and $D = 0.5$ cm$^2$/sec, the self-diffusion coefficient for helium gas at one atmosphere. The only adjustable parameter was the constant $B$. The same value of this constant, 0.71 cm$^{1/2}$, was used to calculate the lines for both values of $V$. The satisfactory agreement between the lines and the experimental points shows that the data are consistent with the $v \propto V^{1/2}$ relationship of Eq. (3).

The experimental results previously reported for the growth rate of camphor crystals also confirm the proportionality between $v$ and $(C_s - C_i)$. The best fit to the data was obtained for $B = 0.57$ cm$^{1/2}$.

Throughout the preceding discussion, it was assumed that crystal growth takes place at a smooth interface. However, we showed earlier that roughening of the interface or even dendrite formation can occur in vapor growth because of interface instability resulting from
Section III

constitutional supercooling. We derived a criterion for interface stability in terms of the temperature gradient in the gas phase at the interface and the growth velocity, considered as two independent variables. We shall now extend the earlier treatment by taking account of the relationship between these quantities.

It was shown in Ref. 3 that the growth interface will be stable if \((dp/dx)_i < (dp_0/dx)_i\), where \(p\) is the partial pressure of the condensing component, \(p_0\) is the saturated vapor pressure, and \(x\) is the distance between the interface and a point in the gas phase. The stability criterion may also be written as \((dC/dx)_i < (dC_0/dx)_i\), where \(C_0\) is the concentration corresponding to \(p_0\).

If the concentration gradient within the boundary layer is assumed to be constant, then for forced convection, \n
\[
\frac{dC}{dx}_i = \frac{C_S - C_i}{\delta}
\]

(4)

If it is assumed that \(p_0\) is proportional to \(\exp[-\Delta H/RT]\) and that \(p_i\) is equal to \(p_0\) at \(T_1\), then differentiating \(C_0 = p_0/RT\) gives

\[
\frac{dC_0}{dT} = \frac{C_i}{T_i} \left(\frac{\Delta H}{RT} - 1\right)
\]

(5)

If it is assumed that the temperature gradient is constant within the thermal boundary layer, and that this layer has the same thickness as the diffusion boundary layer, then

\[
\frac{dT}{dx}_i = \frac{T_\delta - T_1}{\delta}
\]

(6)

Multiplying Eqs. (5) and (6) gives

\[
\frac{dC_0}{dx}_i = \frac{T_\delta - T_1}{\delta} \frac{C_i}{T_i} \left(\frac{\Delta H}{RT} - 1\right)
\]

(7)

To obtain the criterion for interface stability, we set \((dC_0/dx)_i = (dC/dx)_i\). From Eqs. (4) and (7),

\[
\frac{T_\delta - T_1}{T_i} = \frac{(C_S - C_i)/C_i}{\left(\Delta H/RT_1\right) - 1}
\]

(8)

\[
\frac{T_\delta}{T_i} = \frac{(T_1/T_S) \exp[(\Delta H/RT_1) \left(T_S/T_i - 1\right)] - 1}{\left(\Delta H/RT_1\right) - 1} + 1
\]

(9)

The growth interface will be stable only for values of \(T_\delta/T_i\) equal to or greater than those given by Eq. (9). Values of \(T_\delta/T_i\) calculated from Eq. (9) are plotted in Fig. III-3 as a function of \(T_\delta/T_i\) for the case in which \(\Delta H/RT_1 = 15\), the value for a gas obeying Trouton’s rule when \(p_i = 15\) torrs. We see from Fig. III-3 that along the calculated line the value of \(T_\delta/T_i\) is always greater than the corresponding value of \(T_S/T_i\). Therefore, stable growth can occur only if the carrier gas, after passing over the source at \(T_S\), is heated to a temperature higher than \(T_s\) before it reaches the growth interface. It should be noted that the growth velocity does not appear...
in Eq. (9). Therefore, once a suitable temperature profile is established, the growth velocity may be increased indefinitely, without causing interface instability, by increasing the carrier gas velocity.

T. B. Reed
A. J. Strauss

B. OPTICAL TRANSMISSION OF Cd$_{1-x}$Mg$_x$Te ALLOYS

The first investigation of the pseudo-binary CdTe-MgTe system was recently reported by Itoh. Since CdTe has the zincblende structure and MgTe has the wurtzite structure, a complete series of solid solutions cannot be formed. However, Itoh found that there is extensive mutual solid solubility. Alloys with zincblende structure are formed for compositions up to about 60 mole-percent MgTe, and wurtzite-structure alloys are stable for compositions above about 75 mole-percent MgTe. Itoh found that the energy gap of the zincblende-structure alloys increases monotonically with increasing MgTe content.

In the present study, optical transmission measurements have been made on alloy crystals containing up to 46 mole-percent MgTe. The alloys were prepared from the elements in an open-tube reactor, where synthesis can be carried out quite rapidly without the danger of explosion encountered when sizable quantities of the elements are reacted in a sealed quartz ampoule. To obtain single crystals, ingots of the alloys were prepared by the Bridgman method. The fine-grained material prepared in the reactor was placed in a 24-mm i.d. fused silica ampoule, tapered
to a point at the lower end, which had been coated with pyrolytic graphite. After the ampoule was evacuated and sealed, it was heated in a vertical resistance furnace to melt the alloy, and then lowered through the furnace to produce directional crystallization of the melt. Thermal analysis experiments on CdTe-rich melts have shown that the liquidus temperature initially increases linearly with increasing MgTe content. For 35 mole-percent MgTe, the liquidus temperature is 1150°C. The value of 1114°C reported by Itoh for this composition is much too low.

Single-crystal samples between 1 and 3 mm thick were cut from the Bridgman-grown ingots with a wire saw and then mechanically polished. After the initial transmission measurements, a number of samples were annealed several days in saturated Cd vapor at 900°C and then remeasured.

![Fig. III-4. Optical transmission at room temperature vs wavelength for Cd$_{1-x}$Mg$_x$Te alloys.](image)

Optical transmission measurements in the vicinity of the fundamental absorption edge were made at room temperature with a single-beam, prism spectrometer. Figure III-4 shows the transmission curves obtained for CdTe and three representative alloy samples. These results illustrate the monotonic decrease in the absorption edge wavelength with increasing MgTe content, from about 0.86 µm in the infrared for CdTe to about 0.56 µm in the visible for $x = 0.46$. They also illustrate the marked increase in transmission at wavelengths beyond the absorption edge which generally resulted from annealing in saturated Cd vapor. (The as-grown data for the sample with $x = 0.24$ have been omitted from Fig. III-4, since annealing produced no appreciable change in its transmission.) It is probable that the increase in transmission is due primarily to the removal of Te-rich inclusions or microprecipitates formed during growth. This explanation is consistent with microscopic observations made on alloy samples which contained enough MgTe to be transparent to visible light. The as-grown samples contained large numbers of small opaque areas which were greatly reduced in size by annealing.

Transmission measurements between 2 and 15 µm were made on annealed samples at room temperature with a double-beam, prism spectrometer. For each sample, the transmission is

23
Section III

Fig. III-5. Absorption coefficient at room temperature vs photon energy for Cd$_{1-x}$Mg$_x$Te alloys.

Fig. III-6. Energy gap at room temperature vs composition for Cd$_{1-x}$Mg$_x$Te alloys.
almost independent of wavelength and lies between 50 and 65 percent. These results indicate
that the transmission in this region was determined primarily by reflection losses.

In order to determine the energy gaps of the alloys, absorption coefficients were calculated
from the transmission data in the vicinity of the absorption edge. The reflectivity for all samples
was taken to be 0.24, the value for CdTe at its absorption edge. The results are shown in Fig. III-5,
where the absorption coefficient is plotted on a logarithmic scale as a function of photon energy.
The results for CdTe are in reasonably good agreement with those reported by Marple.6 The
absorption edge is not as steep as Marple's, presumably because of the higher purity and surface
perfection of Marple's sample which was zone-refined and chemically polished. The absorption
edges for the alloy samples are considerably less steep than the edge for CdTe. This difference
could easily be due to the lower purity of the alloys. Although they were synthesized from the
best commercially available Mg, this material is much less pure than the Cd and Te used.

An arbitrary but consistent method was used to evaluate the energy gaps of the alloys. The
energy gap for each sample was obtained by adding 0.056 eV to the photon energy for which the
absorption coefficient of the sample was 10 cm⁻¹. The correction term of 0.056 eV was adopted
in order to yield the published value, 1.50 eV, for the energy gap of CdTe at room temperature.
The energy gap values obtained in this manner are plotted against mole-fraction MgTe in Fig. III-6.
The data are well represented by a straight line. Extrapolation to x = 1 gives 3.08 eV as the
energy gap of hypothetical cubic MgTe. As shown in Fig. III-6, energy gap values calculated
from the absorption edge wavelengths reported by Itoh4 are in fairly good agreement with the
present values. However, the present values are not consistent with Itoh's conclusion that the
absorption edge wavelength, rather than the energy gap, varies linearly with MgTe content. Ex-
trapolation of his wavelength vs composition line gives 5.0 eV for the energy gap of cubic MgTe.
This value seems much too high, since published7 optical absorption data for thin films of hex-
agonal MgTe indicate that the energy gap of this phase is less than 3.6 eV. At this energy, the
absorption coefficient has already risen to about 10⁵ cm⁻¹, and there is a peak in the curve of
absorption coefficient vs energy.

A. J. Strauss

C. PHOTOLUMINESCENCE DUE TO OXYGEN IN ZnTe ALLOYS

Thomas and co-workers8 were the first to observe mirror luminescence and absorption
bands in ZnTe due to a center lying about 0.4 eV below the conduction band. They proposed9
that this center is an isoelectronic trap resulting from the substitution of an oxygen atom on a
tellurium site. At low temperatures, the luminescence band peaks close to 6500 Å, and the ab-
sorption band peaks near 5900 Å. Both bands exhibit marked structure due to phonon cooperation.

According to the proposed model, the oxygen acts as an acceptor-like electron trap, since
oxygen is more electronegative than the tellurium it replaces. In the no-phonon process, the
absorption of a photon of energy E₀ results in the formation of a bound exciton, which is com-
posed of an electron strongly bound to the oxygen center and a hole weakly bound to the electron.
Luminescence is observed when the exciton is annihilated. In the no-phonon case, the energy of
the emitted photon is again E₀. The electron trapping energy Eₜ is equal to the band gap energy
E₉ minus E₀. For ZnTe at 4.2°K, where we have performed our luminescence experiments,
E₉ is 2.39 eV, E₀ is 1.986 eV, and Eₜ is therefore 0.40 eV.
Section III

Fig. III-7. Spectra of photoluminescence at 4.2°K due to oxygen in ZnTe$_{1-x}$Se$_x$ alloys. Wavelengths corresponding to no-phonon energy $E_0$ are indicated by arrows.

Fig. III-8. Photoluminescence energies and energy gap for ZnTe$_{1-x}$Se$_x$ alloys at 4.2°K, plotted against mole-fraction ZnSe.

Fig. III-9. Photoluminescence energies for ZnTe$_{1-x}$S$_x$ alloys at 4.2°K, plotted against mole-fraction ZnS.
At the beginning of our investigation, oxygen had not been conclusively identified as the center responsible for the mirror luminescence and absorption, although Hopfield, Thomas, and Lynch\(^9\) had reported observing the most intense absorption in samples grown from a melt doped with ZnO. Similarly, we have found that the absorption coefficient in vapor-grown crystals increases with increasing partial pressure of oxygen in the growth ampoule. Merz\(^10\) has recently presented much more direct evidence for the oxygen model based on isotope substitution and Zeeman experiments.

In this investigation, we have observed the variation in the oxygen luminescence spectrum which results when ZnTe is alloyed with ZnSe, ZnS, or CdTe. On the basis of the oxygen model, the trapping energy \(E_t\) is expected to decrease with increasing ZnSe or ZnS content, since oxygen and tellurium differ more in electronegativity than do oxygen and selenium or oxygen and sulfur. On the other hand, \(E_t\) is expected to remain essentially constant in the ZnTe-CdTe alloys, since changes in the cation lattice should not strongly affect the trapping process. These predictions have been confirmed by the data.

Alloy samples were prepared by annealing weighed mixtures of the powdered compounds in sealed quartz ampoules. In order to enhance the luminescence, excess zinc metal was added to the powder mixtures, and the ampoules were backfilled with oxygen at 400 torrs. The samples were annealed at 1050°C or above for 3 days and then either furnace-cooled or quenched in water. The alloy compositions were determined from x-ray lattice parameters and did not vary from the nominal compositions by more than 2 mole-percent.

Figure III-7 shows representative photoluminescence spectra for ZnTe-ZnSe alloys at 4.2°K excited by 3650 Å radiation. The luminescence band is shifted to higher energies with increasing ZnSe content. Addition of as little as 3 mole-percent ZnSe causes the phonon structure to disappear. This makes it impossible to determine \(E_O\) for the alloys from the position of a distinguishable no-phonon line. On the basis of the data for ZnTe, \(E_O\) for each alloy has been taken as the energy corresponding to the wavelength on the high-energy side of the luminescence band at which the intensity is 15 percent of the maximum intensity for the band.

In Fig. III-8, the 4.2°K values of \(E_O\) and of the photon energy at the peak of the luminescence band are plotted against \(x\), the mole-fraction of ZnSe in the ZnTe\(_{1-x}\)Se\(_x\) alloys. Up to \(x = 0.4\), both energies increase as \(x\) increases, and the data are well represented by two parallel straight lines. This indicates that the shape of the band remains essentially the same over this composition range. Near \(x = 0.4\), however, there appears to be an abrupt change in the character of the luminescence, and we believe that the luminescence above \(x = 0.4\) is not due to oxygen but rather to some unknown impurity.

Figure III-8 also gives the values of the energy gap \(E_g\) for the ZnTe\(_{1-x}\)Se\(_x\) alloys at 4.2°K. The \(E_g\) curve, which passes through a minimum at \(x = 0.4\), was obtained by scaling the room-temperature values determined by Larach, Shrader, and Stocker.\(^11\) It is seen that the trapping energy \(E_t\), which is the difference between \(E_g\) and \(E_O\), decreases with increasing ZnSe content, as expected for the isoelectronic trap model. Extrapolation of the \(E_O\) line indicates that the trapping energy becomes zero at about \(x = 0.5\). Consequently, there is no luminescence due to oxygen at higher concentrations of ZnSe. For these concentrations, the luminescence observed is due to the unknown impurity mentioned above.

Figure III-9 shows the oxygen luminescence data for ZnTe-ZnS alloys containing up to 20 mole-percent ZnS. The photon energies at the peak of the luminescence band and at 15-percent
Section III

intensity increase with increasing ZnS content. The data are well represented by two parallel straight lines, whose slope is somewhat greater than the slope of the corresponding lines in the ZnTe-ZnSe system. Although energy gap data for the ZnTe-ZnS system are very limited, Larach, Shrader, and Stocker have found that \( E_t \) initially decreases with increasing ZnS content. Therefore, \( E_t \) decreases with increasing ZnS content, as expected for the isoelectronic trap model.

![Figure III-10. Photoluminescence energies and energy gap for Zn\(_{1-x}\)Cd\(_x\)Te alloys at 4.2°C, plotted against mole-fraction CdTe.](image)

Figure III-10 shows the luminescence data for the ZnTe-CdTe alloys. In addition to the oxygen band, a second band at somewhat higher energy was observed in all these samples. Because there is some overlap between the oxygen band and the second band (which is presumably due to an unknown impurity originating in the CdTe), the no-phonon energy for the oxygen band cannot be determined from the wavelength at 15-percent intensity. Therefore, Fig. III-10 includes only the photon energy at the peak of the oxygen band, the energy at the peak of the second band, and the energy gap for the ZnTe-CdTe alloys, which is reported to vary linearly or almost linearly with composition. In contrast to the results for the alloys with ZnSe or ZnS, the energy of the oxygen luminescence band decreases with increasing CdTe content. The data are well represented by a straight line whose slope is approximately the same as the slope of the energy gap. Thus, \( E_t \) remains essentially constant over the composition range investigated, as expected for the isoelectronic trap model.

G. W. Iseler
A. J. Strauss

D. COMPOSITION- AND PRESSURE-INDUCED STRUCTURAL CHANGES IN THE Ba\(_{1-x}\)Sr\(_x\)RuO\(_3\) SYSTEM

The structural chemistry of many inorganic compounds with the general formula ABX\(_3\), where A and B are cations and X is an anion, can be described in terms of hexagonal and/or cubic close packing of AX\(_3\) layers with the B cations filling the X\(_6\) octahedra thus formed. When all layers are hexagonal close packed, the octahedra share faces with each other to form chains [Fig. III-11(a)]. When all layers are cubic close packed, the octahedra form a three-dimensional array by sharing only corners, giving the perovskite structure [Fig. III-11(b)].

If structures with mixtures of hexagonal and cubic close-packed layers are allowed, one might expect an infinite number of possible structures. However, there appear to be only three intermediate stacking sequences in actual compounds. The one most closely resembling cubic close packing has a 6-layer (6L) sequence cchcch [Fig. III-11(c)], where c and h represent cubic and hexagonal closed-packed layers, respectively. The structure having equal amounts of hexagonal and cubic close packing has a 4-layer (4L) sequence chch [Fig. III-11(d)]. The last known
Fig. III-11. Schematic of [110] plane of hexagonal cell for ABX₃ structures showing face and corner sharing by octahedra between AX₃ layers; c represents c-parameter of crystal.

The intermediate structure has predominantly hexagonal close packing with the 9-layer sequence hhchhcchhc (Fig. III-11(e)). Katz and Ward have discussed in detail the structural relation of all these types plus some of the unknown possibilities. The system BaₓSr₁₋ₓRuO₃ (Ref. 16) is of interest since one is able to study the effects both of A cation size and of pressure on the structural transformations from the 9-layer compound (BaRuO₃) through the 4- and 6-layer phases to the perovskite (SrRuO₃). The strontium-rich members are also interesting since they exhibit spontaneous magnetism.

In the present investigation, ambient pressure material was prepared by the solid state reaction of BaCo₃-SrCO₃ mixtures with Ru metal at temperatures up to 1100°C. The preparation of high-pressure phases was carried out in cylindrical gold or platinum capsules in a belt apparatus. The temperature was raised after application of pressure, held for one-half hour, and then rapidly quenched before the pressure was released. Phase and structural data were obtained by analyzing x-ray diffraction patterns for powdered samples measured with a Norelco x-ray diffractometer using monochromatic CuKα radiation. The concentration of the components in two-phase samples was estimated from the relative intensities of the lines in the diffraction patterns.
Section III

Fig. III-12. Pressure-vs-composition phase diagram for Ba$_{1-x}$Sr$_x$RuO$_3$ system at 1000°C.

The results of this investigation are summarized in the pressure-vs-composition plot shown in Fig. III-12 for the system at 1000°C. It can be seen that the addition of strontium and the application of pressure both favor structures with more cubic close packing. Both effects tend to decrease the B-B distances and therefore to make the face sharing of octahedra (associated with hexagonal close packing) less stable. In the 6-layer region with high strontium content, distortion of the normal hexagonal unit cell ($a \approx 5.6 \, \text{Å}, \, c \approx 13.9 \, \text{Å}$) produces diffraction line splitting. The splitting can be attributed to a monoclinic distortion with $a \neq b$ and $\gamma \neq 60^\circ$. Even in the most distorted structures, the deviation from a hexagonal unit cell is less than 4 percent.

J. M. Longo  
D. A. Batson  
J. A. Kafalas  
T. W. Hilton

E. DETERMINATION OF EXPERIMENTAL FORM FACTORS ON AN ABSOLUTE SCALE FROM RELATIVE X-RAY INTENSITIES

The controversy about experimental determination of atomic form factors in solids, by means of x-ray diffraction intensity measurements, relates only to results on an absolute scale. On a relative scale, all the available experimental results agree. An alternate method of evaluating the scaling constant would thus be useful.

The form factor can be represented by the parametric expression

$$f(s) = \sum_j \alpha_j \exp \left[ -\frac{\beta_j s^2}{2} \right]$$
where \( s = \frac{|k|}{4\pi} = \frac{(\sin \Theta)}{\lambda} \), with \( \Theta \) the Bragg angle and \( \lambda \) the wavelength, and the \( \alpha \)'s and \( \beta \)'s are Gaussian coefficients. We require the form factor to satisfy the two conditions \( f(s = 0) = Z \), where \( Z \) is the atomic number, and \( f(s > s_c) = f'(s > s_c) \), where \( s_c \) is the reciprocal lattice vector value at which the outer electrons' contribution to the scattering is negligible and \( f'(s) \) is the theoretical free atom form factor. This allows a least-squares determination of the scaling constant as well as the Debye-Waller temperature parameter \( B(T) \) and the \( \alpha \)'s and \( \beta \)'s.

This method has been applied to our relative x-ray intensity data on Ni metal (Table III-1), which are in excellent agreement with previous results collected with the same radiation (filtered MoK\(_\alpha\) radiation). Figure III-13 shows our values for the relative structure factor \( J(s) = \frac{\langle I(s) \rangle}{mP(0)}^{1/2} \), where \( I(s) \) is the integrated intensity on a relative scale, \( m \) is the plane

### Table III-1

<table>
<thead>
<tr>
<th>( \sin \frac{\Theta}{\lambda} )</th>
<th>hkl</th>
<th>( I(s) ) (^\dagger)</th>
<th>( I(s) ) cal(^\dagger)</th>
<th>( P(s) ) (^\S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2458</td>
<td>111</td>
<td>351.84</td>
<td>349.78</td>
<td>351.01</td>
</tr>
<tr>
<td>0.2838</td>
<td>200</td>
<td>169.84</td>
<td>169.06</td>
<td>170.82</td>
</tr>
<tr>
<td>0.4013</td>
<td>220</td>
<td>101.13</td>
<td>100.04</td>
<td>99.60</td>
</tr>
<tr>
<td>0.4706</td>
<td>311</td>
<td>104.65</td>
<td>104.43</td>
<td>103.23</td>
</tr>
<tr>
<td>0.4913</td>
<td>222</td>
<td>28.91</td>
<td>28.84</td>
<td>28.22</td>
</tr>
<tr>
<td>0.5676</td>
<td>400</td>
<td>11.48</td>
<td>11.42</td>
<td>10.88</td>
</tr>
<tr>
<td>0.6185</td>
<td>331</td>
<td>29.29</td>
<td>29.74</td>
<td>29.26</td>
</tr>
<tr>
<td>0.6346</td>
<td>420</td>
<td>26.03</td>
<td>25.56</td>
<td>25.70</td>
</tr>
<tr>
<td>0.6951</td>
<td>422</td>
<td>16.56</td>
<td>16.53</td>
<td>16.16</td>
</tr>
<tr>
<td>0.7373</td>
<td>333,511</td>
<td>16.21</td>
<td>16.29</td>
<td>15.88</td>
</tr>
<tr>
<td>0.8027</td>
<td>440</td>
<td>3.80</td>
<td>3.96</td>
<td>3.85</td>
</tr>
<tr>
<td>0.8394</td>
<td>531</td>
<td>12.79</td>
<td>12.80</td>
<td>12.63</td>
</tr>
<tr>
<td>0.8514</td>
<td>442,600</td>
<td>7.56</td>
<td>7.38</td>
<td>7.58</td>
</tr>
<tr>
<td>0.8974</td>
<td>620</td>
<td>4.45</td>
<td>4.57</td>
<td>4.44</td>
</tr>
<tr>
<td>0.9305</td>
<td>533</td>
<td>3.95</td>
<td>3.87</td>
<td>4.06</td>
</tr>
<tr>
<td>0.9412</td>
<td>622</td>
<td>3.67</td>
<td>3.68</td>
<td>3.75</td>
</tr>
<tr>
<td>0.9831</td>
<td>444</td>
<td>1.02</td>
<td>1.02</td>
<td>1.01</td>
</tr>
<tr>
<td>1.0133</td>
<td>551,711</td>
<td>5.59</td>
<td>5.44</td>
<td>5.58</td>
</tr>
<tr>
<td>1.0232</td>
<td>640</td>
<td>2.73</td>
<td>2.62</td>
<td>2.75</td>
</tr>
<tr>
<td>1.0618</td>
<td>642</td>
<td>4.61</td>
<td>4.62</td>
<td>4.79</td>
</tr>
<tr>
<td>1.0899</td>
<td>553,731</td>
<td>6.33</td>
<td>6.41</td>
<td>6.60</td>
</tr>
<tr>
<td>1.1351</td>
<td>800</td>
<td>0.53</td>
<td>0.48</td>
<td>0.51</td>
</tr>
<tr>
<td>1.1614</td>
<td>733</td>
<td>1.89</td>
<td>1.88</td>
<td>1.92</td>
</tr>
<tr>
<td>1.1701</td>
<td>644,820</td>
<td>3.71</td>
<td>3.69</td>
<td>3.80</td>
</tr>
<tr>
<td>1.2040</td>
<td>660,822</td>
<td>2.65</td>
<td>2.69</td>
<td>2.64</td>
</tr>
<tr>
<td>1.2288</td>
<td>555,751</td>
<td>4.17</td>
<td>4.34</td>
<td>4.26</td>
</tr>
<tr>
<td>1.2370</td>
<td>662</td>
<td>1.82</td>
<td>1.80</td>
<td>1.87</td>
</tr>
<tr>
<td>1.2691</td>
<td>840</td>
<td>1.85</td>
<td>1.83</td>
<td>1.90</td>
</tr>
<tr>
<td>1.2927</td>
<td>753,911</td>
<td>5.79</td>
<td>5.73</td>
<td>5.95</td>
</tr>
<tr>
<td>1.3005</td>
<td>842</td>
<td>3.91</td>
<td>3.87</td>
<td>4.02</td>
</tr>
</tbody>
</table>

\( \dagger \) Observed intensities. The lines joined by a brace were overlapping. They have been counted together and resolved according to the theoretical ratio.

\( \dagger\dagger \) Values calculated from the Gaussian polynomial representing the data.

\( \S \) Experimental results of Ref. 18.
Section III

Fig. III-13. Relative structure factor $J(s)$ as function of $s = (\sin \theta)/\lambda$ for Ni metal.

<table>
<thead>
<tr>
<th>TABLE III-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>VALUES OF X-RAY PARAMETERS FOR Ni BEFORE AND AFTER REFINEMENT</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>0.0020</td>
<td>0.00166</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>1.2640</td>
<td>1.27705</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.0020</td>
<td>0.11825</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>13.2174</td>
<td>13.2296</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>3.7504</td>
<td>3.72131</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>7.1019</td>
<td>7.06452</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>0.2671</td>
<td>0.24092</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>4.1801</td>
<td>4.18757</td>
</tr>
<tr>
<td>$\beta_4$</td>
<td>12.4514</td>
<td>13.14709</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>2.2246</td>
<td>2.24115</td>
</tr>
<tr>
<td>$\beta_5$</td>
<td>60.3462</td>
<td>173.81097</td>
</tr>
<tr>
<td>$\delta(T)$</td>
<td>0.381</td>
<td>0.3705</td>
</tr>
</tbody>
</table>

32
multiplicity, and $P(\theta)$ is the Lorentz and polarization correction. Figure III-13 also shows the Gaussian line best representing the $J$ values. Table III-2 lists the parameters before and after least-squares refinement. The initial $\alpha$ and $\beta$ values are those obtained by Cromer and Waber for the free Ni atom. The accuracy of the fit in Fig. III-13 averages 2 percent, the same as our experimental error and our discrepancy with previous results. In this experiment, the major difficulty is in making the background determinations with sufficient accuracy.

In Fig. III-14, the theoretical free atom form factor for the electronic configuration $3d_{\delta}4s_{2}$ (Ref. 20) is compared with the best Gaussian representation of our results for the form factor of solid Ni. One sees that there is a systematic deviation which reaches a maximum of 3 percent for $s \approx 0.6$. This is small but probably outside the experimental error. Fourier inversion of the two Gaussian representations yields the atomic charge distributions for the free atom and for the solid. The difference between these distributions is shown in Fig. III-15, where one sees that the atom in the solid has more electrons than the free atom in the region from 0.17 to 0.37 Å, and less between 0.37 Å and infinity. This suggests a transfer from the outer levels ($4s$) to the first inner levels ($3d$). Since 0.32 Å is the position of the $3d$ level in the free Ni atom, numerical integration of the real space charge density suggests a transfer of 0.3 electron, a value smaller than suggested by the magnetic moment. However, the accuracy of this determination is poor, and the result should be considered as qualitative.

It appears that the scaling method proposed here preserves the information concerning the outer electron distribution which is lost when the theoretical free atom form factor is used in scaling over the whole experimental range. The very slight difference from the free atom distribution found for Ni suggests an electronic configuration $3d_{\delta}4s_{2-\delta}$, where $\delta = 0.3$. Further work could convert this qualitative result to a quantitative value having a known accuracy.

P. M. Raccah
V. E. Henrich
REFERENCES

A. ELECTRONIC BAND STRUCTURE

1. Optical Properties of Nickel-Copper Alloys from 0.2 to 11 eV

Our investigation of the band structure of nickel, through optical studies, has led us to the nickel-copper disordered alloy system. Experimental measurements and band calculations indicate an energy band picture for copper and nickel, around the L point in the Brillouin zone, as shown in Fig. IV-1. Also given here are the low-energy transitions observed in nickel and the reversal, between copper and nickel, of the L_d-like and the L_p-like states. It seemed logical to test the band model for nickel, which is less well established than that of copper, by looking at the optical properties of the alloy system of these two elements; they lie next to each other in the periodic table, copper having one more electron. As a result, we find that the alloy system is interesting in its own right.

We have measured the reflectance of single crystals of several alloys from 0.2 to 11 eV. Figure IV-2 shows the reflectance of a high-nickel and a high-copper alloy along with pure nickel and pure copper. The curves for the pure metals are virtually the same as those reported by Ehrenreich, et al., and Beaglehole. The 0.4-eV shoulder in nickel is absent at room temperature in the 61-percent nickel alloy. At 77°C, in measurements not shown, a small kink in the curve for the 61-percent nickel alloy does seem to occur at 0.3 eV; this may be related to ferromagnetic behavior. We have previously interpreted this structure in nickel as a minority spin band transition from L_d to L_d (see Ref. 1).
Section IV

In the high-copper curves, even with 16-percent nickel, the reflectance starts dropping immediately rather than staying at a high value. In the three samples with copper, there is consistently a distinct change in slope near 2 eV, characteristic of the first interband transition in copper from the d-bands to the Fermi surface. This edge does not shift as we would expect if an average potential or rigid band model applied to the alloy system. In either of these models, adding nickel to copper would change the d-band Fermi surface separation and shift the energy of the first interband transition. The recent limited data of Schröder and Önengüt on alloys with as low as 2-percent nickel also show a drop in the low-energy reflectance with the edge remaining at 2 eV.

At higher energies, other changes occur. The 61-percent nickel alloy shows a broad peak occurring between 2 and 5 eV, with a distinct narrowing and lowering of the peak at 5.2 eV. A similar but not so distinctive change occurs in the high-copper samples.

Our results are related to band models by using a Kramers-Kronig analysis to compute the imaginary part of the dielectric constant \( \varepsilon_2 \). Figure IV-3 shows \( \varepsilon_2 \), which is proportional to the joint density of states for interband transitions. The suggestion from the reflectance data, that the 2-eV transition in copper does not shift as nickel is added, is confirmed by the \( \varepsilon_2 \) curves. The nonshift of the 2-eV copper absorption is clearly evident as a knee in the 16-percent nickel alloy spectrum and an inflection point in the 61-percent nickel alloy. In the 16-percent nickel alloy, a rise in \( \varepsilon_2 \) above that of the free electron behavior of copper is obtained. This apparently comes from low-energy transitions to the Fermi surface from states near the Fermi surface.

At higher energies, the detailed picture for the alloys is less clear but it appears that other band models, such as the "virtual states" model of Friedel and Anderson, and the "minimum polarity" model recently discussed by Lang and Ehrenreich, must be considered in order to explain the data below 4 eV. The "rigid band" model is inadequate. Recent optical and photoemission results of Seib and Spicer should provide complementary information. We are planning further measurements on high-copper alloys where the change in optical properties is most drastic.

2. Optical Studies in Bismuth-Doped Silicon

Measurements (which were described in the previous Solid State Research Report) have been completed of the optical absorption due to low-energy transitions of isolated bismuth impurity atoms in silicon at low temperatures as a function of the polarization of the infrared light beams.
Section IV

and the orientation of the uniaxial stress applied to the sample. Uniaxial stresses up to $6 \times 10^8$ dynes/cm$^2$ were applied in the [001], [110], and [111] crystal directions, with the $\mathbf{E}$ vector of the light parallel or perpendicular to the applied stress. An example of the data is given in Fig. IV-4, showing the transmission, in arbitrary units, for an applied stress of $1.17 \times 10^8$ dynes/cm$^2$ in a [001] crystal direction. The zero stress transition energies are also indicated on the figure.

All measured relative intensities and transition energies as a function of strain are in agreement with predictions based on the assumption that the transitions are from the $1s(A_1)$ ground level (of $T_d$ symmetry) to the $1s(T_2)$ level, where the $T_2$ level is split by spin-orbit coupling, and the form of the strain Hamiltonian is derived from effective mass and deformation potential theory.

W. E. Krag
W. H. Kleiner
H. J. Zeiger

3. Interband Magnetoreflection in Gray Tin

Two sets of interband transitions have been observed in the magnetoreflection of gray tin. One set has been seen at photon energies between 0.425 and 0.55 eV. Points from these transitions extrapolate to a zero magnetic field energy gap of 0.413 eV. From the band structure of gray tin shown in Fig. IV-5, we identify these transitions as taking place between the $\Gamma_7^-$ valence band and the $\Gamma_8^+$ conduction band, and represent them by arrow A. The second set of transitions (arrow B in Fig. IV-5) has been observed in the range of photon energies between 0.045 and 0.55 eV. These take place from the $\Gamma_8^-$ valence band to the $\Gamma_8^+$ conduction band across the zero thermal energy gap.

Fig. IV-4. Transmission vs photon energy of bismuth-doped silicon for uniaxial applied stress of $1.17 \times 10^8$ dynes/cm$^2$ in [001] crystal direction. The light is polarized parallel and perpendicular to applied stress. Zero stress positions of absorptions are indicated by vertical lines.

Fig. IV-5. Band structure of gray tin showing highest valence bands and lowest conduction band about $k = 0$. Arrows show transitions seen in magnetoreflection.
Section IV

For this experiment, we have used high-purity gray tin which has \( n_0 \sim 5 \times 10^{14} \text{ cm}^{-3} \), where \( n_0 \) is the density of donor impurities minus the density of acceptor impurities. This impurity concentration is at least a factor of 10 lower than that found in the best commercially available tin. The improvement in purity is accomplished with a solvent extraction process using the tin-mercury alloy system. In our experiment, light is reflected off a natural facet of a crystal, and most of our measurements have been made on a crystal with a (100) face. We have worked in the Faraday configuration, with the direction of light propagation parallel to the magnetic field \( \mathbf{H} \); therefore, our data are characteristic of \( \mathbf{H} \) perpendicular to the (100) plane.

The magnetoreflection results for gray tin are very similar to those for HgTe (see Ref. 11) but are more interesting for a comparison with theory for several reasons. First, as mentioned above, they are characteristic of a single, high-symmetry direction; such results could not be achieved in HgTe because of a materials limitation. This is especially important for fitting the \( \Gamma_8^+ \rightarrow \Gamma_8^+ \) transitions. Second, the warping of the \( \Gamma_8^+ \) bands, a parameter which is needed in the theory, has been measured for gray tin.\(^{12}\) Third, the complications which may be introduced by the inversion asymmetry of zincblende HgTe are absent for gray tin, which has inversion symmetry.

A matrix Hamiltonian, which includes the full interaction between \( \Gamma_7^- \), \( \Gamma_7^- \), and \( \Gamma_8^+ \) bands and includes higher band interactions to order \( k^2 \), has been used to calculate the magnetic energy levels.\(^{13}\) A shortcoming of this theory for both gray tin and HgTe is that the interaction between \( \Gamma_8^+ \) and the \( \Gamma_{15}^- \) conduction band (using a mixture of single- and double-group notations) is included only to order \( k^2 \). Thus, while the nonparabolicity of the \( \Gamma_8^+ \) conduction band caused by the interaction between \( \Gamma_7^- \) and \( \Gamma_8^+ \) bands is included, the nonparabolicity of the band caused by the \( \Gamma_{15}^- \) band is not.

Figures IV-6 and IV-7 show the transition energies vs magnetic field for the \( \Gamma_7^- \rightarrow \Gamma_8^+ \) and \( \Gamma_8^+ \rightarrow \Gamma_8^+ \) transitions, respectively. The solid curves are theoretical and give a good fit to both
sets of transitions. The data of Fig. IV-6 were taken with the sample at ~1.5°K, and those of Fig. IV-7 with the sample at ~20°K. We have measured the transitions of Fig. IV-6 at 20° and ~85°K and cannot detect any shift of the resonant energies. This is in marked contrast to HgTe which shows large temperature-induced shifts.

The systematic deviation at high photon energies for both sets of transitions, with the experimental points lying below the theoretical curves, is caused by the nonparabolicity of the \( \Gamma_8^+ \) conduction band induced by the \( \Gamma_{45} \) conduction band, as mentioned above. This effect has been discussed previously. One interesting feature of the low-energy transitions is that they give the \( \Gamma_8^+ \) valence band mass directly. This is evident from an examination of the Landau levels for these transitions, shown in Fig. IV-8. The spin splittings of \( \Gamma_8^+ \) valence and conduction bands are nearly equal, which means the two \( \sigma^+ (\Delta n = +1) \) transitions from the \( n \) valence sub-band to the \( n + 1 \) conduction sub-band are nearly degenerate in energy. The same is true of the \( \sigma^- (\Delta n = -1) \) transitions. Thus, the spacing in Fig. IV-7 between \( \sigma^+ \) transitions, or between \( \sigma^- \) transitions, is
Section IV

Fig. IV-8. Lowest Landau levels for $\Gamma_8^+$ bands at 70 kG. Arrows show optical transitions to $n = 2$ levels of conduction band. Difference between $\sigma^-$ and $\sigma^+$ transition energies to a given conduction band level is direct measure of valence band level spacing.

The lowest $\sigma^+$ transition in Fig. IV-7 is at too high an energy to be part of the Landau level transitions shown in Fig. IV-8. Our suspicion is that it is a transition from an impurity ground state, associated with the $n = 0$ conduction band Landau level to an excited impurity state associated with, and lying below, the $n = 2$ conduction sub-band. The observation of impurity transitions similar to this in p-type InSb and germanium\textsuperscript{15} makes this plausible from an experimental point of view. Evidence has been presented recently for discrete impurity levels in gray tin under uniaxial stress which causes the splitting of the $\Gamma_8^+$ bands.\textsuperscript{16} It would not be surprising if a similar effect were caused by a high magnetic field.

The following parameters\textsuperscript{11} have been used to generate the theoretical curves: $E(\Gamma_8^+) - E(\Gamma_7^+) = 0.413$ eV; $E(\Gamma_8^+) - E(\Gamma_7^+) = 0.80$ eV; $E_P = 24.5$ eV; $\gamma_1 = 4.42$; $\gamma_2 = -1.35$; $\gamma_3 = 1.35$; and $\kappa = -3.0$. The band edge masses corresponding to this set of parameters, in units of the free electron mass, are $m_c(\Gamma_8^+) = 0.028$, $m_v(\Gamma_8^+) = -0.195$, $m(\Gamma_7^+) = -0.057$, and $m(\Gamma_7^+) = -0.051$.

In addition to the work on the lowest $\sigma^+$ transition ($\Gamma_8^+ \rightarrow \Gamma_7^+$), we are hoping to obtain more information in the near future about the $\Gamma_{13}$ conduction band, from its nonparabolic effect on the $\Gamma_8^+$ conduction band, and to make a detailed comparison of our magnetorefectivity results with those from other experiments, especially the conduction band mass determinations from the oscillatory magnetoresistance.\textsuperscript{12,17}

S. H. Groves  A. W. Ewald
C. R. Pidgeon  R. J. Wagner
4. Inversion Asymmetry and Warping-Induced Interband Magneto-Optical Transitions in InSb

We have completed a study of "extra" transitions in the interband magnetoreflection and magneto-electroreflection of InSb, caused by the warping and by the linear-k splitting of the valence band. An unambiguous assignment of the transitions is made from a study of the anisotropy of the spectra, using left- and right-circularly polarized light, with the magnetic field along [100], [110], [111], and [211] directions of the crystal. From the relative strength and energies of these transitions, we are able to determine the size of the warping and linear-k terms in the effective mass Hamiltonian. We find the warping parameter $(\gamma_3 - \gamma_2) = 1.0$, and the linear-k parameter $C = 4.2 \text{eV-cm}$. The error in the determination of $(\gamma_3 - \gamma_2)$ is about 15 percent, and that in the determination of $C$ is about 30 percent. The result for $(\gamma_3 - \gamma_2)$ is in good agreement with the cyclotron resonance work of Bagguley, et al., but not with the more recent work of Tohver and Ascarelli. The value of $C$ is about three times smaller than suggested by Robinson, but is in good agreement with the theoretical estimate of Kane.

A short report of this work has been published in the Physical Review Letters. A longer version, with full account of the experimental and theoretical details, is being prepared currently.

S. H. Groves
C. R. Pidgeon

5. Determination of Debye Temperatures from Thermal Modulation of X-Ray Diffraction

The usual method of measuring the Debye temperature $\Theta_D$ in terms of x-ray diffraction intensities, consists of measuring the difference between the Debye-Waller factors at two fairly distant temperatures. This method precludes the possibility of making detailed studies of $\Theta_D$ in any small temperature range, and thus is not useful for studying critical transitions. We have measured the temperature derivative of the Debye-Waller factor at one temperature directly by synchronous detection of the diffracted x-ray beam from a thermally modulated sample. As the temperature of a crystal used as sample in an x-ray diffractometer is raised, thermal expansion of the lattice shifts the Bragg peaks toward lower angle. For a cubic crystal, this can be written as

$$\frac{d(2\Theta_0)}{dT} = -\frac{\lambda}{a \cos \Theta_0} \left( \frac{1}{a} \frac{da}{dT} \right)$$

where $\Theta_0$ is the Bragg angle, $T$ is the temperature, $\lambda$ is the x-ray wavelength, $a$ is the cell edge, and $(hkl)$ is the diffracting planes. At the same time, the increased atomic motion changes the intensities of the peaks, in general reducing them. For a simple lattice, this is taken into account by the Debye-Waller factor $B(T)$, which multiplies the $T = 0^\circ$ intensity in the form

$$I(T) = I(0) e^{-2B(T) S^2}$$

where $S = \sin \Theta / \lambda$. Thus,

$$\frac{dI}{dT} = -2S^2 B(T) \frac{dB(T)}{dT} I(T)$$

A short report of this work has been published in the Physical Review Letters. A longer version, with full account of the experimental and theoretical details, is being prepared currently.

S. H. Groves
C. R. Pidgeon
Section IV

Fig. IV-9. Experimental setup for thermal modulation.

If the sample temperature is modulated and the diffractometer angle is held constant, the thermal expansion appears in the AC component of the diffracted beam as the angular derivative of the lineshape, while the intensity change gives a signal proportional to the lineshape. Analysis of the resulting signal yields the relative amounts of these two components. Then, if $(1/a)(da/dT)$ is known, $dB/dT$ can be determined.

By using chopped radiation from a projection lamp focused on the sample (Fig. IV-9) to modulate the temperature (modulation amplitude $\sim 0.01^\circ$ to $0.1^\circ$C), signals of the form shown in Fig. IV-10 have been obtained with single-crystal NaCl. Most of the signal is due to thermal expansion, but careful examination shows the presence of a small contribution from the changing phonon density. In practice, only the region near the zero of signal is measured, since the location of the zero uniquely determines the amount of each component present. Several runs have been made with both CuKα and MoKα radiation, and the results are presented in Table IV-1.

When the theory is extended to a diatomic crystal, an average Debye-Waller factor can be defined, and this is the quantity whose derivative is given in Table IV-1. Within the limits of the Debye theory, which predicts $dB/dT > 0$ always, the usual Debye temperature can be determined directly from $dB/dT$. This has been done for the CuKα result, and there is good agreement with the values of $\Theta_D \approx 290^\circ$K determined by other methods.
Section IV

Under any reasonable assumptions, $\text{dB/dT}$ should be independent of $(hkl)$ and the x-ray wavelength, and we should obtain the same value in all our measurements. We believe that the strange results obtained with MoKa radiation are due to extinction.\textsuperscript{24} CuKa radiation penetrates only about 60\,\mu m into NaCl, and any surface damage probably extends this far into the crystal, resulting in a mosaic structure with little extinction. However, MoKa radiation extends about 560\,\mu m into NaCl, where surface damage should be absent and extinction could be expected to occur. Since the amount of extinction depends on the state of perfection of the lattice, we believe that the thermal gradients set up in the sample cause periodic variations in strain which modulate the strength of the extinction and hence the intensity of the diffracted beam. This effect has been observed directly in quartz,\textsuperscript{25} and its size could easily be orders of magnitude larger than the Debye-Waller factor contribution. Tests are currently under way to determine the amount of extinction quantitatively.

Several criteria affect the accuracy obtainable from this type of measurement. Clearly, extinction effects must be eliminated. Sandblasting of the crystal surface and use of very soft x-rays which do not penetrate deeply into the sample should overcome this difficulty in most materials. Also, materials with lower thermal conductivities will have larger temperature oscillations and hence larger signals. The use of faster detector and electronics would permit use of a larger photon flux (we are limited to 30,000 photons per second). Digital rather than analog measurement of the signal would both simplify data analysis and increase accuracy.

With the improvements mentioned above, this technique could be improved to the point of surpassing existing DC methods. In addition, the ability to measure $\Theta_D$ at only one temperature gives this method excellent resolution in temperature, making it valuable in the study of phonon densities around critical transitions.

V. E. Henrich
P. M. Raccah

6. Microwave Acoustic Amplification in n-InSb at 9 GHz

Acoustic amplification was observed on applying a pulsed electric field, up to 40\,V/cm, to a rod-shaped sample of n-InSb at 4.2°K. The electric field, which was on during the transit time of the acoustic pulse down the sample (about 2\,\mu sec), produced a maximum observed change in attenuation of $-41\,\text{db/cm}$. Typical results are shown in Fig. IV-11 for an applied field of 40\,V/cm.
The observed amplification was enhanced by a small magnetic field (typically less than 50 gauss) applied perpendicular to the current flow which presumably eliminated the effect of injection by the end contacts. This small field is sufficient to move any injected plasma away from the center of the rod\textsuperscript{26} (Suhl effect) and out of the 1-mm-diameter path of the acoustic pulse. Since $\omega_c \tau \ll 1$ for $B = 50$ gauss, this small magnetic field was neglected in our theoretical calculations. One end of the rod-shaped sample was coated with aluminum on which a CdS transducer was evaporated. This end extended into a 9.05-GHz coaxial re-entrant cavity which was excited by a 5-W microwave pulse, $\frac{1}{2}$ to $1 \mu$sec wide. The receiver was the highly sensitive interferometer described previously.\textsuperscript{27} With a sample electron concentration of $n = 5 \times 10^{13}$ cm$^{-3}$, the mobility at $4.2^\circ$K is strongly electric field dependent\textsuperscript{28} below $E \approx 0.1$ V/cm, approaching the nitrogen mobility at high electric fields $E > 10$ V/cm. In addition, the electron temperature is affected by the electric field for fields of the order of 10 V/cm. These two effects complicate the theoretical interpretation of the data. Since most of the data were taken with electric fields above $E = 1$ V/cm, we have used a value of mobility (i.e., $q\ell$, where $q$ is the sound wave vector, and $\ell$ is the electron mean free path) in the theoretical calculations appropriate to the higher electric fields.

It should be noted that the zero-field attenuation decreases about 5 db/cm on increasing the temperature to $T = 16^\circ$K (see Ref. 29), where the attenuation reaches a minimum. Hence, if the
pulsed electric field were simply heating the sample, an apparent amplification would result. This effect was minimized by bonding one contact end of the sample to the copper cavity with indium and by using low duty cycle (100-Hz) short electric field pulses. Also, in order to monitor the temperature, a carbon resistor thermistor was placed in good thermal contact with the sample.

Calculation of the amplification due to the free electrons requires essentially only a knowledge of the longitudinal dielectric constant $\epsilon_l$. The lattice dispersion relation for a piezoelectric semiconductor can be written

$$\omega = q\nu_{so} \left[ 1 + K_p^2 \left( \frac{\kappa \epsilon_0}{\epsilon_l} \right) + K_d^2 \left( \frac{\epsilon_l - \kappa \epsilon_0}{\epsilon_l} \right) \right]^{1/2}$$  \hspace{1cm} (4)

where $\omega$ and $\nu_{so}$ are the frequency and sound velocity in the insulating crystal if the piezoelectric coupling is vanishingly small ($K_p^2 << 1$). $K_p^2$ and $K_d^2$ are the dimensionless piezoelectric and deformation potential coupling parameters, $\kappa \epsilon_0$ is the lattice contribution to the dielectric constant, $\epsilon_l$ is the total longitudinal dielectric constant $\epsilon_l = \kappa \epsilon_0 - \sigma / i \omega$, and $\sigma$ is the electrical conductivity. Since $K_p^2$ and $K_d^2$ are small, the attenuation constant $\alpha$ can be written

$$\alpha = 2q_i \left[ -(K_p^2 + K_d^2) q \Im \left( \frac{\kappa \epsilon_0}{\epsilon_l} \right) \right]$$  \hspace{1cm} (5)

where $q_i$ is the imaginary part of the wave vector, and $\Im$ refers to the imaginary part. On substituting the value of $K_p^2 = K_d^2 = 3.6 \times 10^{-4}$ obtained previously,\textsuperscript{30}

$$\alpha = 2.26 \times 10^2 \Im \left( \frac{\kappa \epsilon_0}{\epsilon_l} \right) \text{db/cm}$$  \hspace{1cm} (6)

The longitudinal dielectric constant was calculated assuming a shifted Maxwellian electron distribution with the effect of the DC electric field on the AC response included through the use of a complex temperature.\textsuperscript{31} We note that the classical Boltzmann equation results for the amplification in our experiments differ from the quantum mechanical density matrix results by less than 0.0025 percent, despite the size of the quantity $\hbar q / 2m \nu_{o} \sim 1$. Also, note that, while the complex temperature results from an exact solution of the AC Boltzmann equation, the density matrix equation does not yield this simple result. As in the classical calculation, the quantum mechanical solution for $\omega \tau >> 1$ includes the electric field in the AC conductivity exactly through the use of a drifted distribution and a complex temperature. However, when diffusion current is present (i.e., $\omega \tau < 1$), the quantum mechanical solution does not include the DC electric field in this simple manner.\textsuperscript{32} Experimental data on the change in attenuation with electric field are shown in Fig. IV-12. We are unable to measure the absolute attenuation at zero electric field; however, the calculated value lies between 6 and 10 db/cm for our measured low-field mobilities ($\mu < 100,000 \text{ cm}^2 / \text{V sec}$). The initial sharp decrease in the attenuation is probably the result of the rapid increase of mobility with electric field in this range.

The results of the theoretical calculations are shown in Fig. IV-13. The value of $q \ell = 2$ corresponds to a mobility $\mu \approx 200,000 \text{ cm}^2 / \text{V sec}$ which is nearly the experimentally observed mobility at this temperature for fields $> 1 \text{ V/cm}$. The mobility and concentration at $T = 77^\circ \text{K}$ were $\mu = 630,000 \text{ cm}^2 / \text{V sec}$ and $n = 5 \times 10^{13} \text{ cm}^{-3}$, respectively.
Section IV

The considerable discrepancy between the theoretical curve and experimental data may result from a variety of effects, among which are injection at the contacts and the electric field dependence of the electron mobility and temperature. The latter has not been considered and this may introduce a considerable error.

K. W. Nill

B. MAGNETISM

1. Magnetic Properties of MnAs in the High-Pressure Phase

We have continued our study of the magnetic properties of the high-pressure (orthorhombic) phase of MnAs. Our measurements of the magnetic moment vs temperature in a magnetic field of 10 kOe, as reported in the previous Solid State Research Report, have been extended to a pressure of 11 kbars. In addition, we have now studied the magnetic moment vs temperature in various applied fields throughout the pressure range. A set of such measurements (taken at a pressure of 9 kbars), as given in Fig. IV-14, illustrates the flattening of the magnetization curves in an intermediate temperature region, as well as the onset of a low-temperature transition. Re-expressing the data in terms of isotherms, as shown in Fig. IV-15, enables us to define the magnetic state of the sample in pressure-temperature (P-T) space. Thus, Fig. IV-15 illustrates the apparent ferromagnetism in the intermediate temperature region as well as the metamagnetic behavior of orthorhombic MnAs at both higher [Meta (1)] and lower [Meta (2)] temperatures. These two regions are distinguished from each other by the fact that in state Meta (1), $\frac{dH}{dT} > 0$, and in state Meta (2), $\frac{dH}{dT} < 0$.
Section IV

Fig. IV-14. Variation of magnetic moment of orthorhombic MnAs at 9 kbars with temperature, for various applied magnetic fields.

Fig. IV-15. Magnetic moment of orthorhombic MnAs at 9 kbars as function of applied field at various temperatures, indicating both ferromagnetic and metamagnetic behavior.
Fig. IV-16. Magnetic phase diagram for MnAs.

Fig. IV-17. Inverse susceptibility vs temperature curves of orthorhombic MnAs at indicated pressures.

<table>
<thead>
<tr>
<th>Pressure (kbars)</th>
<th>$\mu_{\text{eff}}$ (Bohr magnetons)</th>
<th>$\theta_p$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.91</td>
<td>220.5</td>
</tr>
<tr>
<td>6</td>
<td>1.87</td>
<td>228</td>
</tr>
<tr>
<td>7</td>
<td>1.83</td>
<td>238</td>
</tr>
<tr>
<td>8</td>
<td>2.02</td>
<td>242.5</td>
</tr>
<tr>
<td>9</td>
<td>2.02</td>
<td>248.5</td>
</tr>
<tr>
<td>10</td>
<td>2.06</td>
<td>256</td>
</tr>
</tbody>
</table>
while in Meta (2), \( \frac{dH_{cr}}{dT} > 0 \); here, \( H_{cr} \) is the critical transition field for departure from antiferromagnetic behavior. Curves similar to those shown in Figs. IV-15 and IV-16 were obtained for various pressures and temperatures. These enabled us to define the region in P-T space in which the high-pressure phase is ferromagnetic or one of the metamagnetic states. These regions are delineated in Fig. IV-16.

In addition, Fig. IV-16 shows the hexagonal-rhombohedral phase transitions, \( \Theta \) the Néel temperatures \( T_N \), and the paramagnetic Curie points \( \Theta_P \). These latter points are based on paramagnetic susceptibility data taken just above \( T_N \) in the pressure range from 4 to 10 kbars. At these temperatures and pressures, MnAs is still in the B31 phase. The resultant curves of inverse susceptibility in this region follow a Curie-Weiss relationship, as seen in Fig. IV-17, and the corresponding values of \( \mu_{\text{eff}} \) and \( \Theta_P \) are given in Table IV-2. The variation of \( \mu_{\text{eff}} \) observed over this pressure range is small and falls within the experimental uncertainties. However, the value of approximately 2 \( \mu_B \) is far below the value \( \mu_{\text{eff}} = 4.56 \mu_B \) which was observed in the hexagonal phase of MnAs. This indicates that virtually the entire change in \( \mu_{\text{eff}} \) occurs discontinuously at the first-order hexagonal-orthorhombic transition, and directly confirms the hypothesis of Goodenough, Ridgley, and Newman that this transition is accompanied by a change from a high- to a low-spin manganese configuration.

The paramagnetic moment value is consistent with the saturation moment value of slightly over 1 \( \mu_B \) obtained in the ferromagnetic state at 11 kbars. In addition, the positive \( \frac{d\Theta_P}{dP} \) indicates a net increase in ferromagnetic interactions with increasing pressure, which is also consistent with the magnetic behavior observed below the ordering temperature.

N. Menyuk  
J. A. Kafalas  
K. Dwight

2. Magnetic Resonance in Spiral Spin Structure Compounds

In an effort to gain some insight into the nature of the normal modes of a conical spiral system, we have studied the equilibrium configurations and spin wave spectra for the linear chain model mentioned in the previous Solid State Research Report. In this model, two species of spins, \( S_A \) and \( S_B \), are coupled by nearest and next-nearest neighbor A-B and B-B interactions. It is found that there exist ranges of exchange interactions for which a conical spiral ground state is stable. Spin wave spectra have also been computed for a number of conical spiral cases. Figure IV-18 shows the spin wave spectrum for the particular choice (in normalized units)

\[
J_{AB}^1 = 3.5, \quad J_{AB}^2 = 1.0, \quad J_{BB}^1 = 2.0, \quad J_{BB}^2 = 1.0, \quad S_A = 1, \quad S_B = 0.8.
\]

These parameters lead to a ferrimagnetic conical spiral structure, with cone angle \( \phi_A = 5.81^\circ \), \( \phi_B = 121.9^\circ \), and turn angle \( 74.8^\circ \).

The modes of particular interest in a microwave resonance experiment are those at \( \vec{k} = \vec{k}_0 \) and \( \vec{k} = 0 \). For the \( \vec{k} = \vec{k}_0 \) modes, those marked 1, 2, and 3 in Fig. IV-18 are exchange modes, while the mode marked 4 is the uniform mode. For modes 1 and 4, each conical spiral precesses rigidly about the cone axis, while for modes 2 and 3, the cones distort as they precess about the cone axis (see Fig. IV-19). Modes 2, 3, and 4 all have net oscillating moment in the plane perpendicular to the cone axes, while mode 1 has no net moment.
Section IV

Fig. IV-18. Spin wave spectrum for linear chain-conical spiral configuration.

Fig. IV-19. Schematic diagram of spin wave modes of linear chain-conical spiral configuration. Arrows show instantaneous displacement of spins in plane perpendicular to spiral axis.
For the \( k = 0 \) case, mode 6 is a pure "twisting" mode, with the two cones moving rigidly, and therefore \( \omega = 0 \). Mode 5 is a "breathing-twisting" mode (see Fig. IV-19), for which the net oscillating moment in the plane vanishes. Each cone separately has an oscillating moment along its cone axis, but the two oscillating moments exactly cancel.

J. J. Stickler
H. J. Zeiger

3. Spherical Model as the Limit of Infinite Spin Dimensionality

Consider the Hamiltonian

\[
H(ν) = -\frac{1}{2} \sum_{i, j=1}^{N} v_{ij} S_i^{(ν)} \cdot S_j^{(ν)}
\]

where \( S_j^{(ν)} \equiv [σ_1^ν (j), σ_2^ν (j), \ldots, σ_l^ν (j)] \) are \( ν \)-dimensional vectors of magnitude \( \sqrt{ν} \). Although it is perhaps not generally appreciated, it seems clear that \( H(ν) \) reduces to the \( S = l/2 \) Ising, classical planar, and classical Heisenberg models for \( ν = 1, 2, \) and \( 3, \) respectively.

Here we argue that in the limit \( ν \rightarrow \infty \), the free energy of \( H(ν) \) approaches that of the spherical model. This result is of particular current interest, besides the geometrical interpretation it attaches to the spherical model, because of recent evidence \(^{38}\) that various "critical properties" of \( H(ν) \) are monotonic functions of \( ν \). Hence, the critical properties of the fairly realistic but hopelessly insoluble Heisenberg model (three-dimensional spins) would appear to be bounded on one side by those of the Ising model (one-dimensional spins) and on the other by those of the spherical model (infinite-dimensional spins). Moreover, the spherical model has in the past been interpreted as a soluble approximation to the Ising model, whereas, in fact, the spherical model would appear to be a much better approximation to the more "realistic" Heisenberg model.

The normalized partition function corresponding to \( H(ν) \) is

\[
Q_N^{(ν)} (K) = \frac{Z_N^{(ν)} (K)}{Z_N^{(ν)} (0)}
\]

where

\[
Z_N^{(ν)} (K) = \left( \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} dσ_1 (1), \ldots, dσ_ν (1) dσ_2 (2), \ldots, dσ_ν (N) \right)
\]

\[
\times \prod_{j=1}^{N} \left( \delta \left[ ν - \sum_{n=1}^{ν} σ_n^2 (j) \right] \right) \times \exp \left[ K Σ_{ij} v_{ij} Σ_{n=1}^{ν} σ_n^i (i) σ_n^j (j) \right]
\]

and \( K \equiv J/2kT \). The \( N \) constraints are then represented as \( N \) delta functions, and we obtain

\[
Z_N^{(ν)} (K) = \frac{(K^2)}{2\pi i} \int_{-i\infty}^{i\infty} \cdots \int_{-i\infty}^{i\infty} \exp \left[ νF(K, \{t_j\}) \right]
\]

where \( F(K, \{t\}) = K Σ_{ij} t_{ij} - \frac{1}{4} ln Δ(\{t\}) \), and where \( Δ(\{t\}) \) is the determinant of the quadratic form \( Σ_{ij} (t_{ij} - v_{ij}) σ_n^i (i) σ_n^j (j) \).
The requirement that \( F(K, \{ t_s \}) \) be stationary leads to the set of conditions

\[
K = \frac{1}{2} \left( \frac{\partial}{\partial t} \ln \Delta(\{ t_s \}) \right) t_s \quad ; \quad t = 1, 2, \ldots, N
\]  

Next, expand \( F(K, \{ t_s \}) \) about the stationary points \( \{ t_s \} \),

\[
F(K, \{ t_s \}) = F(K, \{ t_s \}) + \frac{1}{2} \sum_{m, n=1}^{N} \left( \frac{\partial^2 F}{\partial t_m \partial t_n} \right) (t_m - t_s) (t_n - t_s) + \ldots
\]

We then factor \( \nu F(K, \{ t_s \}) \) out of the integrand of Eq. (10), calling the remaining integral \( R \). Thus, from Eq. (10),

\[
\ln Z_N^{(\nu)}(K) = \frac{1}{2} \nu N \ln \frac{\pi}{K} + \nu F(K, \{ t_s \}) + \ln R
\]

The limiting free energy \( \psi^{(\infty)} \) is related to \( Z_N^{(\nu)}(K) \) by

\[
-\beta \psi^{(\infty)} = \lim_{\nu, N \to \infty} \frac{1}{\nu N} \ln \left[ Z_N^{(\nu)}(K)/Z_N^{(\nu)}(0) \right]
\]

where \( \beta = (kT)^{-1} \). From Eq. (13), we obtain

\[
-\beta \psi^{(\infty)} = -\frac{1}{2} - \frac{1}{2} \ln 2K + \frac{1}{N} F(K, \{ t_s \}) + \lim_{\nu, N \to \infty} \frac{1}{\nu N} \ln R
\]

The last term on the right-hand side of Eq. (15) can be shown to be zero. Now, \( F(K, \{ t_s \}) = NKt_s - \frac{1}{2} \ln \Delta(\{ t_s \}) \) and \( \ln \Delta(\{ t_s \}) = \ln 2^N + \ln \left[ (1/2) t_s \delta_{ij} - (1/2 v_{ij}) \right] \). Thus, Eq. (15) is precisely the spherical model free energy.

H. E. Stanley

4. Eigenvalue Degeneracy as a "Mathematical Mechanism" for Phase Transitions

Kac\(^{39}\) has noted a striking analogy between the Ising model

\[
\hat{H}_I = -J \sum_{\langle i, j \rangle} S_i^{(1)} S_j^{(1)}
\]

(with strong, short-range forces) and the "Kac model"

\[
\hat{H}_K = -\gamma J \sum_{\langle i, j \rangle} e^{-\gamma |i-j|} S_i^{(1)} S_j^{(1)}
\]

(with weak, long-range forces for \( \gamma \) small). In the Ising model, the summation is over nearest-neighbor pairs of sites \( \langle i, j \rangle \), whereas, in the Kac model, the summation is over all sites \( i \) and \( j \) in the lattice. Kac observed that (for both models) the onset of a spontaneous magnetization below a certain transition temperature \( T_c \) is characterized, mathematically, by the asymptotic degeneracy of the maximum eigenvalue of a certain linear operator.

Since the "mathematical mechanisms" responsible for the phase transitions in a strong, short-range force model and in a weak, long-range force model are identical for "one-dimensional"
Section IV

(i.e., Ising) spins, it seems natural to inquire whether this same mathematical mechanism is responsible for the phase transitions in other spin dimensionalities. To this end, we consider the Hamiltonians obtained by replacing the one-dimensional scalar spins $S^{(1)}$ in Eqs. (16) and (17) by isotropically interacting $\nu$-dimensional vector spins $S^{(\nu)}$ and obtain

$$H^{(\nu)} = -J \sum_{\langle i, j \rangle} \vec{S}^{(\nu)}_i \cdot \vec{S}^{(\nu)}_j$$  \hspace{1cm} (18)

$$H^{(\nu)}_K = -\gamma J \sum_{i, j} e^{-\gamma |i-j|} \vec{S}^{(\nu)}_i \cdot \vec{S}^{(\nu)}_j$$  \hspace{1cm} (19)

Thus far, we have observed that, for Eq. (18) with $\nu = 1, 2, 3,$ and $\infty$, the onset of infinite-range order may indeed be described mathematically by the collapse of the entire (discrete) eigenvalue spectrum of an appropriate linear operator into a single value. In particular, the spin-spin correlation function $\langle \vec{S}^{(\nu)}_0 \cdot \vec{S}^{(\nu)}_R \rangle$ may be expressed as $[\lambda^{(\nu)}_1 / \lambda^{(\nu)}_0] R$, where $\lambda^{(\nu)}_0$ is the largest, and $\lambda^{(\nu)}_1$ the next-largest, eigenvalue. Hence, the spontaneous magnetization $M = \lim_{R \to \infty} \langle \vec{S}^{(\nu)}_R \rangle / R^{1/2}$ becomes nonzero as the eigenvalues become degenerate.

H. E. Stanley

5. Finite Temperature Single-Slater Determinant Theory

We have applied standard temperature-dependent Hartree-Fock (HF) theory (without any symmetry restrictions) to a system of $N$ infinitely separated hydrogen atoms in zero external fields. We find that, as temperature $T \to 0$, it leads to the entropy $S \to 0$ rather than to the correct value $S = Nk \ln 2$, although the zero-temperature energy and the absence of spin ordering are correctly predicted. Another, closely related failure of that theory is that as $T \to 0$, the spin susceptibility $\chi \to 0$ rather than $\infty$ as in the (correct) Curie law. This serious failure was traced to the use of a one-electron operator for the effective or approximate Hamiltonian $\tilde{H}$ [defined in Eq. (24) below]. Furthermore, a new finite-temperature HF theory, still involving single determinants as approximate energy eigenstates, was shown to give the correct behavior for the system of isolated hydrogen atoms.

We describe here some of the essential details of this new generalization of HF theory. Basic is the well-known variational principle

$$F(\rho) \equiv \text{tr}(H - \mu N) \rho + kT \text{tr} \rho \ln \rho \geq F_T$$  \hspace{1cm} (20)

where the true free energy, appropriate to a grand canonical ensemble, is

$$F_T = -kT \ln \text{tr} \exp[-\beta (H - \mu N)]$$  \hspace{1cm} (21)

$\rho$ is any density operator, $\beta = 1/kT$, and $H$ is the Hamiltonian

$$H = \sum_{ij} c^+_i c_j + \frac{1}{2} \Sigma_{ijkl} k \epsilon c^+_i c^+_j c_j c_k$$  \hspace{1cm} (22)

c$^+$ are the usual fermion creation operators for some set of orthonormal, one-electron states $\phi_i$. The equality of Eq. (20) is attained when $\rho$ is the true density operator $\rho_T$, where

53
Section IV

\[ \rho_T = Z^{-1} \exp\{ -\beta (H - \mu N) \} \]  

(23)

It is convenient to define an approximate Hamiltonian \( \tilde{H} \) such that

\[ \rho = \exp\{ -\beta (\tilde{H} - \mu N) \}/\text{tr} \exp\{ -\beta (\tilde{H} - \mu N) \} \]  

(24)

Standard T-dependent HF theory is derived from Eq. (20) as follows. First, \( \tilde{H} \) is restricted to be a one-electron operator

\[ \tilde{H} \equiv \sum \epsilon_i N_i \]  

(standard HF theory)

where \( N_i \) are the occupation number operators for a set of one-electron states \( \psi_i \) (called "orbitals," involving both space and spin, in general), and \( \epsilon_i \) are c-numbers. The \( \psi_i \) and \( \epsilon_i \) are then chosen to minimize \( F(\rho) \), yielding the standard T-dependent HF equations

\[ \{ \psi_i, \tau \psi_j \} + \sum_k \left\{ \left( \psi_{i+}, \nu_{j+} \right) - \left( \psi_{i+}, \nu_{j-} \psi_i \right) \right\} N_k = \epsilon_i \delta_{ij} \]  

(26)

where

\[ \overline{N}_k = \text{tr} \rho N_k = 1/\exp\{ \beta (\epsilon_i - \mu) + 1 \} \]  

(27)

As indicated by Blatt, this "standard T-dependent HF theory" (which he calls "Husimi theory") is a natural extension of zero-temperature Hartree-Fock theory to finite temperature.

However, it is not the only such extension. Our purpose here is to describe another, more general, and quite natural extension. Recall that the basic idea of zero-temperature HF theory is to look for a single Slater determinant \( D \) which minimizes the energy \((D, HD)/(D, D)\) over all Slater determinants \( D \). Since the eigenfunctions of the \( \tilde{H} \) in Eq. (25) are determinants, it is clear that the minimum free energy computed with Eq. (25) will, as \( T \to 0 \), approach \( E = (D, HD)/(D, D) \), the correct zero-temperature HF value. Clearly, all that is needed for this is that all the eigenfunctions of \( \tilde{H} \) be single Slater determinants. But \( \tilde{H} \), as given in Eq. (25), is by no means the most general form such that all the eigenfunctions are single determinants. For example, an operator of the form \( \sum \epsilon_i N_i + \sum \epsilon_{ij} N_i N_j \) would also have a complete set of single determinantal eigenfunctions — in fact, \( \tilde{H} \) would have single determinantal eigenfunctions if it were an arbitrary function \( E(N_1, N_2, \ldots) \) of the occupation number operators. Thus, we are led to a new extension to finite temperature of zero-temperature HF theory — choose the \( \psi_i \) and the function \( E(N_1, N_2, \ldots) \) to minimize the free energy \( F \). This theory is just as natural as the standard or Husimi extension, since it has single Slater determinants as "approximate energy eigenfunctions"; furthermore, it can be expected to be "better" in that it will probably yield a lower free energy. It clearly cannot give a higher free energy.

The formal minimization of \( F \) in the new context can be carried out. It requires that the function \( E \) be

\[ E(N_1, N_2, \ldots) = \sum \{ \psi_i, \tau \psi_j \} N_i + \frac{1}{2} \sum \left\{ \left( \psi_i, \nu \psi_j \right) - \left( \psi_i, \nu \psi_j \psi_i \right) \right\} N_i N_j \]  

(28)

†We feel that the most general \( \tilde{H} \) having its eigenfunctions be Slater determinants would lead to a theory which should be considered the most general extension to finite temperature of zero-temperature HF theory. We have not shown that the class of \( \tilde{H} \)'s considered here has that degree of generality.
(which is just the energy of the determinant defined by occupation numbers ..., \(N_i\) ...), and that the \(\phi_i\) be solutions of

\[
(\bar{N}_i - \bar{N}_j) (\psi_i^\dagger \psi_j) + \sum_k \left[(\psi_i^\dagger \phi_k^\dagger \phi_k^\dagger - (\psi_i^\dagger \psi_k^\dagger \psi_k^\dagger)\right] (\bar{N}_i - \bar{N}_j) N_k = 0 \quad \text{all } i \neq j.
\]

Note the similarity between these and the standard HF equations [Eq. (26)]; if it were not for the terms in \(E\) which are quadratic in the \(N_i\)'s, the average in Eq. (29) \(\bar{N}_i - \bar{N}_j\) would factor into \(\bar{N}_i - \bar{N}_j\), and cancellation of \(N_i - N_j\) would lead back to Eq. (26) for \(i \neq j\).

As we have said, this theory completely corrects the physically serious deficiency of the standard theory in the case of infinitely separated hydrogen atoms, but we will not go into the details here. At present, we are studying this theory as applied to hydrogen atoms separated by large but finite distances.

C. LASER SCATTERING AND NONLINEAR EFFECTS

1. Hypersonic Attenuation in Quartz by Thermal Brillouin Scattering

The velocity and attenuation of 28-GHz longitudinal phonons along the x-axis of \(\alpha\)-quartz have been measured in a temperature range from 300° to 600°K. High-resolution Brillouin scattering techniques are employed in this regime where conventional ultrasonics techniques are not applicable. The Brillouin spectrometer consists of a single-mode He-Ne laser and a multisanned confocal spherical Fabry-Perot interferometer. Photoclectron count data from a low dark current photomultiplier are accumulated in a multichannel analyzer for arbitrarily long times to improve the signal-to-noise ratio.

The velocity, or Brillouin shift, variation with temperature agrees within experimental error with previous low-frequency quartz-controlled oscillator measurements. The hypersonic attenuation is obtained from the spectral width of the Brillouin lines and may be compared with theoretical extrapolations of ultrasonics data. There is order of magnitude agreement with the single relaxation theories of Woodruff and Ehrenreich\(^{42}\) and of Bömmel and Dransfeld\(^{43}\); however, both theories generally overestimate the absorption, and poorly represent the details of the temperature dependence.

Further work is in progress to extend the temperature range of the measurements.

A. S. Pine

2. Light Scattering from Single-Particle Electron and Hole Excitations in Semiconductors

Light scattering has been observed for the first time from screened single-particle electron excitations in GaAs, InP, AlSb, and CdTe, as well as from the screened single-particle hole excitations in p-type GaAs doped with cadmium, zinc, and magnesium. The Raman scattering from plasmons and coupled plasmons and phonons, as well as the polarization properties of the scattered light from these excitations, have been reported previously. Both these cases dealt with the collective excitations of the electron gas in a solid. Present results yield the single-particle excitation spectrum of the electron gas. The single-particle scattering is compared with effective-mass calculations based on simple parabolic bands, which involves scattering from...
electron density fluctuations, as well as a more recent effective-mass calculation which predicts a large enhancement due to nonparabolicity. The experimental results, however, are in disagreement with both of those theories.

The scattered light was generated using a 1.06-μm YAG:Nd³⁺ laser which could operate with a continuous output power in excess of 10 W. Figure IV-20 shows the Raman spectrum of an n-type GaAs sample at 300°, 30°, and 5°K. The peaks labeled L₁, L₂, and TO have been described elsewhere, and refer to the coupled modes of the longitudinal optical phonons and the plasmons (L₁, L₂), and the transverse optical phonon (TO). The scattering from the single-particle excitation spectrum of the conduction electrons is seen at lower frequencies near the laser line. At

\[ T = 0^\circ \text{K}, \text{ the single-particle excitation spectrum comes from electrons with momentum } \vec{p} \text{ that are excited from occupied states below the Fermi surface to unoccupied states just above the Fermi surface with momentum } \vec{p} + \vec{q}, \text{ where } \vec{q} \text{ is the momentum change of the scattered electron. At } T = 0^\circ \text{K and for infinite lifetime, the existing theories predict a continuum spectrum increasing linearly with } \omega \text{ to a peak near } 0.7 qv_F, \text{ for the parameter values involved here, and cutting off at } qv_F, \text{ where } v_F \text{ is the Fermi velocity. Samples with electron concentrations ranging from } 2 \times 10^{15} \text{ to } 2.8 \times 10^{18} \text{ cm}^{-3} \text{ were measured. At low temperature, the single-particle spectrum, while smeared by a finite collision time, did show a cutoff consistent with } \omega = qv_F. \text{ At higher temperatures, more electrons can participate in the scattering as the electron distribution becomes Maxwellian. In the high-temperature limit, the spectral shape of the scattered light should resemble a Maxwellian velocity distribution, which was found to be consistent with the experimental results. In the p-type GaAs, scattering from both the heavy and light hole
single-particle excitations was observed at 300°K in samples with hole concentrations of about \(1 \times 10^{16}\) cm\(^{-3}\). A more complete discussion of these results is published elsewhere.\(^{48}\)

A. Mooradian

3. Steady-State Thermal Defocusing of Laser Light

In the previous Solid State Research Report,\(^{49}\) the time dependence of thermal defocusing of laser light was discussed experimentally and the theory was presented.\(^{50}\) We have carried out further work on the steady state and the approach to steady state, which includes a number of new experimental results. A steady-state condition arises when the temperature change due to heat deposition is just counterbalanced by that due to either heat conduction out of the region of the beam or convection currents where material is transported from the volume. In the case of convection, the hot material rises and is replaced by cooler material from below. As a result, a vertical asymmetry will develop for a horizontal laser beam, and the beam will appear to be bent downward and considerably distorted. This is to be contrasted with conduction which is cylindrically symmetric, and should therefore result in no distortions.

Examining convection more carefully shows that the acceleration \(a\), which a particle experiences in the center of the beam, will be proportional to the total power per unit volume absorbed, which is approximately \(aI\); here, \(a\) is the absorption coefficient, and \(I\) is the incident intensity. Also, one would expect convection to be important when \((1/2) \times a t_C = q\), where \(t_C\) is the convection time constant, and \(q\) is the characteristic vertical dimension associated with the beam. In the case of a horizontal laser beam, \(q\) is the beam diameter \(d_0\). From this relation, it follows that

\[
t_C \propto 1/\sqrt{a} \propto 1/\sqrt{aI}.
\]

The acceleration is also proportional to the viscosity of the material. In Fig. IV-21, a plot of the time to reach a maximum beam diameter \(t_{\text{max}}\) vs \(1/\alpha I\) is presented for all our CCl\(_4\) data. However, \(t_{\text{max}}\) differs from the convection time by only a constant. Also included is the best straight line with a slope of 1/2, and it is clear that the fit is quite good.

The theory for conduction effects was presented by Gordon, et al.,\(^{51}\) and was discussed further in Ref. 50 where it was indicated that \(1/t\) should be replaced by \(1/t + 1/t_C\), where

\[
t_C = \frac{d^2 K}{16 \rho C_p}.
\]

\(K\) = thermal conductivity, \(\rho\) = density, and \(C_p\) = heat capacity at constant pressure. In order to study conduction effects, it is necessary to make the conduction time very much shorter than the convection time. There are at least three ways
in which this may be accomplished. The first method is to change the liquid from a material whose ratio of conduction time to convection time is small, to one whose ratio is large. A second technique is to change the direction of propagation of the beam from horizontal to vertical. Now, instead of \( q = d_o \), \( q \) will be of the order of the cell length \( t \), or \( t/a \), depending on which is shorter. Thus, the convection time is greatly increased without changing the conduction time. A third method is to use very low absorption lengths \( 1/a \), as in Ref. 51. The first two of these techniques were tried, and some results are presented in Fig. IV-22. Data were taken with a vertical laser beam and a 10-cm long vertical cell of both CS\(_2\) (curve A) and CC\(_1\)\(_4\) (curve B). In both cases, the intensity (0.8 W/cm\(^2\)), beam diameter (0.294 cm), and absorption length (9.7 cm) were the same. Also, in both cases, cylindrically symmetric patterns resulted for the entire time development. Using the theory for a parabolic intensity profile\(^{51}\) gives the conduction times of \( t_c \) (CC\(_1\)\(_4\)) = 7.33 sec, and \( t_c \) (CS\(_2\)) = 4.33 sec. Curve B can be very accurately reproduced theoretically by using this conduction time for CC\(_1\)\(_4\) and replacing \( 1/t \) by \((1/t + 1/t_c)\). Also given in Fig. IV-22 is a comparison of the vertical cell data for CS\(_2\) (curve A) with that of a horizontal cell with the same constants (curve C). The exception is that the input laser intensity was \( \sim \)50-percent higher in the horizontal cell, causing the intercept to be 50-percent larger in this case. A pronounced ringing or underdamped character was displayed by the change in beam diameter \( \Delta d \) for the case of CS\(_2\) in both the vertical and horizontal cell arrangements. The period of the oscillations was much longer for the vertical than for the horizontal cell and, in both cases, the
Section IV

oscillations were highly damped. Apparently, the value of $q$ increased when switching from the horizontal to vertical cell, but not by as much as expected ($1/d_0 = 32$). Probably because of this, only the early effects of conduction could adequately be predicted by the theory in the case of the CS$_2$ vertical cell data. More careful analysis of the CCl$_4$ data indicated that this ringing was also present in the horizontal, but not in the vertical, cell data. The reason the theory does not predict this oscillation undoubtedly lies with two approximations. One is that

$$
\int_{t_0}^{t} I(t') \, dt' = It
$$

(32)

If the past history of the intensity profile is included with the instantaneous variations, an effective time lag should result, thus causing the oscillations. A second reason is that replacing $1/t$ by $(1/t + 1/t_c)$ is correct only to first order, and higher order terms may be significant for some situations.

R. L. Carman
P. L. Kelley


a. Transverse-Mode Selection

Our most reliable transverse-mode selection technique employed a diamond pinhole and two long focal length lenses, as illustrated in Fig. IV-23(a). The resulting cavity length is approximately 1.5 meters. The output beam from this configuration, using the prism as a Q-switch, is a 4-mm-diameter beam with a 0.5- (theoretical limit) to 1-mrad divergence, and a power of 0.1 to 1 MW which is limited by air breakdown in the pinhole. When the prism was fixed and Q-switching was accomplished with a passive dye, then peculiar near-field patterns as well as air breakdown in the pinhole were unavoidable, even with total output power as low as 50 kW. The air breakdown appears to produce a plasma which is opaque, and thus cuts off further lasing.

In the case of the passive Q-switch, a second method of transverse-mode selection was also tried; this consisted of removing the pinhole and placing a second aperture (optional aperture) as indicated in Fig. IV-23(a). Both apertures were identical in size and centered on a common axis. Using 4-mm-diameter apertures, the laser output consisted of three beams, each approximately 1 mm in diameter with about 1.5-mrad divergence. It was concluded that the passive dye used in conjunction with a flame fusion-grown ruby produces spatial inhomogeneities whose characteristic dimensions are too small to render these beams useful.
Section IV

For the case of the pinhole, the existence of several diffraction-limited hot spots could result in power densities high enough to cause localized air breakdown and, from the ensuing scattering and absorption, a peculiar output near-field pattern. Using the passive dye as a mode-locking element, the requirements on spatial inhomogeneities may well be too high for reliable operation of a diffraction-limited mode-locked laser.

b. Longitudinal-Mode Selection

For non-Q-switched operation, the arrangement in Fig. IV-23(a) produced sufficient mode selection near threshold to allow for operation with linewidths of less than 600 MHz, the resolution limit of our present Fabry-Perot interferometer; i.e., less than six modes were present. A typical interferogram is shown in Fig. IV-23(b). An interferometer with a resolution less than 100 MHz is now being constructed to confirm single-mode operation.

When the laser was Q-switched by rotating a prism, the scheme illustrated in Fig. IV-23(a) was insufficient for producing single-longitudinal-mode operation. By adding a second feedback arrangement, which comprised the second arm of an inverted Michelson interferometer, single-mode operation was obtained. The $45^\circ$ beamsplitter had a 60-percent reflectivity, while the remaining mirror had a 100-percent reflectivity. The only mode which will oscillate in this scheme is the one for which reflection from the 100-percent mirror destructively interferes with the light directly reflected out of the cavity by the beamsplitter. Reliable longitudinal-mode selection requires stable mirror mounts; we are now investigating this problem.

R. L. Carman
F. H. Perry

REFERENCES

24. R.W. James, The Optical Principles of the Diffraction of X-rays (G. Bell and Sons Ltd., London, 1958), Chapter II.
32. K.W. Nill, to be published.
47. P.A. Wolff, Phys. Rev., to be published.
This report covers in detail the solid state research work at Lincoln Laboratory for the period 1 February through 30 April 1968. The topics covered are Solid State Device Research, Optical Techniques and Devices, Materials Research, and Physics of Solids.