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TECHNICAL PROGRESS REPORT
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ABSTRACT

The vibrational and electronic properties of amorphous and crystalline solids and in some cases their gaseous and liquid counterparts have been studied using Raman spectroscopy, infrared spectroscopy, optical mixing, and high pressure uniaxial stress techniques.

1. Inelastic Light Scattering From Amorphous and Crystalline Solids with $2\mu\text{m}$ Excitation

A. Mott Transition in Ge(As)--We have shown that the semiconductor to metal transition in Ge(As) is gradual and that semiconductor-like and metallic-like regimes coexist near the critical arsenic concentration.¹ Thus our results are in agreement with the model of Cohen and Jortner² and in disagreement with the model of Mott.³

The temperature dependence and polarization properties of the single particle spectrum of Ge(As) have been studied and explained theoretically.⁴ Several electronic Raman lines in the spectrum of Ge(Ga) have been resolved and observed to broaden significantly with increased gallium concentration.⁴

B. Uniaxial Stress Apparatus--A low temperature uniaxial stress apparatus has been constructed and successfully tested.⁵ With this apparatus we have achieved the highest uniaxial stress, 23 kBar, yet obtained along the [110] axis of germanium. Preliminary measurements have been made of the stress dependence of the electronic valley-orbit Raman transition. We have verified the theoretical piezo-Raman selection rules and demonstrated that the electronic eigenstates can easily be tuned through the optical phonon energy of Ge.

C. Brillouin Scattering--Construction work has been completed on a Brillouin scattering laboratory physically contiguous to our Raman scattering laboratory and comprising a sample preparation area and a light tight measurement room. A scanning Fabret-Perot interferometer specially fitted with mirrors designed for $2\mu\text{m}$ spectroscopy has been received and is being installed. This interferometer in conjunction with an ABC-YAG laser⁶ comprises the basic units of a system designed for transmission Brillouin spectroscopy in the near IR.

II. Inelastic Light Scattering From Amorphous and Crystalline Solids with Visible Excitation

A. Photostructural Changes in Amorphous As_2S_3 Films--By carefully studying the polarized Raman spectra of As_4S_6 vapor and As_4S_4 molecular crystals we have established that the photostructural mechanism in amorphous As_2S_3 films involves photon induced crosslinking of As_4S_6 molecular units.⁷ Our results are in basic agreement with the x-ray work of De Neufville *et al.*,⁸ but unlike the x-ray analysis provide definitive evidence of the type of molecular restructuring that one obtains when As_2S_3 films are exposed to radiation.

B. The As_2O_3 System--Raman and infrared spectra have been recorded from As_2O_3 in the gas, liquid glass and crystalline forms.^{9,10} The spectra have been studied at temperatures ranging from 4 K to 1300 K with particular emphasis on the glass-liquid transition. The bond angle in the basic AsO_3 structural unit of the glass has been determined from depolarization spectra and from a valence force field molecular-model calculation to be 126° . A model for the structural changes involved in the glass-liquid transition has been proposed and is in excellent agreement with experimental observations.

C. Silicon-Carbide--The Polk Random Network Model for the structure of amorphous Ge and Si has recently been adapted to tetrahedrally coordinated binary amorphous solids.¹¹ One of the basic characteristics of the Polk model is the large number of odd membered rings of bonds that the model predicts. But odd membered rings in a binary system necessitate the presence of chemically unattractive like-atom or "wrong" bonds if one assumes that the system possesses short range compositional order.

We have searched for and found evidence of like-atom carbon-carbon bonds in amorphous SiC.¹² However, because the C-C bonds have both graphite-like and diamond-like character one cannot assume amorphous SiC possesses short-range compositional order. Therefore the "wrong" bonds in SiC are not evidence of odd membered rings and can not be invoked in support of the Polk model for binary amorphous solids.

D. Boron Nitride--Boron Nitride like carbon can be prepared in a turbostratic form and in crystallite sizes ranging from $30 \text{ \AA}$ up to 1 mm.¹³ The material can also be prepared as an amorphous film. Thus, boron nitride is an ideal material for the study of the applicability of the microcrystallite model of the amorphous phase to binary systems. We have chemically prepared BN in various crystallite sizes and have determined the L_c and L_a parameters of each crystallite composition from x-ray measurements using the Scherer formula.¹⁴ We find that the width of the high frequency "in plane" optical phonon varies inversely with L_c , clear evidence of finite wave vector effects. We have also prepared amorphous BN films but have to date been unable to record Raman spectra of these films because of their intense luminescence emission. [The same problem has been encountered in our study of amorphous diamond.] To overcome the luminescence

problem two approaches have been taken: (a) A vacuum optical oven capable of temperatures in excess of 1500°C has been constructed. Initial measurements using this device indicate that the luminescence from BN is effectively quenched at 1300°C . (b) A high speed mechanical chopper ($\approx 1\text{ MHz}$) has been designed to take advantage of the difference in response times for the Raman effect ($\approx 10^{-14}\text{ sec}$) and luminescence ($\approx 10^{-6} - 10^{-9}\text{ sec}$) signals.

E. The Lens of the Eye--A Special Amorphous Solid--A small portion ($\approx 1/8$ time) of the effort of the principal investigator is spent on ophthalmological laser research in collaboration with Dr. R. Schachar of the University of Chicago Billings Hospital. During the course of that research we have carried out a fundamental study of Raman scattering from the lens. Because the lens is a non-crystalline solid and because the analysis of its optical properties was heavily dependent upon (see acknowledgement, page 24 of Ref. 18) and contributed significantly to the understanding of the basic physics of amorphous solids it is appropriate to include a description of the lens research in this progress report.

From our Raman studies of the lens we have determined its protein microstructure and have established the positional correlation of specific chemical bonds with the lens optic axis.¹⁸ Based on our analysis we suggest a mechanism for cataract formation that depends on disorder induced long-wavelength fluctuations in protein orientational configuration.

F. Hot Phonons and Polaritons--Visible argon-laser and infrared CO_2 laser radiation have been successfully mixed in the noncolinear configuration in α -quartz.¹⁵ The conversion efficiencies exceed those observed in RbClO_3 ¹⁶ and the tuning range is quite broad. The dispersion of the third order nonlinear susceptibility of α -quartz has also been measured.

G. Polar Isotope Modes--A general theory of the effect of isotopes on polar-phonons in crystals has been formulated.¹⁷ From this theory, a generalized Lyddane-Sachs-Teller relationship has been deduced and the effect of the presence of isotopes on the static and high frequency dielectric constants has been calculated. When applied to the polar modes in RbClO_3 the theory gives excellent agreement with experiment.

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