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REPORT SUMMARY

The research described in this report was carried out under the direction of Professors W. Flygare, Jr. and J. Jonas of the Department of Chemistry, Professors M. Klein and W. McMillan of the Department of Physics, and Professors N. Holonyak, Jr., C. T. Sah, and G. Stillman of the Department of Electrical Engineering as an integral part of the interdisciplinary research program of the Materials Research Laboratory of the University of Illinois.

Technical Problem

The research described in this report investigates two areas of major concern for the development of improved materials.

(a) Research on Semiconductors: The principal concern is to develop improved light emitting, laser, semiconducting diodes, near infrared photodiode detectors, and control defects and impurities in silicon diodes, transitors and integrated circuits. Emphasis has been on the properties of the compound semiconductors GaAs, InP, $GaAs_xP_{1-x}$, $In_{1-x}Ga_xP$, $In_{1-x}Ga_xP_{1-z}As_z$ for light emitters and detectors and on silicon for solid state circuit devices.

(b) Research on Disordered Materials: Emphasis has been placed on the determination of the dynamic structure of liquids including water, polymers, liquid crystals, superionic conductors, layer compounds and hydrogen in metals.

General Methodology

(a) Research on Semiconductors: Diodes and single and double heterojunctions were fabricated by liquid phase expitaxial growth. Optical absorption and luminescence measurements were made to determine the performance of the devices and clarify the electronic mechanisms involved in their operation. A novel capacitance technique was used to determine the concentration and properties of defects introduced into silicon devices during thermal processing and integrated circuit manufacture.

(b) Research on Disordered Materials: Sophisticated light scattering techniques, nuclear magnetic resonance, viscosity and elastic constant measurements as a function of pressure were the principal techniques. The experimental research was closely coupled with extensive theoretical developments.

Technical Results

(a) Research on Semiconductors

Laser diodes of InGaPAs which operate in the visible yellow region of the spectrum were developed. These laser diodes operate at shorter wavelengths than any other III-V compound system.

Liquid phase expitaxial layers of controlled thickness and properties on GaAs and InP substrates for photodiode detector devices were prepared and the initial evaluation of the device characteristics begun.

The properties of tantalum, gold, and aluminum-oxygen centers in silicon were determined.

(b) Research on Disordered Materials

Intermolecular forces and orientational pair correlation of molecules in liquids were determined and correlated with electric dipole moments. Molecular size and shape were found to determine primarily the orientational pair correlations.

The limitations of the hard sphere model of a liquid were quantitatively revealed by NMR, self-diffusion, viscosity and pressure-volume-temperature data. Angular momentum correlation time data showed that the effective hard sphere diameter of molecules is temperature dependent. The Stokes-Einstein equation was found to be remarkably precise with the slipping boundary condition well satisfied. The molecular conditions that yield these results were clarified by the data. At high pressure, the interesting result was obtained that the anomalous properties of water revert to more normal behavior with major changes in the hydrogen bond network. The effect of pressure on the glass transition of several elastomers including natural rubber was determined.

Raman scattering studies yielded detailed information concerning the silver ion mobility in the superionic conductor β-Ag_2HgI_4 and AgI. Information concerning interatomic forces and bonding in titanium carbide were obtained by this technique. The growth of oxide layers on niobium was studied by Raman scattering and scattering from hydrogen in palladium observed.

Proposed theories of the critical behavior near the smectic A to nematic phase transition of liquid crystals were shown to be faulty. Theoretical molecular models of the smectic C and F phases were completed.

Experimental data were obtained that exposed the inadequacy of current theories of charge density waves in the transition metal dichalogenides and A15 compounds. The reasons for the failure of the theories was determined to be primarily the neglect of phonon entropy. As a result, a satisfactory theory has been developed. A two dimensional version of Landau's quantum hydrodynamics was used to establish a theory of superfluidity in two dimensional submonolayer He^4 films.

Special Comments

Examination of the individual project reports which follow reveal the extensive pattern of collaboration among the investigators supported by this contract. This collaboration included the preparation and sharing of materials, the performance of measurements, and cooperation in the development of theories based on the experimental data. Collaboration was not confined to the groups supported by this contract but extended to important interactions with groups and individuals supported by other Federal agencies. The semiconductor research of Prof. N. Holonyak benefited immensely as a result of cooperation with investigations of the Monsanto Chemical Company and the liquid crystals and phase transition work similarly was assisted by interactions with the Bell Telephone Laboratories.

Of the 77 publications resulting from the research supported by the contract, 26 publications or 34% were coauthored by collaborating investigators.

Final Project Report
Luminescence, Lasers, Carrier and Impurity Effects in Compound Semiconductors
N. Holonyak, Jr.

Technical Problem

In this project we have been concerned with two areas of work: 1) The quaternary $In_{1-x}Ga_xP_{1-z}As_z$ has been grown, via liquid phase epitaxy (LPE), and fabricated into single and double heterojunction laser diodes that extend further into the visible (yellow) than does any other III-V system. As part of this work, we have studied the behavior of the quaternary and its two ternary boundaries $GaAs_{1-y}P_y$ and $In_{1-x}Ga_xP$. 2) Because of its practical importance (in making the indirect crystal quasi-direct) and its fundamentally different behavior in a ternary than in a binary, we have studied further the behavior of the nitrogen trap in $GaAs_{1-y}P_y$; this has been accomplished by means of absorption, photoluminescence, and high pressure measurements, the last on homo- and heterojunctions. We have established that the N trap in $GaAs_{1-y}P_y$, and in $In_{1-x}Ga_xP$, exhibits both short range and long range behavior.

Technical Results

InGaPAs HETEROJUNCTIONS

Although it is certain that $In_{1-x}Ga_xP_{1-z}As_z$ can be grown via vapor phase epitaxy (VPE), in this work it has been more convenient to use LPE to grow single and double heterojunctions on $GaAs_{1-y}P_y$ substrates. For both single and double heterojunctions we have employed a cylindrical slider boat (positioned in a small temperature gradient) and have determined that melt wipe-off after the growth of each layer is perhaps the most important LPE process problem,[1] particularly for In-rich melts suitable for large energy gap layers.

For the case of single heterojunctions, the active region of the structure lies in the $GaAs_{1-y}P_y$ substrate.[2,3] This has made it possible to study a number of the fundamental properties of the N trap in $GaAs_{1-y}P_y$ in the region near the direct-indirect transition.[4-8] We mention that as part of this work we have determined, via the first successful direct-gap exciton absorption measurements in a III-V alloy,[9,10] that the direct-indirect transition in $GaAs_{1-y}P_y$ lies at $y \equiv y_c \approx 0.45$ (77°K) and in $In_{1-x}Ga_xP$ at $x \equiv x_c \approx 0.72$ (77°K).

Utilizing $GaAs_{1-y}P_y$ as a substrate, we have succeeded in growing $In_{1-x}Ga_xP_{1-z}As_z$ DH laser diodes that operate in the yellow at 77°K.[11,12] These laser diodes have been operated also in external grating cavities and have demonstrated to what extent "homogeneous" or "inhomogeneous" broadening can be expected in a diode laser.[13,14] As the LPE crystal growth art has improved, it has proven possible to operate $In_{1-x}Ga_xP_{1-z}As_z$ DH laser diodes ($\sim$140 meV heterobarrier) at room temperature with pulsed current densities of $\sim 2\text{x}10^4 \mathring{A}/cm^2$.[15] The heterobarrier height can be increased to $\sim$250 meV without sacrificing the capability of laser operation (300°K) at $\sim$6500 Å.[16] These results indicate that when more sophisticated stripe-geometry diode structures are employed, and the LPE layer growth is further developed, it should be possible to operate red-orange $In_{1-x}Ga_xP_{1-z}As_z$ DH laser diodes continuously at room temperature. The composition (x_c, z_c) at which these quaternary laser diodes become limited by the direct-indirect transition ($x_c - 0.52z_c = 0.73$, 77°K; $x_c - 0.51z_c = 0.72$, 300°K) has been determined by pressure measurements[17] and by observation of diode "freeze-out" (300→77°K) or impedance increase for lattice-matched wide-gap $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim x_c$, $z \lesssim 0.01$) layers grown on successively higher composition $GaAs_{1-y}P_y$ substrates.[18]

NITROGEN TRAP IN III-V ALLOYS

By means of absorption, photoluminescence and electroluminescence measurements on $In_{1-x}Ga_xP$:N[10,19,20] and by a large series of measurements on $GaAs_{1-y}P_y$:N,[7,8,21-26] we have shown that the previous assignment of an NN-pair recombination transition[27] in these alloys (analogous to GaP:N behavior) is in error, and that this transition, now labeled N_X, is due to recombination at a single N site. Theory, with measurement,[8] shows that the N trap in $GaAs_{1-y}P_y$ (and in $In_{1-x}Ga_xP$) exhibits a combination of long-range and short-range behavior, the latter being most important for light emitting purposes (indirect crystal).[26,27] The two long-range states, N_Γ and N_X, are associated with the Γ and X band minima.[7,8] The state N_X, which is useful in indirect crystal for light emitting diodes (LED's),[27] is basically fairly weak except for the oscillator strength coupled into this transition by the short-range state, N.[8,26] Pressure measurements on $In_{1-x}Ga_xP_{1-z}As_z$ - $GaAs_{1-y}P_y$:N heterojunctions[2,7,25] in the composition range where the short-range trap, N, is degenerate with N_Γ and where N_X is degenerate with N_Γ indicate strong interaction and splitting of these states at the crossover compositions.[7]

Implications for Future Research

We have demonstrated that the quaternary $In_{1-x}Ga_xP_{1-z}As_z$ can be used to fabricate single and double heterojunctions, the latter able to operate well into the yellow portion of the spectrum. This is the highest energy diode laser system yet demonstrated. Although it is not yet proven, the $In_{1-x}Ga_xP_{1-z}As_z$ system potentially is capable of lattice-latching when one layer is grown epitaxially on another. For technological reasons it is important that this alloy is free of Al and its difficult oxides.

Based on experiments conducted on $In_{1-x}Ga_xP$ and $GaAs_{1-y}P_y$, we have been able to show that the N trap in these alloys exhibits a combination of long range and short range behavior and that NN-pair recombination transitions (unlike in GaP:N) are not important. This work is useful in helping to clarify the recombination mechanisms that are important in certain classes of LED's.

Both of these areas of study are far from complete and require more work. Based on the work reported here, it is likely that a CW, room temperature visible (∿6500Å) DH diode laser can be built; also, it is likely that the work we describe here, pursued further, will improve LED's by a factor of 10.

References

1. J. J. Coleman, N. Holonyak, Jr., and M. J. Ludowise, "Melt Removal and Planar Growth of $In_{1-x}Ga_xP_{1-z}As_z$," Appl. Phys. Lett. 28, 363-365 (1976).
2. J. J. Coleman, W. R. Hitchens, N. Holonyak, Jr., M. J. Ludowise, W. O. Groves, and D. L. Keune, "Liquid Phase Epitaxial $In_{1-x}Ga_xP_{1-z}As_z$/$GaAs_{1-y}P_y$ Quaternary (LPE)-Ternary (VPE) Heterojunction Lasers," Appl. Phys. Lett. 25, 725-727 (1974).
3. J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, and D. L. Keune, "Liquid Phase Epitaxial $In_{1-x}Ga_xP_{1-z}As_z$/$GaAs_{1-y}P_y$ Heterojunction Lasers," IEEE J. Quantum Electron. QE-11, 471-476 (1975).
4. J. J. Coleman, N. Holonyak, Jr., A. B. Kunz, W. O. Groves, D. L. Keune, and M. G. Craford, "Resonant Enhancement (?) of the Recombination Probability at the Nitrogen-Trap, Γ-Band Edge Crossover in $GaAs_{1-x}P_x$:N ($E_N = E_\Gamma$, $(x \equiv x_N)$)," Solid State Commun. 16, 319-322 (1975).

5. J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford, "Heterojunction Laser Operation of N-Free and N-Doped $GaAs_{1-y}P_y$ ($y = 0.42$-0.43, $\lambda \sim 6200$ Å, 77°K) near the Direct-Indirect Transition ($y \sim y_c \approx 0.46$)," J. Appl. Phys. 46, 3556-3561 (1975).

6. J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, R. J. Nelson, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford, "Heterojunction Laser Operation of $GaAs_{1-x}P_x$:N on NN-pair (E_{NN}) and A-line (E_N) Transitions near the Direct (Γ) Band Edge," J. Appl. Phys. 46, 4835-4841 (1975).

7. R. J. Nelson, N. Holonyak, Jr., J. J. Coleman, D. Lazarus, W. O. Groves, D. L. Keune, M. G. Craford, D. J. Wolford, and B. G. Streetman, "Effect of Composition and Pressure on the Nitrogen Isoelectronic Trap in $GaAs_{1-x}P_x$," Phys. Rev. B14, 685-690 (1976).

8. George G. Kleiman, R. J. Nelson, N. Holonyak, Jr., and J. J. Coleman, "A Direct Study of the Nature of Nitrogen Bound States in $GaAs_{1-x}P_x$:N," Phys. Rev. Lett. 37, 375-378 (1976).

9. R. J. Nelson, N. Holonyak, Jr., and W. O. Groves, "Free Exciton Transitions in the Optical Absorption Spectra of $GaAs_{1-x}P_x$," Phys. Rev. B13, 5415-5419 (1976).

10. R. J. Nelson and N. Holonyak, Jr., "Exciton Absorption, Photoluminescence and Band Structure of N-Free and N-Doped $In_{1-x}Ga_xP$," J. Phys. Chem. Solids 37, 629-637 (1976).

11. W. R. Hitchens, H. Holonyak, Jr., P. D. Wright, and J. J. Coleman, "Low Threshold LPE $In_{1-x'}Ga_{x'}P_{1-z'}As_{z'}/In_{1-x}Ga_xP_{1-z}As_z/In_{1-x'}Ga_{x'}P_{1-z'}As_{z'}$ Yellow Double Heterojunction Laser Diodes ($J < 10^4$ Å/cm^2, $\lambda \approx 5850$ Å, 77°K)," Appl. Phys. Lett. 27, 245-247 (1975).

12. J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and P. D. Wright, "Yellow $In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunction Lasers," J. Appl. Phys. 47, 2015-2019 (1976).

13. P. D. Wright, J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and G. E. Stillman, "Homogeneous or Inhomogeneous Line Broadening in a Semiconductor Laser: Observations on $In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunctions in an External Grating Cavity," Appl. Phys. Lett. 29, 18-20 (1976).

14. P. D. Wright, J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and G. E. Stillman, "$In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunction Laser Operation (77°K, Yellow) in an External Grating Cavity," J. Appl. Phys. 47, 3580-3586 (1976).

15. J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, R. Chin, W. O. Groves, and D. L. Keune, "Pulsed Room Temperature Operation of $In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunction Lasers at High Energy (6470 Å, 1.916 eV)," Appl. Phys. Lett. 29, 167-169 (1976).

16. J. J. Coleman, N. Holonyak, Jr., R. Chin, B. L. Marshall, W. O. Groves, A. H. Herzog, and D. L. Keune, "Room Temperature Visible $In_{1-x}Ga_xP_{1-z}As_z$ Heterojunction Lasers," North American Gallium Arsenide Symposium, September, 1976, St. Louis (to be published, Institute of Physics Conference Series).

17. R. J. Nelson, N. Holonyak, Jr., W. R. Hitchens, D. Lazarus, and M. Altarelli, "Pressure Experiment Determination of the Direct-Indirect Transition in the Quaternary $In_{1-x}Ga_xP_{1-z}As_z$," Solid State Commun. 18, 321-325 (1976).

18. N. Holonyak, Jr., R. Chin, J. J. Coleman, D. L. Keune, and W. O. Groves, "Limitations of the Direct-Indirect Transition on $In_{1-x}Ga_xP_{1-z}As_z$ Heterojunction," J. Appl. Phys. (Submitted)

19. R. J. Nelson and N. Holonyak, Jr., "Nitrogen Trap Bound States in $In_{1-x}Ga_xP$," Solid State Commun. 20, 549-551 (1976).

20. R. J. Nelson and N. Holonyak, Jr., "Effect of Crystal Composition on the Optimization of Radiative Recombination in N-Free and N-Doped $In_{1-x}Ga_xP$ Light Emitting Diodes," J. Appl. Phys. 47, 1704-1707 (1976).

21. D. J. Wolford, B. G. Streetman, R. J. Nelson, and N. Holonyak, Jr., "Identification of Recombination Luminescence Transitions in N-Doped $GaAs_{1-x}P_x$ ($x=0.87$)," Solid State Commun. 19, 741-747 (1976).

22. D. J. Wolford, B. G. Streetman, R. J. Nelson, and N. Holonyak, Jr., "Stimulated Emission on N_X("A-line") Recombination Transitions in Nitrogen-Implanted $GaAs_{1-x}P_x$ ($x \approx 0.37$)," Appl. Phys. Lett. 28, 711-713 (1976).

23. D. J. Wolford, B. G. Streetman, W. Y. Hsu, J. D. Dow, R. J. Nelson, and N. Holonyak, Jr., "Evidence for Radiative Recombination in $GaAs_{1-x}P_x$:N ($0.28 \lesssim x \lesssim 0.45$) Involving an Isolated Nitrogen Impurity State Associated with the Γ_1 Minimum," Phys. Rev. Lett. 36, 1400-1403 (1976).

24. R. J. Nelson, N. Holonyak, Jr., W. O. Groves, and D. L. Keune, "Electron-Hole Recombination in Nitrogen-Doped Direct Bandgap $GaAs_{1-x}P_x$," J. Appl. Phys. 47, 3625-3629 (1976).

25. R. J. Nelson, N. Holonyak, Jr., J. J. Coleman, D. Lazarus, D. L. Keune, W. O. Groves, and M. G. Craford, "Pressure Study of the N_Γ and N_X Bound State Interaction in Nitrogen-Doped $GaAs_{1-x}P_x$," Phys. Rev. B14, 3511-3515 (1976).

26. R. J. Nelson, N. Holonyak, Jr., J. J. Coleman, D. Lazarus, D. L. Keune, A. H. Herzog, W. O. Groves, and George G. Kleiman, "Pressure Study of the External Quantum Efficiency of N-doped $GaAs_{1-x}P_x$ Light-Emitting Diodes," Appl. Phys. Lett. 29, 615-617 (1976).

27. M. G. Craford and N. Holonyak, Jr., "The Optical Properties of the Nitrogen Isoelectronic Trap in $GaAs_{1-x}P_x$," in *Optical Properties of Solids: New Developments*, ed. B. O. Seraphin (North-Holland Publ. Co., Amsterdam, 1976), Chap. 5, pp. 187-253.

PUBLICATIONS (SINCE JUNE 1, 1975)

J. J. Coleman, N. Holonyak, Jr., and M. J. Ludowise, "Melt Removal and Planer Growth of $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}_{1-z}\mathrm{As}_z$ Heterojunctions," Appl. Phys. Lett. 28, 363-365 (1976).

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, R. J. Nelson, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford, "Heterojunction Laser Operation of $\mathrm{GaAs}_{1-x}\mathrm{P}_x$:N on NN-pair ($E_{NN}$) and A-Line ($E_N$) Transitions near the Direct (Γ) Band Edge," J. Appl. Phys. 46, 4835-4841 (1975).

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and P. D. Wright, "Yellow $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}_{1-z}\mathrm{As}_z$ Double Heterojunction Lasers," J. Appl. Phys. 47, 2015-2019 (1976).

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, and D. L. Keune, "Liquid Phase Epitaxial $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}_{1-z}\mathrm{As}_z/\mathrm{GaAs}_{1-y}\mathrm{P}_y$ Heterojunction Lasers," IEEE J. Quantum Electron. QE-11, 471-476 (1975).

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, and D. L. Keune, "Pulsed Room-Temperature Operation of $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}_{1-z}\mathrm{As}_z$ Double Heterojunction Lasers at High Energy (6460 Å, 1.916 eV)," Appl. Phys. Lett. 29, 167-169 (1976).

J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, P. D. Wright, W. O. Groves, D. L. Keune, and M. G. Craford, "Heterojunction Laser Operations of N-Free and D-Doped $\mathrm{GaAs}_{1-y}\mathrm{P}_y$ ($y=0.42-0.43$, $\lambda \sim 6200$ Å, 77°K) near the Direct-Indirect Transition ($y \sim y \gtrsim 0.46$)," J. Appl. Phys. 46, 3556-3561 (1975).

M. G. Craford and N. Holonyak, Jr., "The Optical Properties of the Nitrogen Isoelectronic Trap in $\mathrm{FaAs}_{1-x}\mathrm{P}_x$," in *Optical Properties of Solids: New Developments*, ed. B. O. Seraphin (North-Holland Publ. Co., Amsterdam, 1975), Chapt. 5, pp. 189-253.

W. R. Hitchens, H. Holonyak, Jr., P. D. Wright, and J. J. Coleman, "Low-Threshold LPE $\mathrm{In}_{1-x'}\mathrm{Ga}_{x'}\mathrm{P}_{1-z'}\mathrm{As}_{z'}/\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}_{1-z}\mathrm{As}_z/\mathrm{In}_{1-x'}\mathrm{Ga}_{x'}\mathrm{P}_{1-z'}\mathrm{As}_{z'}$ Yellow Double Heterojunction Laser Diodes ($J < 10^4$ Å/cm^2, $\lambda \gtrsim 5850$ Å, 77°K)," Appl. Phys. Lett. 27, 245-247 (1975).

N. Holonyak, Jr., R. Chin, J. J. Coleman, D. L. Keune, and W. O. Groves, "Limitations of the Direct-Indirect Transition on $In_{1-x}Ga_{x}P_{1-z}As_{z}$ Heterojunction," J. Appl. Phys. (Submitted)

George G. Kleiman, R. J. Nelson, N. Holonyak, Jr., and J. J. Coleman, "Direct Study of the Nature of Nitrogen Bound States in $GaAs_{1-x}P_{x}$:N," Phys. Rev. Lett. 37, 375-378 (1976).

R. J. Nelson and N. Holonyak, Jr., "Effect of Crystal Composition on the Optimization of Radiative Recombination in N-Free and N-Doped $In_{1-x}Ga_{x}P$ Light Emitting Diodes," J. Appl. Phys. 47, 1704-1707 (1976).

R. J. Nelson and N. Holonyak, Jr., "Nitrogen Trap Bound States in $In_{1-x}Ga_{x}P$," Solid State Commun. 20, 549-551 (1976).

R. J. Nelson and N. Holonyak, Jr., "Exciton Absorption, Photoluminescence, and Band Structure of N-Free and N-Doped $In_{1-x}Ga_{x}P$," J. Phys. Chem. Solids 37, 629-637 (1976).

R. J. Nelson, N. Holonyak, Jr., J. J. Coleman, D. Lazarus, W. O. Groves, D. L. Keune, M. G. Craford, D. J. Wolford, and B. G. Streetman, "Effect of Composition and Pressure on the Nitrogen Isoelectronic Trap in $GaAs_{1-x}P_{x}$," Phys. Rev. B14, 685-690 (1976).

R. J. Nelson, N. Holonyak, Jr., J. J. Coleman, D. Lazarus, D. L. Keune, W. O. Groves, and M. G. Craford, "Pressure Study of the N_{Γ} and N_{X} Bound State Interaction in Nitrogen-Doped $GaAs_{1-x}P_{x}$," Phys. Rev. B14, 3511-3515 (1976).

R. J. Nelson, N. Holonyak, Jr., J. J. Coleman, D. Lazarus, D. L. Keune, A. H. Herzog, W. O. Groves, and George G. Kleiman, "Pressure Study of the External Quantum Efficiency of N-doped $GaAs_{1-x}P_{x}$ Light-Emitting Diodes," Appl. Phys. Lett. 29, 615-617 (1976).

R. J. Nelson, N. Holonyak, Jr., and W. O. Groves, "Free-Exciton Transitions in the Optical Absorption Spectra of $GaAs_{1-x}P_{x}$," Phys. Rev. B13, 5415-5419 (1976).

R. J. Nelson, N. Holonyak, Jr., W. O. Groves, and D. L. Keune, "Electron-Hole Recombination in Nitrogen-Doped Direct Bandgap $GaAs_{1-x}P_{x}$," J. Appl. Phys. 47, 3625-3629 (1976).

R. J. Nelson, N. Holonyak, Jr., W. R. Hitchens, D. Lazarus, and M. Altarelli, "Pressure Experiment Determination of the Direct-Indirect Transition in the Quarternary $In_{1-x}Ga_xP_{1-z}As_z$," Solid State Commun. 18, 321-325 (1976).

D. J. Wolford, B. G. Streetman, R. J. Nelson, and N. Holonyak, Jr., "Stimulated Emission on N_X ("A-Line") Recombination Transitions in Nitrogen-Implated $GaAs_{1-x}P_x$ ($x \approx 0.37$)," Appl. Phys. Lett. 28, 711-713 (1976).

P. D. Wright, J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and G. E. Stillman, "Homogeneous or Inhomogeneous Line Broadening in a Semiconductor Laser: Observations on $In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunctions in an External Grating Cavity," Appl. Phys. Lett. 29, 18-20 (1976).

P. D. Wright, J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and G. E. Stillman, "$In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunction Laser Operation (77°K, Yellow) in an External Grating Cavity," J. Appl. Phys. 47, 3580-3586 (1976).

Theses

J. J. Coleman, "Indium Gallium Phosphide Arsenide - Gallium Arsenide Phosphide Single Heterojunction Lasers," Ph.D. Thesis (1975), H. Holonyak, adviser.

William Robert Hitchens, "Liquid-Phase-Epitaxial Growth and Properties of Indium Gallium Phosphide and Indium Gallium Phosphide Arsenide Injection Lasers," Ph.D. Thesis (1975), N. Holonyak, adviser.

Ronald Jarl Nelson, "Luminescence, Absorption, and Pressure Studies of Nitrogen-Doped and Nitrogen-Free Gallium Arsenide Phosphide and Indium Gallium Phosphide," Ph.D. Thesis (1976), H. Holonyak, adviser.

Final Project Report
Compound Semiconductors for Near Infrared Detectors
G. Stillman

Technical Problem

This project was initiated in July 1975, to study various III-V compounds for applications in near infrared photodiode detectors. The performance of silicon photodetectors that are available commercially is limited by a response time-quantum efficiency product at wavelengths longer than about 0.9 μm because of the low absorption coefficient of silicon in this wavelength range. Photodiodes in direct band gap III-V compound semiconductors do not have the same limitation and are inherently capable of much shorter (transit time limited) response times at a given quantum efficiency. For highest sensitivity in wide bandwidth detection applications it is also desirable to operate the detectors with avalanche gain, and the larger the difference in electron and hole ionization coefficients, the higher the sensitivity that can be obtained in a properly designed device. The initial objective of this project was to establish a laboratory for the liquid phase epitaxial growth of GaAs and InP, the general characterization and evaluation of semiconductor material, and for the fabrication and evaluation of photodiode detectors. The second objective was to fabricate special device structures which will permit the accurate determination of the electron and hole impact ionization coefficients over a wide range of electric fields above and below room temperature. Besides being of interest for the design or avalanche photodiodes, these parameters are also of great importance in IMPATT device analyses.

General Methodology

The slider boat liquid phase epitaxial technique was chosen for the initial growth of GaAs and InP to be used in near infrared detector applications because of its versatility for multiple layer growth and because of its relative simplicity. Separate systems have been set up for the growth of GaAs and InP. The InP LPE system incorporates a transparent gold furnace to permit accurate determination of the liquidus and solidus temperatures for a given melt composition. The growth techniques presently being utilized include supersaturation, constant-temperature, and ramp down growth.

For the characterization of the semiconductor material grown, facilities have been set up for Hall effect measurements at room temperature and liquid nitrogen temperature, and for C-V measurements and analyses using Schottky barrier diodes. In addition, optical facilities exist for the measurement of transmission and/or absorption over the wavelength range from the near ultraviolet out to about 50 μm, and these measurement techniques are used to evaluate the quality of the material (deep levels, etc.) and to determine the band gap of semiconductor alloys.

The fabrication of wide bandwidth photodiode detectors requires the use of photolithographic processing techniques, and a small facility which permits this processing has been set up in collaboration with Professor Nick Holonyak, Jr. Included in this facility are photoresist and two inch mask alignment equipment, and the capability of depositing pyrolytic SiO_2, SiON and Si_3N_4 for use in passivation, pattern definition, and masking for diffusion and etching. An alloy station which uses an HCl-H_2 atmosphere is employed for the low temperature preparation of ohmic semiconductor contacts.

The characterization of the photodiode detectors includes measurements of quantum efficiency, relative spectral response, noise, and response time. For the measurement of quantum efficiency, a spot measurement is made using a HeNe laser and a calibrated photodiode. The spectral quantum efficiency and the spectral responsivity are then determined by using the spot measurement to calibrate relative spectral measurements made using a thermocouple reference detector and a monochrometer with a tungsten light source. Standard laboratory techniques are used for the noise and response time measurements.

Technical Results

Liquid phase epitaxial layers with good morphological and electrical characteristics can now be grown routinely on <100> and <111> N^+ and high resistivity Cr-doped substrates. There is generally good agreement between the experimental layer thickness and that calculated using diffusion limited growth models, so that the layer thickness can be controlled quite accurately for thicknesses greater than 1 μm. This is important for the design and fabrication of both photodiodes and particular structures for electron and hole ionization coefficient measurements. The doping can generally be controlled quite well in the low 10^{15} cm^{-3} range, as confirmed by Hall coefficient measurements of the layers grown on insulating substrates and by C-V measurements of the layers on conducting substrates. This growth technique is now being used to fabricate special structures for the measurement of electron and hole impact ionization coefficients. As the InP growth parameters are determined, these measurements will be extended to this material, and following this to InGaAsP quaternary epitaxial layers for longer wavelength near infrared applications.

PUBLICATIONS (SINCE JUNE 1, 1975)

G. E. Stillman, "Ionization Coefficients in GaAs and Related Compounds," International Symposium on Gallium Arsenide and Related Compounds, Edinburgh, September 1976.

G. E. Stillman, C. M. Wolfe, and D. M. Korn, "Donor Impurities in GaAs: Evidence for a Stoichiometric Hydrogenic Shallow Donor Level," Thirteenth International Conference on Physics of Semiconductors, Rome, 1976.

P. D. Wright, J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise and G. E. Stillman, "Homogeneous or Inhomogeneous Line Broadening in a Semiconductor Laser: Observations on $In_{1-x}Ga_xP_{1-z}As_z$ Double Heterojunctions in an External Grating Cavity," Appl. Phys. Lett. 29, 18-20 (1976).

P. D. Wright, J. J. Coleman, N. Holonyak, Jr., M. J. Ludowise, and G. E. Stillman, "$In_{1-x}Ga_xP_{1-z}As_z$ Double-Heterojunction-Laser Operation (77°K, Yellow) in an External Grating Cavity," J. Appl. Phys. 47, 3580-3586 (1976).

Theses

None

Final Project Report
Properties of Recombination Centers in Semiconductors
C. T. Sah

Technical Problem

This project studies the recombination and diffusion kinetic properties of impurity and defect recombination centers in silicon introduced during crystal growth and subsequent high temperature processing steps commonly used in integrated circuit manufacturing. The capacitance-voltage and transient capacitance techniques are used to determine thermal emission rates of electrons and holes, the energy level and the concentration profile of these centers. Detailed studies were made for Ta and aluminum-oxygen centers as well as low temperature diffusion of gold into an aluminum sink in silicon.

Technical Results

Detailed measurements of the parameters characterizing the generation and recombination properties of electrons and holes at Ta centers in silicon have been made and reported.[1] High concentrations of Ta were introduced into the silicon melt but only a small fraction is electrically active in the grown silicon crystal.

The effect of the stationary trapped charges at recombination centers located at the edge of the space charge region of p-n or Schottky barrier junction has been analyzed and determined experimentally. The model including this stationary charge has been used to evaluate the spatial variation of the concentration of the recombination centers in the region very near the p-n junction or the metal-semiconductor interface. One interesting result obtained is the high diffusion rate of gold from silicon into the aluminum sink at 450°C in an Al on n-Si Schottky barrier diode structure. It shows that gold outdiffuses into the aluminum sink following the simple diffusion law which gives an erf concentration profile with diffusivities consistent with those extrapolated from 800 to 1200°C.[2]

The capacitance-voltage method has been applied to the determination of impurity concentration, resistivity and conductivity mobility in p-type silicon. The impurity and carrier concentrations are obtained from the capacitance-voltage measurements made on Al on n-Si Schottky barrier diodes while the resistivity is measured on an ohmic diode adjacent to the Schottky diode. The analyses[3] of the data had neglected the deionization effect at low temperatures which is not justifiable. A revised calculation of the experiment has been undertaken and will be submitted for publication.

The capacitance transient technique has also been applied to the study of the traps produced during heat treatment in aluminum-doped silicon. There has been some interest in Al-doped p-type silicon in certain IR applications due to the larger thermal activation energy of aluminum in silicon. Detailed measurements have shown that the defect centers detected are aluminum-oxygen complexes which produce three hole-trap levels and one electron-trap level in the silicon band gap. The complexes break up at 1000°C or above and the oxygen member of the complex diffuses toward a heavily phosphorus doped layer.

References

1. K. Miyata and C. T. Sah, "Thermal Emission rates and Activation Energies of Electrons at Tantalum Centers in Silicon," Solid-State Electron. 19, 471 (1976).

2. A. Neugroschel and C. T. Sah, "Concentration Profiles of Recombination Centers in Semiconductor Junction Evaluated from Capacitance Transients," IEEE Trans. Electron Devices 23, 1069-1074 (1976).

3. K. Y. Tsao and C. T. Sah, "Temperature Dependence of Resistivity and Hole Conductivity Mobility in P-type Silicon," Solid-State Electron. 20, 949-953 (1976).

PUBLICATIONS (SINCE JUNE 1, 1975)

K. Hess, G. Dorda and C. T. Sah, "The Current-Voltage Characteristics of Field-Effect Transistors with Short Channels," Solid State Commun. 19, 471 (1976).

H. Maes and C. T. Sah, "Application of the Equivalent Circuit Model for Semiconductors to the Study of Au-Doped p-n Junctions under Forward Bias," IEEE Trans. Electron Devices Ed-23, 1131-1143 (1976).

M. J. McNutt and C. T. Sah, "Determination of the MOS Oxide Capacitances," J. Appl. Phys. 46, 3090-3193 (1975).

M. J. McNutt and C. T. Sah, "Exact Capacitance of a Lossless MOS Capacitor," Solid-State Electron. 13, 225-257 (1976).

M. J. McNutt, C. T. Sah, R. Van Overstraeten, G. Declerck and P. Muls, "Comments on 'Effects of Spatially Inhomogeneous Oxide Charge Distribution on the Capacitance-voltage Characteristics,'" J. Appl. Phys. 46, 5057 (1975).

Kenji Miyata and C. T. Sah, "Thermal Emission Rates and Activation Energies of Electrons at Tantalum Centers in Silicon," Solid-State Electron. 19, 611-613 (1976).

Arnost Neugroschel and C. T. Sah, "Concentration Profiles of Recombination Centers in Semiconductor Junctions Evaluated from Capacitance Transients," IEEE Trans. Electron Devices Ed-23, 1069-1074 (1976).

T. H. Ning and C. T. Sah, "Photoionization Cross-Sections of a Two-Electron Donor Center in Silicon," Phys. Rev. B14, 2528-2533 (1976).

C. T. Sah, "Bulk and Interface Imperfections in Semiconductors," Solid-State Electron. 19, 975-990 (1976).

C. C. Shiue and C. T. Sah, "Studies of Electron Screening Effects on the Electron Mobility in Silicon Surface Inversion Layers," Surf. Sci. 58, 163-172 (1976).

K. Y. Tsao and C. T. Sah, "Temperature Dependence of Resistivity and Hole Conductivity Mobility in p-type Silicon," Solid-State Electron 20 (1976).

Theses

Ching Ho Chan, "Application of Equivalent Circuit Model to the Study of Properties of Gold in N-Silicon," M.S. Thesis (1975), C. T. Sah, adviser.

James William Holtkamp, "Differential Equation Solution of Metal-Oxide-Semiconductor Capacitance," M.S. Thesis (1975), C. T. Sah and M. J. McNutt, advisers.

Thomas Ying-Ching Lo, "Computer-Automated Electrical Characterization of Semiconductor Devices," PH.D. Thesis (1976), C. T. Sah, adviser.

Final Project Report
Liquid Crystals and Phase Transitions
W. McMillan

Technical Problem

This research was concentrated in two areas: liquid crystals and charge density waves.

In liquid crystals the technical problem is to gain a microscopic understanding of the liquid crystal phases and their phase transitions. The principal experimental method used is Rayleigh light scattering and a new optical method for measuring elastic constants. The principal theoretical tools have been microscopic mean field theory, phenomenological Landau theory, and renormalization group methods. We have perfected a new high precision optical method for measuring elastic constants and viscosity coefficients of liquid crystals in the nematic phase. We have used this method to study the critical behaviour near the smectic A to nematic phase transition in CBOOA (cyanobenzylidene-octyloxyaniline). These new results, together with our Rayleigh scattering measurements, show that all the proposed theories of the critical behaviour are incorrect. On the theoretical side we have completed a series of papers on the Landau theory approach on several phase transition problems.

General Methodology

In the study of charge density waves (CDW) in metals the thrust has been mainly theoretical, in collaboration with experimenters Fred Brown, Bob Craven, Miles Klein and the Bell Labs group. The overall objective is to construct a quantitative theory of CDWs in the transition metal dichalcogenides (2H-$TaSe_2$) and to test it by comparison with experiment. A Landau approach has been very useful in describing the phase transitions and the defects (CDW dislocations and discommensurations). We have recently shown that previous microscopic theories cannot describe CDWs in 2H-$TaSe_2$ and have reformulated the theory. We have calculated lattice dynamics in the distorted phase in order to interpret Klein's Raman data. In addition we have studied superlattice formation in 1T-$TiSe_2$ with x rays.

Technical Results

We measured the twist elastic constant K_{22} and the viscosity γ_1 of CBOOA near the smectic A-nematic transition T_{AN} using the standard Rayleigh scattering technique and with temperature control and homogeneity better than .001°C (at 83°C). Our results fit

$$K_{22}(T) = K_{22}^{\circ} + C/(T - T_{an})^{\nu}$$

with $\nu = 0.5$ with a similar expression for γ_1. This result contradicts deGennes analogy to liquid helium ($\nu = 2/3$) and Halperin et al.'s prediction of a first order transition.

We have developed a new experimental technique of forcing a small distortion on the liquid crystal using an external magnetic field and measuring the distortion using a sensitive optical interference technique. The method yields higher precision than Rayleigh scattering and is useful within $\sim$ .003°C of the phase transition. The standard Freedericksz method imposes large distortions and fails .1°C above the transition. Our results for the band elastic constant are similar to (1) with $\nu = .73$. This result contradicts mean field theory ($\nu = .5$). We have therefore shown that all the theories of the critical behaviour are wrong. These results also indicate that there is an essential anisotropy in the critical behaviour with the transverse and longitudinal correlation length having different exponents, a result suggested by my early x-ray study and by Litster's light scattering study in the smectic A phase. The experiments indicate that the theory will have to be reformulated keeping the anisotropy in mind.

The molecular theory of the smectic phases is essentially complete; a model of the smectic F phase will soon be published. The molecular model of the smectic C phase (orientational ordering due to dipole-dipole interactions) is still controversial. However, experiments in progress (Doane at Kent State and Blinc in Yugoslavia) should settle the question.

In a series of papers we have established the Landau theory approach to charge density waves in transition metal dichalcogenides and in A 15 compounds. This approach has been very useful and very successful. With the completion of the heat capacity (Cravens) and Raman (Klein) experiments in Urbana there is enough experimental data to test the proposed microscopic theories of CDWs. The proposed theories all fail to describe the data. The technical reason that the theories fail is that they assume a long correlation length in a BCS-like energy gap model. The theories simply neglect the phonon entropy. We have shown that for 2H-$TaSe_2$ the phonon entropy is dominant and have reformulated the theory accordingly. The next step is to include the correct band structure in the theory and to check it against the deHaas-van Alphen (Graebner) and deHaas-Shubnikov (Coleman) data. At least for the dichalcogenides the experiments seem to be pushing us rapidly toward a viable microscopic theory. A very fruitful collaboration with Miles Klein on the Raman experiments, Bob Craven on the heat capacity measurements and Fred Brown on the study of 1T-$TiSe_2$ has developed within the Materials Research Laboratory.

We have made a great deal of progress in understanding superfluidity in submonolayer He^4 films in the last year due to a collaboration with Jack Mochel. Mochel has very beautiful, high precision measurements of third sound velocity and attenuation from .1°K to 1°K. We have interpreted these measurements using a theoretical model which is a two-dimensional version of Landau's quantum hydrodynamics. The model predicts an elementary excitation spectrum which can be used to calculate the temperature dependence of third sound, thermal boundary resistance and critical velocity effects.

References

1. K. C. Chu and W. L. McMillan, Phys. Rev. A11, 1059 (1975).
2. P. G. deGennes, Solid State Commun. 10, 753 (1972).
3. B. I. Halperin, T. C. Lubensky, and S. K. Ma, Phys. Rev. Lett. 32, 292 (1974).
4. W. L. McMillan, Phys. Rev. A7, 1419 (1973).
5. F. Garcia-Golding and J. D. Litzter, VI Intl. Liquid Crystal Conf. (1976).
6. A. W. Overhauser, Phys. Rev. 167, 691 (1968).
7. S. K. Chan and V. Heine, J. Phys. F3, 795 (1973).
8. T. M. Rice and G. K. Scott, Phys. Rev. Lett. 35, 120 (1975).

PUBLICATIONS (SINCE JUNE 1, 1975)

Ravindra N. Bhatt and W. L. McMillan, "Theory of Phonon Dynamics Near a Charge Density Wave Instability," Phys. Rev. B12, 2042-2044 (1975).

K. C. Chu and W. L. McMillan, "Theory of Nonlinear Elastic Behavior of Nematic Liquid Crystals Near the Nematic-Smectic A Phase Transition," Phys. Rev. (Submitted)

K. C. Chu and W. L. McMillan, "Unified Landau Theory for the Nematic, Smectic A and Smectic C Phases of Liquid Crystal," Phys. Rev. (Accepted)

John A. Holy, Miles V. Klein, W. L. McMillan, and S. F. Meyer, "Raman-active Lattice Vibrations of the Commensurate Superlattice in 2H-TaSe$_2$," Phys. Rev. Lett. 37, 1145-1148 (1976).

W. L. McMillan, "Landau Theory of Charge Density Waves in Transition-Metal Dichalcogenides," Phys. Rev. B12, 1187-1196 (1975).

W. L. McMillan, "Time Dependent Landau Theory of Charge Density Waves in Transition Metal Dichalcogenides," Phys. Rev. B12, 1197-1199 (1975).

W. L. McMillan, "Theory of Discommensurations and the Commensurate-Incommensurate Charge Density Wave Phase Transition," Phys. Rev. B14, 1496-1502 (1976).

W. L. McMillan, "Time Dependent Unified Landau Theory for the Nematic, Smectic A and Smectic C Phases of Liquid Crystals," Phys. Rev. (Submitted)

R. J. Meyer, "Molecular Theory of the Smectic E, H, and VI Phases," Phys. Rev. A12, 1066-1075 (1975).

R. Jay Meyer, "Molecular Order in the Smectic E Phase," Phys. Rev. A13, 1613-1618 (1976).

R. Jay Meyer, "Lattice Distortions and Phase Transitions in Crystalline Methanes," Phys. Rev. B14, 4094-4099 (1976).

R. Jay Meyer, "Theory of Angular-Resolved Photoemission at Low Energy and High Atomic Number: 1T-TaS$_2$," Phys. Rev. B. (Submitted)

K. C. Woo, F. C. Brown, W. L. McMillan, R. J. Miller, M. J. Schaffman and M. P. Sears, "Superlattice Formation in Titanium Diselenide," Phys. Rev. B14, 3242-3247 (1976).

Theses

None

Final Project Report
Light Scattering from Non-Vibrational Modes in Solids
M. S. Klein

Technical Problem

The main objective of this work has been to study non-vibrational motions in disordered solids. Particular emphasis has been placed on two classes of system in which atoms or ions diffuse very rapidly: hydrogen in metals and fast-ion conductors. The technique used is Raman scattering, which has not been applied extensively to metals. A secondary objective of this work has been to broaden knowledge of Raman scattering in metals by applying the technique to study lattice vibrations in disordered metals and in metals that have electronically driven phase transitions.

General Methodology

Our general technique is laser-excited Raman scattering. Because of the great deal of disorder in the materials under investigation, much of the work requires a third monochromator to be added to the usual double monochromator to cause a further reduction in the parasitic elastically scattered laser light. Much of our effort on hydrogen in metals has involved the bcc metals niobium and tantalum, which oxidize readily, especially at the temperatures necessary to obtain high equilibrium hydrogen concentrations. Thus the experiments have been carried out in an ultra-high vacuum system. This has allowed the beginnings of a study of Raman scattering from a thin oxide layer on niobium and from adsorbed molecules on the oxide.

None of the samples studied in this work has been readily available, and a great deal of effort has been expended in sample preparation. The fast ion conductors studied, $RbAg_4I_5$ and $NH_4Ag_4I_5$, have been grown from aqueous solution in a joint effort involving members of three research groups: Salamon, Klein, and Lazarus. The niobium:hydrogen and tantalum:hydrogen work has been done in collaboration with Prof. H. Birnbaum, who has prepared the samples and has been closely involved in various treatments given the samples during the Raman measurements. The crystals for the TiC measurements were supplied by Prof. W. Williams, who has highly characterized them. The samples of 2H-$TaSe_2$ came from Dr. S. F. Meyer of Prof. C. Slichter's group. Transport and specific heat measurements on them were made by Dr. R. Craven of IBM, formerly a member of Dr. Salamon's group. The samples of 1T-$TiSe_2$ were prepared by K. C. Woo of Dr. F. Brown's group. The Raman and infrared work on TCNQ was performed on samples prepared by Prof. G. DePasquali.

Technical Results

(a) Pre-resonance Raman spectra have been obtained by Professor Klein working with Dr. Wozniak and Professor DePasquali for TCNQ and LiTCNQ in acetonitrile solution using an Ar^+ - Kr^+ laser and a tunable rhodamine 6G dye laser.[1] The theory of Albrecht and Hutley has been used to calculate frequency factors for the intensity variations for several symmetric vibrational modes of each molecule. The observed spectra for TCNQ and LiTCNQ with violet, blue, and green excitation give evidence of resonance enhancement due to vibronic mixing between at least two violet and ultraviolet transitions. The Raman spectra for LiTCNQ with yellow, orange, and red excitation show enhancement due to a single electronic excitation in the near infrared.

(b) Professor M. Klein has developed a theory of light scattering from the relaxation modes of rapidly diffusing atoms or ions using the independent particle approximation.[2]

Professor Klein and D. Gallagher have obtained Raman data on the superionic conductor Ag_4RbI_5 at temperatures of 136 K to 448 K.[3] At 209 K there is a second order phase transition from a highly ionic conducting phase to one with less conductivity. The Raman spectrum shows no abrupt changes at the transition. At high temperatures there are two main features--a symmetric peak centered at 105 cm^{-1}, and a shoulder on the Rayleigh line at about 23 cm^{-1}. As the temperature is lowered, the shoulder resolves itself into three peaks. Polarized Raman spectra cannot be taken below the transition at 209 K because the crystal becomes a random superposition of uniaxial ferroelastic domains.

The Ag ions are surrounded by a distorted tetrahedral cage of I ions. A similar local geometry is found in $\beta - Ag_2HgI_4$[4] and in phase IV of AgI.[5] The Raman spectrum of these materials shows a peak at 20 - 30 cm^{-1} and one at about 110 cm^{-1}. Tentative explanations of the spectra in all materials are the same--the 100 cm^{-1} peak is a "breathing" mode of the I-tetrahedra, and the 20 - 30 cm^{-1} mode is the "attempt frequency" of the silver ion oscillating in its potential well. This is presumably the same attempt vibration involved in the diffusive jumping of the Ag ions from site to site. The 100 cm^{-1} breathing mode is presumably the polaron mode responsible for dressing the Ag ion's motion. Thus the two Raman features may directly relate to two processes that are very important to an understanding of the microscopic dynamics of this superionic conductor.

(c) Raman spectra have been obtained by Professor Klein, Mr. Holy, and Professor Williams on samples of TiC containing various concentrations of carbon vacancies. The vacancies "induce" Raman scattering that would otherwise not be allowed. The first-order impurity-induced spectra show broad peaks at 285 and 410 cm^{-1} in the acoustical phonon region, a gap, and peaks at 570 and 680 cm^{-1}. Some of the details of the spectra depend on the vacancy concentration; the general features do not. These data reveal new information about interatomic forces and bonding in these materials. For instance, the data suggest strongly that the first shell of C atoms around a C vacancy (next-nearest neighbors) have their electronic polarizability more strongly affected by the vacancy than do the first nearest neighbor Ti atoms.

(d) Raman spectra have been obtained by Professor Klein and Mr. Holy on 1T and 2H polytypes of TaS_2 obtained from Dr. S. Meyer of Professor Slichter's group. This material is a nearly 2-dimensional layered compound with very weak bonding between layers. In the 1T polytype, two Raman modes have been seen, as predicted by symmetry arguments. Two weaker "forbidden" modes are also observed. These may be caused by a distortion of symmetry breaking associated with a charge density wave known to be present in 1T-TaS_2 at room temperature. In 2H-TaS_2 four Raman are observed; the lowest one at 24 cm^{-1} is a direct measure of the interlayer force constants.

Polarized Raman spectra have been obtained on 2H-$TaSe_2$ at temperatures from 300 K to 27 K, below the transition to a commensurate charge-density wave and superlattice.[6] At room temperature all the allowed Raman modes of the 2H structure are seen along with a very strong, broad band at 148 cm^{-1} that is assigned to a combination of two LA phonons having wave vectors on the line Σ from about 0.40 to 1.00 q_M. The dispersion curve for this branch shows softening and a Kohn anomaly.[7]

Diffraction studies on 2H-$TaSe_2$[7,8] show a transition from a normal lattice to one with an incommensurate charge density wave (CDW) at 122 K followed at 90 K by a transition to a commensurate state. These studies strongly suggest, but do not prove, the coherent superposition of three CDW's. Neutron diffraction studies give the static displacements in the distorted state, but they are relatively insensitive to the absolute phase angle. At low temperatures six new low frequency Raman modes are seen. These are interpreted as new zone center optical phonons that result from folding in the anomalous LA mode at $2/3q_M$. Their number and Raman symmetries are consistent only with an inversion-symmetric, 3CDW state. The Raman data have removed the ambiguities remaining from the diffraction studies and allowed a determination of the space group of the commensurate CDW state. W. L. McMillan has produced a microscopic model of the lattice dynamics of this state.[6] The parameters in this model are fitted to the frequencies of the four strongest new Raman lines, which are assigned to amplitude and phase modes of the charge density wave.

Raman studies have been performed on 1T-$TiSe_2$ by J. A. Holy and Prof. M. Klein in collaboration with K. C. Woo and Prof. F. Brown. Below the transition to a CDW state new Raman-active and infrared-active phonon modes are seen. This is a more complicated system than 2H-$TaSe_2$ because the new modes are derived from the folding of more than one phonon branch. Detailed understanding may require more far infrared measurements and the results of inelastic neutron measurements.

(e) Attempts extending over a two-year period to see Raman scattering from the vibrations of hydrogen and deuterium in niobium and tantalum have not been successful. Raman scattering was seen from pure Ta in the form of a nice two-phonon density of states. This altered somewhat upon hydrogenation, but no high frequency hydrogen modes appeared. In the case of tantalum this negative result has a positive significance: the vibrations of the hydrogen atoms do not appreciably couple to the optical susceptibility at the laser photon energy, 2.4 eV. This implies that the hydrogen does not introduce an electronic level within 2.5 eV of the Fermi level that can be reached from the Fermi level via electric dipole transitions. There was some oxide contamination during the experiment on hydrogen in niobium and no two-phonon spectrum was seen, thus the negative result on that system is not as significant as it is for tantalum.

The Raman work on niobium showed one broad peak at 640 cm^- that is probably due to an oxide layer. To better understand this peak the oxidation of clean Nb surfaces at very low partial pressure of O_2 was studied. At 200°C an amorphous NbO layer initially forms giving a very broad Raman peak. As the oxide film thickens the NbO crystallizes and the broad peak develops into several sharp Raman peaks characteristic of NbO. Continued exposure results in the growth of an amorphous layer of Nb_2O_5 on top of the NbO, and this results in a broad Raman peak. The Nb_2O_5 develops into a crystalline form as it thickens, and sharp Raman lines characteristic of Nb_2O_5 are then observed.

Higher frequency Raman peaks were also observed at 1350 and 1600 cm^{-1} on Nb samples held in a high vacuum system. They were not due to intentional additions of hydrogen. Their positions coincide exactly with some infrared lines observed with deposited Al and Cu films exposed to formic acid vapors.[9] The adsorbed ions were thought to be HCO_2^-. The niobium samples were electropolished in lactic acid before being placed in the vacuum system, and lactic acid contains HCO_2 units. If such units are responsible for the Raman lines, they are probably formed on an oxide layer rather than on the niobium itself.

Implications for Further Research

There are several immediate implications of the above results that are affecting the continuation of this work. The Raman work on the fast ion conductor $RbAg_4I_5$ is currently being extended to $NH_4Ag_4I_5$, which has the same properties of ionic conduction and low frequency vibrational modes but has in addition the internal vibrational modes of the ammonium ion that will be affected by the static and dynamical disorder.

Theoretical work has been started and additional experiments are planned to explain why the charge-density-waves in compounds such as $TaSe_2$ produce such strong new Raman-active modes in the low temperature phases.

Attempts to observe Raman scattering from hydrogen in metals are being extended to fcc metals. A positive result has recently been observed in Pd:H. Additional feasability studies are planned to determine if Raman scattering can be used to study chemisorbed species and thin oxide layers on metal surfaces under controlled conditions.

References

1. W. T. Wozniak, G. DePasquali, and M. V. Klein, Chem. Phys. Lett. 40, 93 (1976).
2. M. V. Klein in Light Scattering in Solids, eds. M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p 351.
3. D. Gallagher and M. V. Klein, J. Phys. C (Solid State) (Accepted).
4. D. F. Shriver, G. Joy, and D. Greig, J. Electrochem. Soc. 123 , 588 (1976).
5. R. C. Hanson, T. A. Fjeldly, and H. D. Hochheimer, Phys. Status Solidi B 70, 567 (1975).
6. J. A. Holy, M. V. Klein, W. L. McMillan, and S. F. Meyer, Phys. Rev. Lett. 37, 1145 (1976).
7. D. E. Moncton, J. F. Axe, and F. J. DiSalvo, Phys. Rev. Lett. 34, 734 (1975).
8. J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).
9. Ito and Suetaka, J. Phys. Chem. 79, 1190 (1975).

PUBLICATIONS (SINCE JUNE 1, 1975)

John A. Holy, Miles V. Klein, W. L. McMillan, and S. F. Meyer, "Raman-Active Lattice Vibrations of the Commensurate Superlattice in 2H-$TaSe_2$," Phys. Rev. Lett. 37, 1145-1148 (1976).

Kanti Jain and M. V. Klein, "Valley-Orbit Raman Scattering from Bound and Delocatlized Electrons in n-Si," Proc. 3rd Int. Conf. on Light Scattering in Solids, Campinas, SP, Brazil, 1975. In Light Scattering in Solids, eds. M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), pp. 298-307.

K. Jain, S. Lai, and Miles V. Klein, "Electronic Raman Scattering and the Metal-Insulator Transition in Doped Silicon," Phys. Rev. B13, 5448-5464 (1976).

M. V. Klein, "Electronic Raman Scattering," Proc. First USA-USSR Seminar-Symposium on Theory of Light Scattering in Condensed Matter, Moscow, 1975. In The Theory of Light Scattering in Solids, eds. V. M. Agvanovich and J. L. Birman (Nauka Publ. House, Moscow, 1976), Vol. II, pp. 558-573.

Miles V. Klein, "Light Scattering from Relaxation Modes of Rapidly Diffusing Atoms or Ions," *Proc. 3rd Int. Conf.* on Light Scattering in Solids, Brazil, 1975. In Light Scattering in Solids, eds. M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), pp. 351-355.

Wayne T. Wozniak, G. DePasquali, and Miles V. Klein, "Pre-Resonance Raman Intensity Studies of TCNQ and $TCNQ^-$," Chem. Phys. Lett. 40, 93-97 (1976).

W. T. Wozniak, G. DePasquali, M. Klein, R. Sweany, and T. Brown, "Vibrational Spectra of TTF-TCNQ: Evidence for TTF° and TCNQ° in Thin Films," Chem. Phys. Lett. 33, 33-36 (1975).

Jim E. Clemans, "The Thermal Condctivity of Solid Neon," Proc. 14th Int. Conf. on Thermal Conductivity, University of Connecticut, Storrs, Conn. (1975).

David Gallagher and Miles V. Klein, "Polarized Raman Scattering in the Solid Electrolyte $RbAg_4I_5$," J. Phys. C (Accepted).

Theses

Kantilal Jain, "Electronic Raman Scattering from Doped Silicon," Ph.D. Thesis (1975), M. V. Klein, adviser.

Final Project Report

High Pressure Nuclear Magnetic Resonance and Raman Study of
the Dynamic Structure of Liquids, Disordered Solids and Polymers

J. Jonas

Technical Problem

The goal of this research was to improve our understanding of the dynamic structure of liquids, disordered solids and polymers by studying motion and interactions at a molecular level. Simple polyatomic molecular liquids and water were of main interest. In this research summary we emphasize in particular the work and results on dense liquids composed of molecules approaching spherical shape because these studies enabled us to draw a number of conclusions of general validity about the dynamic structure of these liquids. In a sense our experiments on disordered organic solids and polymers must be still regarded as exploratory and in fact represent an initial successful stage of our systematic effort in this specific direction.

General Methodology

In order to obtain detailed information about molecular motions in liquids and provide meaningful experimental tests for current theories of liquids one has to separate the effects of temperature and density, i.e., one has to use both temperature and pressure as experimental variables. It is not surprising to find that the volume changes often play a dominant role in affecting molecular motions in dense liquids because of the close packing of the molecules. The capability of carrying the NMR and Raman experiments at high pressure over a wide range of temperatures represents an important and unique feature of our experiments.

Nuclear magnetic resonance relaxation experiments provide detailed information about reorientational motions, angular momentum correlation times and self-diffusion coefficients. Since the NMR experiments yield the zero Fourier transform of the correlation functions for the appropriate motions, we started using laser Raman scattering experiments to obtain detailed time dependence of the correlation functions. The question of applicability of various hydrodynamic equations on a molecular level was of interest and therefore shear viscosities were also measured as a function of temperature and pressure.

Technical Results

The results of our studies provided direct experimental evidence on the validity of the idea that the dynamic structure of a dense liquid is dominated by the harsh repulsive intermolecular forces and that the slowly varying attractive forces can be neglected. The experimental data were analyzed in terms of the rough hard sphere model of liquids based on the modified Enskog theory. A rough hard sphere model of a liquid is a model for spherical particles for which interparticle binary collisions occur instantaneously and are capable of changing angular as well as linear momentum of a particle. In addition, the rotational and translational motions are coupled. Our experiments established that the rough hard sphere model provides good description of the dynamics in dense liquids. The results provided experimental verification of the molecular dynamics calculations for hard spheres as reported by Alder et al. From the experimental relaxation, diffusion and viscosity data we obtained effective hard sphere diameters and their temperature dependence for a variety of molecular liquids (e.g., benzene, tetramethylsilane, sulfur hexafluoride, etc.). One specific result worth emphasizing was the experimental finding that the time dependence of the angular momentum correlation function can be approximated as a series of uncorrelated binary collisions. In contrast our results showed the importance of many body correlation effects on diffusion and shear viscosity in agreement with the results of the molecular dynamics calculations. We showed the limitations of the hard sphere model at high packing where predictions from this simple model strongly deviated from experimental data for all molecular liquids studied. The hydrodynamic Stokes-Einstein equation was found valid in the slipping boundary condition for the liquids investigated.

The experiments on liquid water and heavy water showed that compression leads to significant distortion of the hydrogen bond network with the important result that the dynamic behavior of water under high compression resembles that of normal molecular liquid of comparable molecular size. At high densities, the hard core repulsive interactions begin to dominate over the directional interactions which are mainly responsible for the open structure of liquid water at low temperatures and pressures.

The results of two studies were published in the area of disordered organic solids and elastomers. The self-diffusion study of the disordered fcc crystalline phase of neopentane indicated that self-diffusion proceeds via a relaxed vacancy mechanism. The pressure effects on the glass transition were of main interest in the NMR study of several elastomers including natural rubber.

For clarity's sake, the detailed discussion of technical results is divided into three sections. The first section deals with the experimental and theoretical results obtained in our studies of dense liquids composed of molecules approaching spherical shape. This part of our discussion can be regarded as a final report on this specific class of liquids because we arrived at a number of conclusions of general validity and further progress in this area must come from development of better theoretical models. The second section is devoted to hydrogen bonded water and heavy water which exhibit many anomalous properties when compared to normal atomic and/or molecular liquids. The third section summarizes the results on disordered solids and polymers and serves mainly as an illustration of future directions of our studies

i) Molecular Liquids

The NMR spin-lattice relaxation times, self-diffusion coefficients, shear viscosities and PVT data have been measured in a variety of simple polyatomic molecular liquids over a wide range of temperatures and pressures. The dense liquids[1-6] such as benzene, pyridine, tetramethylsilane, neopentane, perfluorocyclobutane, sulfur hexafluoride, carbon tetrafluoride, etc., are composed of molecules close to a spherical shape. The analysis of the NMR relaxation data and transport data was based on molecular dynamics calculations of transport coefficients for a hard sphere fluid as performed by Alder et al.[7] and on the rough hard sphere model of a liquid as proposed by Chandler.[8] These models are based on the Enskog theory[9] and the ideal that in dense liquid the molecules are so closely packed that the dynamic structure is dominated by the intermolecular repulsive forces depending on the shape of the molecules. As far as our results are concerned the predictions of the rough hard sphere model agree well with the experimental data. Our data confirm the molecular dynamics calculations[7] for diffusion and shear viscosity of a hard sphere fluid and clearly show that many body correlations affect in a major way the self-diffusion coefficients and cause deviations from predictions based on the simple Enskog theory. At intermediate densities the self-diffusion coefficient of a liquid is enhanced due to long persistence of velocity currents (vortex effect), whereas at high densities the self-diffusion coefficient is much lower than the Enskog self-diffusion coefficient. This effect can be ascribed to backscattering caused by the high probability of reversal of velocity of a particle upon collision with its nearest neighbor in dense systems. The experimental data enabled us to calculate the effective hard sphere diameters for the various liquids studied and also obtain their temperature dependence. For all liquids we found that at high packing the predictions based on hard sphere model deviate significantly from the observed values of self-diffusion coefficient and shear viscosities.[3-4]

There are several possible reasons for the interesting behavior of the self-diffusion coefficients at high densities. First, there is a distinct possibility that the extrapolated values from the molecular dynamics calculations may be in serious error at high densities. Secondly, the effective hard-core diameters can become a function of density at the high packing fractions. This possible dependence of σ upon density may have its origin in the following. One has to realize that the rough-hard sphere model is still a qualitative model, and that the real liquids we deal with in this study could perhaps be represented as the soft sphere liquid. A softness of the potential may have a significant effect on the self-diffusion coefficients because the relationship between the hard spheres and the soft spheres is not well understood for the transport processes.[10]

In contrast to the behavior of the self-diffusion coefficient and shear viscosity no correlation effects were observed for the angular momentum correlation times.[2,5,6,11] The angular momentum correlation time, τ_J, reflects the time for a molecule to lose memory of its initial angular momentum and as such it may be expected to be closely related to the molecular collision frequency. These correlation times were obtained from NMR measurements for liquid systems where spin-rotation interactions dominate the relaxation mechanism. For all liquids studied (SF_6, C_4F_8, CF_4, $CFCL_3$ C_6D_5F) we found that the experimental data can be analyzed in terms of the rough hard sphere theory assuming that the process determining the time dependence of the angular momentum correlation function can be approximated as a series of uncorrelated binary collisions. It is satisfying to note that the hard sphere diameters obtained from the analysis of spin-rotation relaxation data agree well with those obtained from diffusion and viscosity experiments. One should emphasize that in our studies we provided a direct experimental evidence that the effective hard sphere diameter is temperature dependent. This, of course, makes physical sense because the repulsive part of the intermolecular potential in a real fluid has a finite slope and molecules with higher kinetic energy come closer to each other during a harsh collision and thus exhibit a smaller hard sphere diameter.

Since our experiments provided self-diffusion coefficients and shear viscosities of various liquids over a wide range of temperatures and densities it was possible to test the validity of the hydrodynamic Stokes-Einstein equation on a molecular scale.[4,6] This relation states that the product of the diffusion coefficient and the viscosity is a constant related to the diameter of the spherical particle moving through a fluid. The many body correlations which led to a decrease of diffusion below the Enskog theory are compensated for by correlations which enhance viscosity by nearly that much. Over a wide range in volume and temperature the Stokes-Einstein equation is remarkably precise and shows that the slipping boundary condition is satisfied well for most of the molecular liquids studied. It is interesting to note that this is true in spite of the fact that the velocity autocorrelation function is not exponential as required by the application of the Stokes theory.

ii) Water and Heavy Water

It is well known that water exhibits anomalous behavior[12] with pressure when compared with normal atomic or molecular liquids. All the anomalies and the consequent "strange" behavior of water under compression have their origin in the open tetrahedral structure of water at lower temperatures due to a well developed hydrogen bond network. We measured[13-15] the proton and deuteron spin-lattice relaxation times, self-diffusion coefficients, shear viscosity of water and heavy water over a wide range of pressures and temperatures. Thanks to the capability of performing our experiments under high pressure we were able to take advantage of the phase diagram of water and heavy water and carry out experiments[15] on liquid water at temperatures below 0°C down to -15°C. In this region the extremes of our measurement were ice I and a high pressure ice V.

Analysis of our experimental NMR relaxation, diffusion and viscosity data lead to several important conclusions about the motional behavior of water molecules in compressed liquid water and heavy water. First, the initial increase in density at low temperatures produces a faster motion of the water molecules. This is easily understood in terms of a simple physical picture. Since reorientation and diffusion of water molecules must proceed via breaking and reforming of hydrogen bonds, one can readily see that high compression which changes the optimal tetrahedral hydrogen bond network will facilitate such dynamic processes. Only at higher densities or higher temperatures further compression will hinder molecular motions due to increased packing and stronger short-ranged repulsive interactions. Under these conditions the behavior is already analogous to that found for normal atomic and molecular liquids where compression slows down the motional processes. Second, compression results in a decreased coupling between the rotational and translational motions as reflected in the relationship between the reorientational correlation time of water molecules and shear viscosity. Therefore, the Debye equation fails to describe the effect of density on the reorientation of water molecules. Third, we find that the activation energies for relaxation, diffusion and shear viscosity decrease with increasing density. Fourth, at high temperatures and high compression the dynamic structure of water resembles that of a hard sphere system. From these findings we conclude that compression of water produces major changes in the random hydrogen bond network with the result that water begins to behave more as a normal liquid under high compression. All our experimental results are in agreement with recent molecular dynamics calculations on water by Stillinger and Rahman.[16]

iii) Disordered Solids and Polymers

Due to its spherical shape neopentane ($C(CH_3)_4$) represents an excellent example of a molecule exhibiting a high temperature disordered solid phase, a so-called plastic phase. The dominant feature of this fcc lattice is the large degree of reorientational freedom but there is also evidence suggesting a substantial amount of translational freedom. The NMR proton spin-lattice relaxation times have been measured in the disordered crystalline phase of neopentane[17] as a function of temperature and pressure. The molecular reorientation and self-diffusion contributions to observed relaxation time were separated and the activation parameters were calculated for these two processes. In contrast to weak pressure dependence of the overall molecular reorientation, the self-diffusion exhibited a strong pressure dependence. The activation volume for self-diffusion was found to be close to the molecular volume of neopentane. Based on analogy with close-packed metals this finding indicates that self-diffusion in the plastic phase of neopentane proceeds via vacancy mechanism.

The work dealing with the high pressure NMR study of molecular motions and glass transition in several elastomers[18] can be regarded as a successful, preliminary study for future experiments related to glass transition in amorphous polymers. The NMR proton spin-lattice relaxation times, T_1, have been measured in natural rubber, synthetic cis-1,4-polyisoprene, cis-1,4-polybutadiene and natural rubber gum stock over a range of pressures from 1 bar to 3 kbar at temperatures from -10° to 100°C at 24.2 and 56.4 MHz. Using the concept of the most probable correlation times for the motion of main chain segments the activation enthalpy and activation volume were calculated from the temperature and pressure dependencies of the T_1 minimum. The finding that $\Delta V^{\ddagger}$ increases with increasing temperature, and the relative role of thermal and volume effects on relaxation were briefly discussed. The observed pressure dependence of the glass transition temperature for these elastomers indicated that configurational entropy rather than volume plays an important role in determining the glass transition.

As it is clear from the above discussion, our NMR relaxation experiments were performed under conditions of extreme pressure and temperature.

Changes in those conditions produce subsequent changes of electrical parameters in the NMR sample probe, which in turn lead to variations of effective radio-frequency field and its phase. Thus, frequent reoptimization of rf pulse lengths and phases are always necessary. Therefore we decided to develop a computer-directed automated system[19] for the measurement of the NMR spin-lattice relaxation times. This system automatically generates and optimizes the pulse sequences and carries out the measurement of spin-lattice relaxation times automatically. We found three major advantages of this system: i) substantially improved precision; ii) reduction of measurement time; iii) more accurate optimization of pulse lengths and phases than for manual operation. Further work is in progress on an automated system for NMR relaxation experiments in the rotating coordinate frame.

References

1. J. Jonas, Annu. Rev. Phys. Chem. 26, 167 (1975).
2. J. DeZwaan and J. Jonas, J. Chem. Phys. 62, 4036 (1975).
3. H. G. Parkhurst, Jr. and J. Jonas, J. Chem. Phys. 63, 2705 (1975).
4. H. G. Parkhurst, Jr. and J. Jonas, J. Chem. Phys. 63, 2698 (1975).
5. J. DeZwaan and J. Jonas, J. Chem. Phys. 63, 4606 (1975).
6. R. J. Finney, M. Wolfe, and J. Jonas, J. Chem. Phys. 66, 0000 (1977).
7. B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).
8. D. Chandler, J. Chem. Phys. 60, 3500 and 3508 (1974).
9. S. Chapman and T. G. Cowling, Mathematical Theory of Non-Uniform Gases (Cambridge U. P., Cambridge, England, 1970), 3rd Ed.
10. P. Protopapas, H. C. Anderson, and N. A. D. Parlee, J. Chem. Phys. 59, 15 (1973).
11. J. DeZwaan, R. J. Finney, and J. Jonas, J. Chem. Phys. 60, 3223 (1974).

12. D. S. Eisenberg and W. Kauzman, The Structure and Properties of Water (Oxford U. P., New York, 1969).

13. J. Jonas, T. DeFries, and D. J. Wilbur, J. Chem. Phys. 65, 582 (1976).

14. D. J. Wilbur, T. DeFries and J. Jonas, J. Chem. Phys. 65, 1783 (1976).

15. T. DeFries and J. Jonas, J. Chem. Phys. (In press).

16. F. H. Stillinger and A. Rahman, J. Chem. Phys. 61, 4973 (1974).

17. W. C. Allen, N. I. Liu, and J. Jonas, J. Chem. Phys. 63, 3317 (1975).

18. N. I. Liu and J. Jonas. J. Magn. Resonance 18, 465 (1975).

19. D. M. Cantor and J. Jonas, Anal. Chem. 48, 1904 (1976).

PUBLICATIONS (SINCE JUNE 1, 1975)

W. C. Allen, N. Liu, and J. Jonas, "NMR Study of the Pressure Effects on the Molecular Dynamics in the Disordered, Crystalline Phase of Neopentane," J. Chem. Phys. 63, 3317-33240 (1975).

D. M. Cantor and J. Jonas, "Automated Measurement of Spin-Lattice Relaxation Times: Optimized Pulsed Nuclear Magnetic Resonance Spectrometry," Anal. Chem. 48, 1904-1909 (1976).

J. Jonas, "Nuclear Magnetic Resonance at High Pressure," Annu. Rev. Phys. Chem. 26, 167-190 (1975).

J. Jonas, T. DeFries, and D. J. Wilbur, "Molecular Motions in Compressed Liquid Water," J. Chem. Phys. 65, 582-588 (1976).

H. J. Parkhurst, Jr. and J. Jonas, "Dense Liquids. I. The Effect of Density and Temperature on Self-Diffusion of Tetramethylsilane and Benzene-d_8," J. Chem. Phys. 63, 2698-2704 (1975).

H. J. Parkhurst, Jr. and J. Jonas, "Dense Liquids. II. The Effect of Density and Temperature on Viscosity of Tetramethylsilane and Benzene," J. Chem. Phys. 63, 2705-2709 (1975).

D. J. Wilbur, T. DeFries, and J. Jonas, "Self-Diffusion in Compressed Liquid Heavy Water," J. Chem. Phys. 65, 1783-1786 (1976).

D. J. Wilbur and J. Jonas, "Fourier Transform NMR in Liquids at High Pressure. III. Spin-Lattice Relaxation in Toluene-d_8, J. Chem. Phys. 62, 2800-2807 (1975).

Final Project Report
Structure of Liquids
W. H. Flygare

Technical Problem

The purpose of this research is to examine the dynamics and static structure of liquids including liquid crystal systems above the liquid crystal phase transition temperature. We are primarily interested in the intermolecular forces which are important in determining the orientational structure in liquids. However, we have also examined the behavior of a binary system with respect to hard core repulsive forces and their role in dynamic properties such as mutual diffusion.

General Methodology

The general experimental technique is light scattering. Starting with a monochromatic optical source (Ar^+ ion laser), both the intensity and spectrum of the scattered light are examined to gain information about the static and dynamic features of scattering medium. The above data is interpreted by using a correlation function theory for the scattering medium. The experimental correlation function, which is the Fourier transform of the scattered light spectrum, is written (according to the ergodic hypothesis) as a function of the space-time-orientation correlation function of the particles in the scattering medium. A model of the scattering medium then allows a comparison with the experimental data. By carefully studying the correlation function as a function of temperature and density (in a high pressure bomb) we are able to infer the nature of the close range forces causing both the static and dynamic features of the liquid structure.

Technical Results

Building on our earlier work on p-methoxybenzlidene-n-butylaniline (MBBA)[1] which concluded that orientational pair correlations (OPC) were determined by the size and shape of the molecule, we examined several chemical analogs of MBBA which changed considerably the electric dipole moments in these molecules.[2] The OPC were analyzed as a function of density and temperature as a function of size, shape, and moment of the molecules. We found that the molecular size and shape (repulsive) largely determined the OPC in these liquid crystal forming molecules.

At this time we initiated a study of intermolecular forces in the system of substituted benzenes where the size and shape remained relatively constant with substitution, but the electrical moments changed markedly. Before this, however, three important studies were necessary in interpreting accurately the OPC data in these systems. These studies included the first quantitative attempt to understand on an experimental and theoretical basis the nature of the "local field" at the scattering molecule,[3] a careful study of mutual diffusion in binary systems, which showed for the first time that hard core diameters could be transferred from one binary system to another,[4] and finally a careful study of the polarizability anisotropies and their dispersions was also completed.[5] These above studies were a prelude to the main study of orientational pair correlations in systems of equal size and shape with different electric dipole moments.[6]

The nature of the intermolecular forces which are important in determining the magnitude of orientational pair correlations (OPC) in liquids was studied by combining high pressure and depolarized Rayleigh light scattering techniques. For molecules of similar shape (toluene, bromobenzene, and nitrobenzene) we find that the magnitude of the OPC as measured by depolarized light scattering is not simply a function of the packing of the molecules. For sixteen monosubstituted derivatives of benzene of similar size and shape, we find that the magnitude of the OPC correlates well with the square of the molecular dipole moment. This correlation of OPC with dipole moment is understood by relating both the molecular dipole moment and the magnitude of the OPC to the detailed distribution of molecular electronic charge. The light scattering reorientational relaxation times for toluene, bromobenzene, and nitrobenzene as a function of pressure have also been measured and found to be linear functions of viscosity.

References

1. T. D. Gierke and W. H. Flygare, J. Chem. Phys. 61, 2231 (1974).
2. G. R. Alms, T. D. Gierke, and W. H. Flygare, J. Chem. Phys. 61, 4083 (1974).
3. A. K. Burnham, G. R. Alms, and W. H. Flygare, J. Chem. Phys. 62, 3289 (1975).
4. S. J. Bertucci and W. H. Flygare, J. Chem. Phys. 63, 1 (1975).
5. G. R. Alms, A. K. Burnham, and W. H. Flygare, J. Chem. Phys. 63, 3321 (1975).
6. S. J. Bertucci, A. K. Burnham, G. R. Alms, and W. H. Flygare, J. Chem. Phys. 00, 0000 (1977).

Implications for Further Research

The most obvious implication for future research would be to try and determine the effects of an orientating electric field on the orientational pair correlations in liquids composed of molecules with large dipole moments. These studies may have some bearing on the nature of molecular pyroelectric materials such as polyvinylidene difluoride. Can molecular polarization be frozen into an amorphous material by fast cooling in an electric field?

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G. R. Alms, A. K. Burnham, and W. H. Flygare, "Measurement of the Dispersion in Polarizability Anisotropies," J. Chem. Phys. 63, 3321-3327 (1975).

S. J. Bertucci, A. K. Burnham, G. R. Alms, and W. H. Flygare, "Light Scattering Studies of Orientational Pair Correlations in Liquids Composed of Anisometric Molecules," J. Chem. Phys. 00, 0000 (1977).

S. J. Bertucci and W. H. Flygare, "Rough Hard Sphere Treatment of Mutual Diffusion in Binary Liquid Mixtures," J. Chem. Phys. 63, 1-10 (1975).

W. H. Flygare, "Light Scattering," in Encyclopedia of Physics, ed. R. G. Lerner and G. L. Trigg (Dowden, Hutchison, and Ross, Inc., Shoudsburg, Pennsylvania, 1977).

W. H. Flygare, "Light Scattering in Pure Liquids and Solutions," Chem. Soc. Rev. 00, 0000 (1977).

W. H. Flygare, S. L. Hartford, and B. R. Ware, "Electrophoretic Light Scattering," in Molecular Electro-Optics, ed. C. T. O'Konski (Marcel-Dekker, Inc., 1976).

Theses

Tilak Raj, "Applications of Laser Light Scattering Spectroscopy to Biopolymers," Ph.D. Thesis (1976), W. H. Flygare, adviser. First job: Postdoc, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

Sidney J. Bertucci, "Light Scattering Studies of Orientational Pair Correlations in Pure Liquids and Mutual Diffusion in Binary Solutions," Ph.D. Thesis (1976), W. H. Flygare, adviser. First job: Central Research, Eastman Kodak Co., Rochester, NY 14614.

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The quaternary semiconductor $In_{1-x}Ga_xP_{1-z}As_z$ has been exploited to construct light emitting and laster diodes with selective emission from the yellow of the visible spectrum to the infrared.

The properties of deep traps which affect the performance of silicon devices has been characterized.

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