THE STUDY OF VIBRATIONAL AND ELECTRONIC EXCITATIONS
IN ORDERED AND DISORDERED SOLIDS

Progress Report
For Period September 1, 1976 - August 31, 1977

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TECHNICAL PROGRESS REPORT

ABSTRACT

The vibrational and electronic excitations of ordered, partially ordered, and disordered solids have been studied using various techniques including Raman, Brillouin, infrared, and X-ray spectroscopy together with extrinsic perturbations which include temperature and stress.

During the academic year September 1976 - June 1977 the Principal Investigator was on sabbatical leave from The University of Chicago and was a visiting staff member of the University of Cambridge, Cambridge, England. The entire period at Cambridge was spent on research activities which were closely coupled with those which received ERDA support under Contract EY-76-S-02-2126. Therefore, progress made by the Principal Investigator while at Cambridge constitutes part of this report. Moreover, by maintaining close telephone and mail contacts with students and staff at The University of Chicago and through periodic return visits, the Principal Investigator was able to sustain his research activities at Chicago throughout the sabbatical period. The progress made on research supported by Contract EY-76-S-02-2126 for the period November 30, 1976 - August 15, 1977 is described under appropriate subcategories below.

Disordered Solids

(1) Amorphous Diamond Films.--Following the seminal work of Aisenberg and Chobot¹ Dr. J. Wong and co-workers at the General Electric Company Research Laboratories have prepared amorphous films of carbon which in contrast to the normal graphitic amorphous carbons² have physical properties akin to diamond. We have undertaken in collaboration with Dr. Wong a study of the vibrational excitations of these remarkable films and hope thereby to obtain some understanding of their microstructures. Our preliminary results are very intriguing. We have obtained the Raman spectrum of several amorphous

diamond films (a very difficult task because the films emit intense luminescence characteristic of crystalline diamond³) and find the spectra to contain no features which are qualitatively distinct from the corresponding spectra of amorphous carbon in the graphitic form.² This is remarkable because unlike graphitic amorphous carbon, amorphous diamond is transparent, insulating, superhard, and has other diamond-like physical properties. Our preliminary results have raised fundamental questions concerning the relationship between structure and physical properties of amorphous carbon films.

(2) Low Frequency Inelastic Light Scattering from Chalcogenide Glasses and Alloys.--We have recently shown that chalcogenide glasses exhibit a temperature dependent light scattering intensity at very low frequency shifts which is in excess of what we would expect from Debye-like phonon excitations.⁴ As can be seen from the low frequency Raman spectra of As_2S_3 glass shown in Figure 1, the intensity at $\approx 0 \text{ cm}^{-1}$ Stokes Raman shift decreases to zero with decreasing temperature. In contrast, the first order phonon scattering intensity is proportional to ω^2 , the Debye-like density of states and to the Raman coupling coefficient $C(\omega)$ where $C(\omega) \propto \omega^n$, $n > 0$. Thus the phonon scattering intensity should approach zero at zero Raman shift for all sample temperatures.

The above described "light scattering excess," which was first observed in fused silica glass,⁵ has been attributed to polarizability fluctuations of the double well defect potentials to which the anomalous linear term in the specific heat of glass has been attributed.⁵ To test this assertion we have determined for the first time the frequency dependence of the excess scattering as well as the temperature dependence and compared our results with the corresponding theoretical results¹ based on the double well potential. As can be seen from Figure 2, it is not possible to account for both the frequency and temperature dependence of the light scattering excess with currently available theoretical models for any reasonable choice of the parameters characterizing the distribution in double well potentials. However, the "light scattering excess" can be quantitatively attributed to multi-phonon processes even though such an explanation is less appealing esoterically.

(3) Irreversible Photostructural and Thermostructural Transformations.--The initiation of this project, though anticipated for the current funding period, has been delayed primarily because the facilities necessary for the preparation of bulk metastable As_2O_3

glass were not readily available at Cambridge. However, we are keenly interested in this project and have included it again in our proposed research.

Partially Ordered Solids

(1) Graphite Intercalate Compounds.--Although most modern work on alkali graphite intercalates is limited to stages 1-3, a detailed understanding of the electronic, structural, and vibrational properties of those materials necessitates the study of higher stage (more dilute) materials. Therefore, using the methods of Herald⁷ and the data of Nixon and Parry,⁸ we have successfully prepared a series of compounds of graphite intercalated with rubidium.⁹ This series spans the range from stage 1 to stage 6 and possibly stage 9 (the highest stage alkali intercalate yet reported), i.e. C_8Rb , $C_{12n}Rb$ $n = 2 \dots 6, 9?$. All samples were characterized by using X-ray spectroscopic techniques and examining multiple (00 ℓ) c axis reflections. The room temperature Raman spectrum of each sample in the series was recorded. Stage 1 C_8Rb yields a spectrum which, like the corresponding spectra of C_8K and C_8Cs ,¹⁰ consists of a continuum on which were superposed a pair of Breit-Wigner (BW) resonances. For $n \geq 3$ a Raman doublet at $\approx 1600 \text{ cm}^{-1}$ is observed and has, for each stage, been successfully computer fit with a pair of Lorentzian lines.⁹ The ratio of the integrated intensities of the components of the doublet varies linearly with n and is zero at $n = 2$ in agreement with the "nearest layer" model of Nemanich, Solin, and Guérard.¹⁰ We find that the ratio of the Raman scattering cross sections for type C and B layers is $\sigma_C / \sigma_B = 0.3 \pm 0.1$. This result is an indication that type B layers contain more charge than type C layers, i.e. that charge is localized along the "c" axis in contrast to the results of X-ray measurements on $C_{12n}K$.¹¹

(2) Raman Active Soft Modes and Phase Transitions in the Non-Stoichiometric Compounds Na_xWO_3 .--The sodium tungsten bronze compounds Na_xWO_3 are known to exhibit unusual electronic transport properties including a metal-nonmetal transition at $x \sim 0.2$, enhanced superconducting properties at $x \sim 0.2$, and a large concentration-dependent Kohn anomaly for $0.56 < x < 0.83$.¹² Naturally these electronic properties are closely related to structural features. In this regard, the high-concentration Na_xWO_3 compounds ($x > 0.56$) have usually been treated as cubic substances with a

perovskite-like ABO_3 structure in which the A sites are randomly occupied by sodium atoms.

Several large single crystals of high concentration Na_xWO_3 were prepared in our materials preparation laboratory. Sample composition was accurately determined by J. Ito using flame spectroscopy. The homogeneity of the samples was established from depth profile studies carried out at our microprobe facility. Finally, the crystal quality and orientation were established through preliminary analyses at our X-ray facility. Only after the samples were characterized in the manner described above could precise structural studies using sophisticated Raman and X-ray scattering techniques be undertaken.

We have studied the temperature dependence of the Raman spectra of Na_xWO_3 ($x > 0.5$) and have observed several Raman-active soft modes.¹³ As can be seen from Figure 3, the soft mode frequencies exhibit temperature dependent discontinuities which are indicative of multiple structural phase transitions. In collaboration with R. Clarke, who carried out very accurate X-ray studies of concentrated Na_xWO_3 ,¹⁴ we have established that Na_xWO_3 ($x > 0.5$) has four distinct structural phases, only two of which are cubic. Moreover, we have performed a group theoretical analysis of the vibrational excitations which occur in each of the four distinct structures and have compared our results with polarized Raman spectra. The agreement between theory and experiment was excellent and allowed us to identify the specific rigid rotations of the WO_6 octahedra which are responsible for the unique sequence of structural phase transitions exhibited by concentrated Na_xWO_3 . Finally, the partial phase diagram of concentrated Na_xWO_3 is shown in Figure 4. This phase diagram has been established independently from the Raman and X-ray results which are in excellent agreement.

Ordered Solids

(1) Graphite.--Our previous results¹⁵ indicated that of the several current lattice dynamics calculations on graphite, the prototypical layer material, only that due to Nicklow et al.¹⁶ was compatible with a sharp feature at 3248 cm^{-1} in the second order Raman spectrum. We also noted, however, that even the calculation of Nicklow et al. did not provide a satisfactory explanation of the full second order spectrum. An additional

point of considerable discrepancy in the lattice dynamics models of graphite is the frequency of the out of plane A_{2u} mode for which theoretical values span the broad range from 600-1300 cm^{-1} . Therefore, we have prepared samples of highly oriented pyrolytic graphite with faces polished in a plane containing the "c" axis, a necessary requirement for observing the A_{2u} mode which we have detected for the first time.¹⁷ The infrared reflectivity of graphite and the Raman spectrum were measured with $E \perp C$ and $E \parallel C$, and the frequencies of the A_{2u} mode and E_{1u} (in plane) mode were determined to be 868 cm^{-1} and 1588 cm^{-1} , respectively. Macroscopic effective charges for each mode have also been calculated and are 0.08 e and 0.41 e, respectively. It is noteworthy that when the proper A_{1u} frequency is used with the model of Nicklow et al., that model no longer accounts for the key feature at 3248 cm^{-1} in the second order Raman spectrum. The assignment of the A_{2u} frequency has, however, enabled us to evaluate the magnitude of a four-body force constant k_u ¹⁸ that is characterized by a puckering of the layer planes and which must necessarily be contained in any lattice dynamics model which accounts for the A_{2u} mode. We find that $k_u = 1.34 \times 10^5 \text{ dynes/cm}^2$ and is of the same order as the bond stretching force constant k_r .

(2) Tungsten Trioxide.--We have studied the temperature dependence of the polarized Raman spectra of WO_3 for fixed low power laser excitation¹⁹ in an effort to establish the nature of the threshold-like photodarkening previously observed. The temperature dependence of the Raman spectra, when compared with the spectral dependence on laser excitation power density, indicates that the observed photodarkening is a thermal process associated with a temperature-dependent shift in the optical gap. It appears that WO_3 may be a useful material for a reversible optical threshold switch in the visible region of the spectrum in addition to possessing fundamentally interesting properties associated with multiple phase transitions. However, only very small thin platelets of WO_3 have been produced by the usual vapor transport growing methods.²⁰ We have, therefore, developed a new technique for growing larger WO_3 defect-free crystals from solution. The method used is based on the phase diagram studies by Levin of $\text{B}_2\text{O}_3 - \text{WO}_3$ mixtures.²¹ Our initial results are quite encouraging. We have been able to grow WO_3 platelets of typical 5 mm x 4 mm x .5mm.

The Principal Investigator has devoted 50% of his time since December 1, 1976 to research funded under Contract EY-76-S-02-2126 and will continue to devote one-half of his time during the renewal period.

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Figure Captions

Figure 1. Temperature dependence of the low frequency Raman spectra of As_2S_3 glass.

Figure 2. (a) The temperature dependence of the As_2S_3 spectra at $\omega = 5 \text{ cm}^{-1}$ and (b) the spectral distribution of the light scattering excess. The solid circles in (b) represent the experimental spectral contribution due to the light scattering excess while the open circles are the data from which the excess is deduced. The three different solid lines in (a) and (b) are plots of the theoretical excess intensity calculated using three different sets of parameters for the distribution of double-well potentials. The dashed line in (a) is the contribution due to scattering from Debye phonons.

Figure 3. Temperature dependence of the square of the frequencies of the Raman active soft modes of Na_xWO_3 . The solid lines are drawn to aid presentation.

Figure 4. Phase diagram for Na_xWO_3 . $\square$ Raman $\odot$ X-ray $\triangle$ NMR, + specific heat, $\circ$ birefringence.

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Fig.2

Fig.3

Fig. 4