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RESEARCH ON THE DYNAMIC STRUCTURE OF  
LIQUIDS, LIQUID CRYSTALS AND DISORDERED  
SOLIDS. RESEARCH ON SEMICONDUCTOR  
MATERIALS AND DEVICES

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| 13. ABSTRACT<br>The dynamic structure of liquids and disordered solids is investigated by Rayleigh, Brillouin and Raman light scattering, by nuclear magnetic resonance and by infrared absorption. Simple liquids, liquid crystals, polymers, glasses, organic semiconductor and hydrogen in metals are the objects of investigation.<br><br>The properties of light emitting and laser diodes of the semiconductors GaAsP, InGaAs and InGaP are investigated to improve and extend their behavior. Impurities and imperfections in silicon which affect the properties of solid state devices are investigated for the purpose of controlling and improving device performance. |  |  |                       |

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Research on Semiconductor Materials and Devices.

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## TECHNICAL REPORT SUMMARY

### Technical Problem

Two general areas of research are reported:

1. The dynamic structure of liquids and disordered solids.
2. Semiconductor materials and devices.

The goal of the research on liquids and amorphous solids is an improved understanding of molecular motion and interactions in highly disordered materials of technological importance.

The research on semiconductors is focused on two areas: 1. The understanding and improvement of the light emitting and laser properties of semiconductor devices fabricated from gallium arsenide phosphide, indium gallium arsenide, and indium gallium phosphide. 2. Knowledge of the properties of electron and hole traps in silicon which are of importance for the operation of solid state devices. Both controlled impurities and imperfections resulting from manufacturing processes are under investigation.

### General Methodology

The research on the structure of liquids and disordered solids makes use of novel light scattering techniques (Rayleigh, Brillouin and Raman scattering), of nuclear magnetic resonance, and of infrared absorption as a function of temperature and pressure. The systems investigated include solutions of importance in chemical processing, liquid crystals of significance for device applications, polymers, glasses, solid state electrolytes organic semiconductors, and hydrogen in metals.

Semiconductor diodes are fabricated by constant temperature, liquid phase epitaxial growth and diffusion of appropriate impurities. The effects of composition, impurity concentration and structural perfection on the wavelength, intensity, and efficiency of light emission and laser action are investigated.

Electron and hole traps in silicon are investigated by sensitive capacitance and junction techniques. The effect of deep traps due to deliberate by added impurities and of imperfection traps introduced by manufacturing processes on silicon device behavior are investigated.

#### Technical Results

Collective reorientational relaxation times have been measured for binary solutions of carbon tetrachloride and the nematic liquid crystal MBBA (p-methoxybenzylidene-p-n-butylaniline) and compared with the viscosity. At high concentrations MBBA molecules shear more easily than they rotate and major rotational correlations occur.

The effect of pressure and temperature on the structure of electrolytic solutions and liquid methyl fluoride- $d_3$  has been investigated. The transition pressure hysteresis of ammonium chloride has been interpreted. Preliminary experiments on polymers (rubbers) have been useful in selecting the best theoretical model.

Apparatus for light scattering experiments on hydrogen in metals and glasses is being constructed. Preliminary data on the organic charge transfer molecule TTF-TCNQ has been obtained.

A dynamical theory of phase transitions in liquid crystals has been completed and data to test the theory are being taken.

Substantial progress has been made in the explanation of the effects of nitrogen impurity and of Zn doping in GaAsP. Major progress has been made in the synthesis of InGaP and the shortest wavelength laser operation yet achieved in a III-IV semiconductor (5500 Å, green) has been demonstrated. High quality, Zn diffused junction lasers of InGaAs have been fabricated.

The cause of the double donor center in silicon has been shown to be strain introduced during boron diffusion. The effects of transition metal and heavy metal impurities like chromium and gold in silicon are under study.

TECHNICAL REPORTTechnical Problem

The research supported by this Contract No. DAHC-15-73-G-10 falls into two broad areas. First, there is the investigation of molecular interactions and motion in liquids and disordered crystals. Second, there is the effort to understand and improve semiconductor devices.

The motivation for the first area of research is that, although the liquid state is poorly understood, it is of enormous importance in almost all manufacturing processes and in numerous critical operations like lubrication. Also, modern technology is extending the use of liquids to extremes of temperature and pressure where their properties differ significantly from normal. It would be most useful to technology to have available for liquids an understanding of their structure and dynamic properties comparable with that which has been achieved in the case of crystalline solids. The problems of the liquid state include those of amorphous solids which are supercooled liquids. Liquid crystals and polymers are technologically important materials in themselves and in structure occupy a position between that of the highly disordered liquids and slightly imperfect crystals.

The development of lasers and electronic instrumentation has made possible sophisticated light scattering experiments whose potential value for liquid state research has not been explored. The motion of an atomic or molecular unit in a liquid scatters radiation and an analysis of the frequency, polarization and intensity of the scattered radiation enables deductions to be made concerning the character of the molecular motion

and the molecular interactions responsible for the motion. Such scattering experiments and nuclear magnetic resonance and infrared absorption measurements are capable of yielding new and important information concerning the dynamic structure of liquids.

Professors W. Flygare, J. Jonas, M. Klein and W. McMillan are applying these techniques to a variety of liquids and disordered solids. Much of the research is exploratory in nature and of the "high risk" type. These statements are particularly relevant to the attempts to investigate the motion of hydrogen in metals, the motion of molecular units in glasses, and the motion of ions in superionic conductors like beta alumina.

The research on semiconductor materials and devices is focused on the trapping, release, and recombination of electrons and holes. Of chief interest is the effects of these processes upon two technologically important areas--light emitting diodes and lasers and junctions important for transistor devices. Professor N. Holonyak, Jr. is growing crystals of ternary III-IV semiconductor compounds, constructing diodes, and attempting to improve and understand the behavior of light emitting diodes (LED's) and semiconductor lasers. Professor C. T. Sah is investigating impurities and imperfections in silicon crystals that are of decisive importance for the performance of silicon based semiconductor devices.

### General Methodology

The planning for the investigations of liquids and disordered solids recognize that both theory and experiment have been unable to handle the more difficult problems posed by these phases in as adequate a manner as has been possible with single crystals. It is generally accepted among solid state physicists and chemists, however, that recent theoretical and experimental advances have opened new possibilities for understanding the liquid state. Among the experimental techniques are those included under the names of Rayleigh, Brillouin and Raman scattering as implemented by modern lasers, electronic equipment, computers and powerful theoretical techniques. In many cases, nuclear magnetic resonance and infrared absorption can also be employed in a uniquely valuable manner.

Experiments on the dynamic structure of liquids are usefully carried on in conjunction with studies of phase transitions and atomic motion in glasses and polymers not only because the same experimental techniques are useful but because the same basic molecular interactions are under study.

Because the experimental techniques are either novel or pushed to the state of the art and materials are frequently being examined under extreme conditions of pressure and temperature where their properties may be highly unusual, many of the experiments are not only exploratory but "high risk" in the sense that feasibility and results are uncertain.

In the development of ternary semiconductor III-IV compounds for light emitting diodes and lasers it is assumed that these materials, particularly GaAsP, will be of unique importance in the near future. It is also assumed that the known properties of the present materials can be substantially

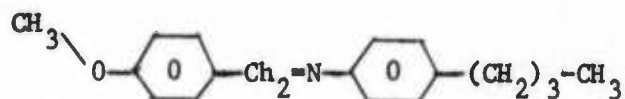
improved and extended by preparation of better materials through improved crystal growth and processing techniques. Finally, it is assumed that the problems involved are sufficiently complex and sophisticated that progress cannot be made by Edisonian methods but that a substantial increase in fundamental understanding of electronic behavior in these materials at the atomic level must parallel practical developments. This same point of view pervades the planning of the research on electron and hole centers in silicon.

The attempted development of semiconductor ternary III-IV compounds as light emitting diodes and lasers depends heavily on unique crystal growth techniques and expertise which has been acquired by Holonyak and his coworkers, in particular techniques for constant temperature, liquid phase epitaxial growth (CT-LPE).

The capacitance technique for studying electron and hole centers in silicon which was developed by Sah and his coworkers is unique in sensitivity, precision, simplicity and speed. Coupled with computer analysis of the experimental data, capacitance and junction current methods enable precise examination of the properties of deep level centers in silicon.

### Technical Results

A complete study has been made of the anisotropic Rayleigh light scattering from binary solutions of  $\text{CCl}_4$  and the nematic liquid crystal MBBA (p-methoxybenzylidene-p-n-butylaniline)



which is approximately  $17\text{\AA}$  long with a  $7\text{\AA}$  diameter. The temperature dependence of spectral linewidths of the binary solutions has been measured. The linewidths are inversely proportional to the collective reorientational relaxation time

$$(\Delta\nu)^{-1} = \tau_{\text{OR}}^{\text{coll.}}$$

According to the Debye-Einstein relationship, the single particle reorientational relaxation time is related to the viscosity,  $\eta$ , by

$$\tau_{\text{OR}}^{\text{sing}} = \left(\frac{4}{3} \pi a^3\right) \frac{\eta}{kT}$$

$k$  is Boltzmann's constant,  $T$ , the temperature, and  $a$  is the effective radius of the molecule. If this relation is valid, the temperature dependence of  $(\tau_{\text{OR}} \cdot T)$  should be equivalent to the temperature dependence of the viscosity,  $\eta$ , which is known to be Arrhenius in nature; i.e.,

$$\eta = \eta_0 \exp[-E/RT]$$

The experimental data show that at low concentrations the Debye-Einstein relation is valid but above 0.5 mole fraction, there is a definite divergence. This indicates that MBBA molecules can shear more easily than rotate at high concentrations.

A concentration and temperature-dependent study of the depolarized integrated intensity of the light scattered from MBBA in  $\text{CCl}_4$  has also been completed. The data show relatively weak two-body rotational correlations until the MBBA mole fraction is above 0.9. Above this concentration major rotational correlations are evident. Similar studies have been conducted on other molecules in other solvents.

A substantial beginning has been made in measuring mutual diffusion constants in binary solutions to examine the mass and size dependence in these processes. (Flygare)

W. H. Flygare and T. D. Gierke, "Light Scattering in Noncrystalline Solids and Liquid Crystals," submitted to Annual Review of Materials Science for publication.

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A study of the effects of pressure and temperature on the dynamic structure of several electrolyte solutions, including both so called structure breaker and structure former ions has been finished. This work is a part of a systematic effort directed to solving some of the problems of density and temperature effects on aqueous solutions.

Raman and NMR techniques have been used in a detailed investigation of molecular motions in liquid methyl iodide- $d_3$ . The main emphasis is on separation of the density and temperature effects on the reorientational and vibrational correlation functions and on constant volume

experiments in particular. The method of Fourier transform deconvolution was used in the treatment of the Raman data.

In the area of disordered solids, a study of the temperature and density effects on the order-disorder transition in compressed powders of  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  has been finished. Of main interest is the transition pressure hysteresis accompanying the order-disorder transition and its temperature dependence. The experimental results have been successfully interpreted in terms of a phenomenological theory based on a compressible Ising lattice as recently proposed by C. P. Slichter and collaborators of this Laboratory.

The results of several preliminary experiments on polymers have been encouraging. Using NMR relaxation measurements, the effects of pressure on molecular motions and the glass transition temperature in several types of rubber have been investigated. The results obtained determine the theoretical model for the glass transition which best describes the experimental data. (Jonas)

The following manuscripts are in preparation for publication:

"Effect of Pressure on Deuteron Spin-Lattice Relaxation in Several Concentrated Deuterium Oxide Diamagnetic Electrolyte Solutions," Y. Lee, J. H. Campbell and J. Jonas.

"Fourier Transform NMR in Liquids at High Pressure III: Spin-Lattice Relaxation in Toluene- $d_8$ ," D. J. Wilbur and J. Jonas.

"High Pressure NMR Study of Molecular Motions and Glass Transition Temperature in Several Amorphous Elastomers," N. Liu and J. Jonas.

"NMR Study of Pressure Effects on Order-Disorder Transition in  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$ ," N. Liu and J. Jonas.

"Raman and NMR Study of Density and Temperature Effects on Molecular Motions in Liquid Methyl Iodide," J. H. Campbell and J. Jonas.

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A specimen holder to maintain a metal sample in a controlled hydrogen atmosphere or high vacuum at a controlled temperature during back reflection light scattering experiments has been built. A multiply-passed Fabry Perot interferometer is being designed for the optical experiments.

For the experiments on Brillouin and Rayleigh light scattering from glasses and imperfections in crystals, the optical system has been assembled and is being tested.

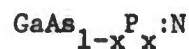
Preliminary Raman and infrared data have been obtained from TTF, the donor molecule in the TTF-TCNQ organic charge transfer complex, and a theoretical analysis of the data is in progress. (Klein)

. . . . .  
Molecular theories for the five liquid phases of liquid crystals for which the molecular order is understood have been completed. Three of the phase transitions are predicted to be second order and a theory of the critical region near the phase transition is being developed. The Wilson method of handling critical exponents is being used to treat the second order smectic A-nematic phase transition. A simple dynamical theory has been developed.

A self-beating Rayleigh light scattering apparatus has been placed in operation and the first data have been obtained from several liquid crystals. The relaxation time of the director in the nematic phase is

measured directly to test the dynamical theory of the smectic A-nematic phase transition. Present theory makes specific predictions concerning the temperature dependence of the relaxation time near this phase transition. (McMillan)

In the past year major advances in the study and understanding of the three alloys  $\text{GaAs}_{1-x}\text{P}_x$ ,  $\text{In}_{1-x}\text{Ga}_x\text{P}$ , and  $\text{In}_x\text{Ga}_{1-x}\text{As}$  has been made.

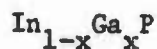


Since Craford and co-workers first demonstrated the importance of the N isoelectronic trap in yielding bright electroluminescence in the indirect region of  $\text{GaAs}_{1-x}\text{P}_x$  ( $x > x_c \approx 0.50$ , 300°K;  $x_c \approx 0.46$ , 77°K),<sup>1,2/</sup> we have shown that the N trap can be involved in stimulated recombination transitions in both the direct ( $x < x_c$ ) and indirect ( $x > x_c$ ) crystal composition regions.<sup>3-6/</sup> In spite of the extensive studies already performed, it has not been previously very clear to what extent the N trap differs in behavior in the direct and indirect bandgap regions.

In the direct crystal composition region, laser operation has been consistently possible on N trap transitions provided that the trap energy is reasonably close to the direct ( $\Gamma$ ) band edge. In the indirect region ( $x > 0.46$ , 77°K) stimulated emission has been possible to composition  $x = 0.56$  and, as recently demonstrated, laser operation has been achieved at crystal composition  $x = 0.47 > x_c$ .<sup>7/</sup> Clearly, the effect of the N trap in the indirect composition region has been to make the crystal quasi-direct. Recent results demonstrate that the effect of the N trap in the direct composition region is the opposite and makes the crystal behave as quasi-indirect.<sup>8/</sup>

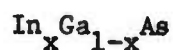
In experiments on: a)  $x=0.24\text{GaAs}_{1-x}\text{P}_x:\text{Te}$  ( $\text{Te}\approx 10^{19}/\text{cm}^3$ ), b)  $\text{GaAs}_{1-x}\text{P}_x:\text{N}^+:\text{Te}$  ( $\text{N}^+\geq 10^{19}/\text{cm}^3$ ,  $\text{Te}\approx 10^{19}/\text{cm}^3$ ), and c)  $\text{GaAs}_{1-x}\text{P}_x:\text{N}^+:\text{Te}:\text{Zn}$  ( $\text{N}^+\geq 10^{19}/\text{cm}^3$ ,  $\text{Te}\approx 10^{19}/\text{cm}^3$ ,  $\text{Zn}\approx 10^{19}/\text{cm}^3$ ), all prepared from the same constant-composition vapor phase epitaxial (VPE) wafer, laser operation has been obtained successively (a) at energies  $>E_g$ , (b) at energies  $\approx E_g$  on the NN pair trap states, and (c) at energies  $<E_g$  on the Te donor band tail states.<sup>8/</sup> The fact that the  $\text{GaAs}_{1-x}\text{P}_x:\text{N}^+:\text{Te}$  sample (b) can just barely be made to lase (near  $E_g$ ) and the other two samples (a) and (c) lase easily, triple doping ( $\text{Zn}+\text{Te}+\text{N}$ ) notwithstanding for the (c) case, is very good evidence that the N trap (which has no energy states in the donor tail for the  $\text{Zn}+\text{Te}+\text{N}$  case) is a very effective trapping center and source of non-k=0 recombination components for the  $\text{Te}+\text{N}$  case. These experiments<sup>8/</sup> provide for the first time direct evidence that the N impurity tends to make direct crystals quasi-indirect, which is of course consistent with the fact that the N trap is a very short range acceptor center. Note that for the  $\text{Zn}+\text{Te}+\text{N}$ -doped crystal (c) the N trap is not effective because the Zn doping has made the crystal p-type and photopumping fills the donor tail states to an energy well below that of the NN pair states (i.e.,  $E_{\text{Te}} < E_g < E_{\text{NN}}$ ) at the threshold for laser operation.

In addition to this work, the effect of Zn doping in conjunction with N in  $\text{GaAs}_{1-x}\text{P}_x$  has been explained.<sup>9/</sup> Besides its intrinsic interest, the Zn impurity in  $\text{GaAs}_{1-x}\text{P}_x:\text{N}$  is important for its role in the doping and fabrication of LED's. An electron trapped at a single N center or NN pair recombines via a hole trapped by a Zn atom, which is not the case for GaP. This behavior of  $\text{GaAs}_{1-x}\text{P}_x:\text{N}:\text{Zn}$  persists to the direct-indirect transition and then weakens.



Major progress has been made in the past year in the synthesis and laser operation of  $\text{In}_{1-x}\text{Ga}_x\text{P}$ .<sup>13/</sup> By constant-temperature liquid phase epitaxial (CT-LPE) crystal growth from In-Ga solution, high quality single crystal  $\text{In}_{1-x}\text{Ga}_x\text{P}$  on [100] oriented  $\text{GaAs}_{1-y}\text{P}_y$  substrates ( $y=0-0.40$ ) have been grown recently.<sup>14/</sup> This material when photopumped has operated as a laser to wavelengths as short as  $5500\text{\AA}$  (green), which is in the region of peak eye sensitivity and is, furthermore, the shortest wavelength laser operation yet achieved in a III-V semiconductor. Some of these CT-LPE crystals ( $x=0.52$ ) have been operated cw ( $77^\circ\text{K}$ ) as lasers, and have been pulse-operated at  $300^\circ\text{K}$  and a pulse rate of  $140 \times 10^6/\text{sec}$ .

Since both p-type and n-type  $\text{In}_{1-x}\text{Ga}_x\text{P}$  (homogeneous doping) exhibit laser operation when photopumped,<sup>14/</sup> laser junctions can undoubtedly be constructed in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  in the wavelength region  $6000-5500\text{\AA}$  (orange-yellow-green). These junctions will be prepared by Zn diffusion into n-type crystals since this approach to junction construction is of utmost practicality and value for large-scale LED processing. The diffusion of Zn into  $\text{In}_{1-x}\text{Ga}_x\text{P}$  is not without problems; apparently the Zn impurity can disturb the In-Ga sublattice if it is not properly introduced into  $\text{In}_{1-x}\text{Ga}_x\text{P}$ .<sup>15/</sup> Recent experiments indicate that this problem can be overcome.



Using the same constant-temperature crystal synthesis methods employed successfully to grow  $\text{In}_{1-x}\text{Ga}_x\text{P}$ ,<sup>13/</sup> n-type  $\text{In}_x\text{Ga}_{1-x}\text{As}$  has been grown that has yielded high quality Zn-diffused junction lasers ( $\lambda=1\mu\text{m}$ ).<sup>16/</sup> These lasers have been pulse-operated to temperatures as high as  $265^\circ\text{K}$ , and

no doubt can be further improved if the crystal is improved by CT-LPE synthesis. Also, the possibility exists that the improved methods of Zn diffusion into  $\text{In}_{1-x}\text{Ga}_x\text{P}$  now concerning us will have equal effect on the preparation of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  p-n junctions. (Holonyak)

#### References

1. W. O. Groves, A. H. Herzog, and M. G. Craford, *Appl. Phys. Lett.* 19, 184 (1971).
2. M. G. Craford, D. L. Keune, W. O. Groves, and A. H. Herzog, *J. Electron. Mater.* 2, 137 (1973).
3. N. Holonyak, Jr., D. R. Scifres, R. D. Burnham, M. G. Craford, W. O. Groves, and A. H. Herzog, *Appl. Phys. Lett.* 19, 254 (1971).
4. N. Holonyak, Jr., D. R. Scifres, M. G. Craford, W. O. Groves, and D. L. Keune, *Appl. Phys. Lett.* 19, 256 (1971).
5. N. Holonyak, Jr., R. D. Dupuis, H. M. Macksey, M. G. Craford, and W. O. Groves, *J. Appl. Phys.* 43, 4148 (1972).
6. N. Holonyak, Jr., R. D. Dupuis, H. M. Macksey, G. W. Zack, M. G. Craford, and D. Finn, *IEEE J. Quant. Elect.* QE-9, 379 (1973).
7. N. Holonyak, Jr., J. C. Campbell, M. H. Lee, J. T. Verdeyen, W. L. Johnson, M. G. Craford, and D. Finn, *J. Appl. Phys.* 44, to be published (December, 1973).
8. M. H. Lee, N. Holonyak, Jr., J. C. Campbell, W. O. Groves, and M. G. Craford, *J. Appl. Phys.*, submitted.
9. J. C. Campbell, N. Holonyak, Jr., M. H. Lee, M. J. Ludowise, M. G. Craford, D. Finn, and W. O. Groves, *J. Appl. Phys.* 45, to be published (February, 1974).

10. M. G. Craford and D. L. Keune, to be submitted for publication.
11. J. A. Rossi, A. R. Chinn, and H. Heckscher, Appl. Phys. Lett. 23, 25 (1973).
12. D. L. Keune, N. Holonyak, Jr., R. D. Burnham, D. R. Scifres, H. R. Zwicker, J. W. Burd, M. G. Craford, D. L. Dickus, and M. J. Fox, J. Appl. Phys. 42, 2048 (1971). D. R. Scifres, N. Holonyak, Jr., R. D. Burnham, H. R. Zwicker, D. L. Keune, W. O. Groves, M. G. Craford, and J. W. Burd, Solid-State Electron. 14, 949 (1971).
13. H. M. Macksey, N. Holonyak, Jr., R. D. Dupuis, J. C. Campbell, and G. W. Zack, J. Appl. Phys. 44, 1333 (1973).
14. H. M. Macksey, M. H. Lee, N. Holonyak, Jr., W. Hitchens, R. D. Dupuis, and R. C. Campbell, J. Appl. Phys. 44, to be published (November, 1973).
15. H. M. Macksey, N. Holonyak, Jr., D. R. Scifres, R. D. Dupuis, and G. W. Zack, Appl. Phys. Lett. 19, 271 (1971).
16. H. M. Macksey, J. C. Campbell, G. W. Zack, and N. Holonyak, Jr., J. Appl. Phys. 43, 3533 (1972).
17. R. D. Burnham, N. Holonyak, Jr., and D. R. Scifres, Appl. Phys. Lett. 17, 455 (1970). R. D. Burnham, N. Holonyak, Jr., H. W. Korb, H. M. Macksey, D. R. Scifres, J. B. Woodhouse, and Zh. I. Alferov, Appl. Phys. Lett. 19, 25 (1971).

During the present grant year, the capacitance technique has been used to determine the process and physical origin of the double donor center in the upper half of the silicon band gap ( $E_C-0.3$  and  $E_C-0.6$  eV). Exhaustive

sets of experiments have been designed. It was found that under all high temperature cycles, these centers are not detected in Schottky barrier diodes at sensitivity of  $10^{10}$  centers/cm<sup>3</sup>. These centers were previously generated and studied at high concentrations (greater than  $10^{12}$  centers/cm<sup>3</sup>) in boron diffused P+N diodes, suggesting that the center is associated with lattice strain introduced by the high concentration of boron in the p+ layer. Additional and new devices are being fabricated to test this hypothesis. This detective experiment represents, probably for the first time, the use of a highly sensitive and extremely simple and rapid electrical measurement technique to the study of process induced carrier generation-recombination centers. The importance of controlling, in particular reducing, the concentration of these centers is well known in MOSIC and CCD and need not be elaborated. This particular project will be completed early in 1974.

Studies are in progress and will continue to investigate the properties of transition and heavy metal impurities for possible device applications. A crystal grower has been set up to introduce these impurities during growth. The first element being studied is chromium.

A detailed study using carefully designed and fabricated gold-doped P-I-N diodes, has been made on the electron and hole capture and emission rates at the gold donor and acceptor centers in silicon to obtain their temperature dependences accurately at low electric field and to verify the thermal equilibrium mass action law. It is anticipated that this project will be completed during the current grant.

Online computer equipment has been set up to allow rapid analysis of a large amount of experimental data. This effort will be extended during the next grant year to a larger and faster machine which has a higher level programming language than what we presently have in order to analyze a variety of different experiments rapidly.

Since the beginning of ARPA support in 1964, this group has published about 100 papers of which 34 are directly concerned with the use of the junction current and capacitance methods to study deep level centers in silicon. A review of this work was presented in the Sherman Fairchild Lecture at Lehigh University on November 7, 1973 by Professor C. T. Sah. A copy of the text was sent to ARPA. (Sah)

#### References

1. C. T. Sah, L. Forbes, L. L. Rosier, and A. F. Tasch, Jr., Sol. St. Elec. 13, 759-788 (1970).
2. C. T. Sah, W. W. Chan, H. S. Fu, and J. W. Walker, Appl. Phys. Lett. 20, 193-195 (1972).
3. L. D. Yau and C. T. Sah, Appl. Phys. Lett. 21, 157-158 (1972).
4. C. T. Sah and J. W. Walker, Appl. Phys. Lett. 22, 384-385 (1973).
5. C. T. Sah and H. S. Fu, Physica Status Solidi (a) 11, 297-319 (1972).
6. C. T. Sah and H. S. Fu, Physica Status Solidi (a) 14, 59-70 (1972).
7. T. H. Ning and C. T. Sah, Phys. Rev. B4, 3469-3481 (1971).
8. T. H. Ning and C. T. Sah, Phys. Rev. B4, 3484-3488 (1971).
9. S. T. Pantelides and C. T. Sah, Sol. State Comm. 11, 1713-1718 (1972).

10. L. D. Yau and C. T. Sah, Sol. St. Elec., in press.
  11. J. W. Walker and C. T. Sah, Phys. Rev. B7, 4587-4605 (1973).
  12. J. W. Walker and C. T. Sah, Rad. Effects J., in press.
  13. J. W. Walker and C. T. Sah, Phys. Rev. B15, in press, (December 1973).
  14. L. L. Rosier and C. T. Sah, Sol. State Elec. 14, 41-54 (1971).
  15. C. T. Sah, T. H. Ning, L. L. Rosier, and L. Forbes, Sol. State Comm. 9, 917-920 (1971).
  16. L. L. Rosier and C. T. Sah, J. Appl. Phys. 42, 4000-4005 (1971).
  17. J. M. Herman and C. T. Sah, Physica Status Solidi (a) 14, 405-415 (1972).
  18. J. M. Herman III and C. T. Sah, J. Appl. Phys. 44, 1259-1262 (1973).
  19. J. M. Herman III and C. T. Sah, Sol. St. Elec. 16, 1133-1139 (1973).
  20. L. L. Rosier, Ph.D. thesis, Department of Physics, University of Illinois, 1969.
  21. T. H. Ning, Ph.D. thesis, Department of Physics, University of Illinois, 1971.
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### Implications for Future Research

The study of rotational correlations should be pursued in order to relate these two body correlation processes to other molecular processes. Extensions of the work should include the temperature, pressure, and concentration dependence. Rotational correlations should be studied in the vicinity of the critical point of liquids where there is considerable information available concerning translational diffusion and the shear viscosity.

Studies of mutual diffusion in binary liquids should be continued with extension to systems of molten salts, beta alumina type compounds, and, if possible, binary metals. The properties of molten salts are of obvious technological interest because of their use in high temperature, non-aqueous electrolytic processes.

The Rayleigh light scattering technique offers such a unique technique for the study of transport properties (diffusion and mobility of charged macromolecules that the modest beginning of this research should be continued. Of particular interest is the opportunity to examine charge shielding from counterions and many body forces. (Flygare)

It is most attractive to consider the extension of the use of nuclear magnetic resonance methods to higher pressures of 10 kilobars and, in particular, to temperatures up to 1000°C which appear feasible. Supercritical dense water gas can be studied under conditions where its electrical conductivity is comparable to that of fused salts, and polymers can be studied under extreme conditions. The experimental problems are severe but the possible rewards in terms of finding novel phenomena are so interesting that they justify this relatively high risk experiment. (Jonas)

The feasibility of the present experiments on hydrogen in metals and of molecular motion in glasses must be determined, and the results of the preliminary investigation of organic charge transfer conductive compounds must be assessed before future planning in this area can be realistically performed. (Klein)

The future work on liquid crystals should include the acquisition of better x-ray data on the smectic A-nematic transition, and acquisition of Rayleigh light scattering data to test the dynamical theory of this transition. With the implementation of the light scattering experiments, it appears that the apparatus may make possible some interesting experiments in a related area—that of atomic motion of the liquid like state of the ions in superionic conductors. Many of these materials exhibit important phase transitions which are susceptible to the experimental and theoretical techniques presently being applied to liquid crystals. The feasibility of research in this area is being examined. (McMillan)

The importance of GaAsP as a material for light emitting diodes warrants continued research, particularly of stimulated emission and laser effects in the indirect composition range  $x > x_c$ . Is it possible to operate  $\text{GaAs}_{1-x}\text{P}_x$ :N as a laser in the range from  $x_c$  to  $x=0.65$ ? The behavior of the N trap should be studied as its energy is varied (with  $x$ ) relative to  $\Gamma$  band edge. It is important to measure the possible improvement of the oscillator strength for recombination on the N trap as  $E_N$  or  $E_{NN}$  approaches  $E_\Gamma$ . These effects can be measured by using the grating tuning recently introduced by Rossi and determining the phase shift between repetitive pulse photoexcitation and the recombination radiation.

An attempt should be made to prepare laser junctions in  $\text{In}_{1-x}\text{Ga}_x\text{P}$  by Zn diffusion into n type crystals. Also, nitrogen doping should be attempted by addition of  $\text{NH}_3$  to the  $\text{H}_2$  now used during crystal growth. Nitrogen doping will be important for the improvement of light emission in the orange, yellow and green regions of the spectrum and possibly for the construction of short wavelength lasers.  $\text{In}_x\text{Ga}_{1-x}\text{As}$  should be developed in parallel with  $\text{In}_{1-x}\text{Ga}_x\text{P}$  by employing the same ideas applied to this material. It should be possible to grow by CT-LPE methods  $\text{AlInGaP/InGaP}$  and  $\text{AlInGaAs/InGaAs}$  heterojunctions for possible use as optoelectronic devices. Such heterojunctions are a long range goal of the present research. (Holonyak)

In addition to the work on double donor centers in silicon, other centers generated by radiation or high temperature processes should be studied. New devices should be constructed to verify the conclusion that the double donor center is due to lattice strain resulting from boron diffusion into silicon. Transition metal impurities like Mo, W, Fe, Ta, Ti and others should be investigated for their possible device applications. Isovalent traps (sometimes called isoelectronic traps) deserve continuing study because of their effect on radiative and nonradiative recombination and generation. It is highly desirable that studies of simple donors and acceptors, like sulfur and zinc, be studied in low electric fields to provide a basis for a quantum mechanical theory of thermal emission and capture of electron and holes at these centers. (Sah)