UNIVERSITY OF CHICAGO
TECHNICAL PROGRESS REPORT
COVERING

SEPTEMBER 1, 1974 - AUGUST 31, 1975

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TECHNICAL PROGRESS REPORT

ABSTRACT

The electronic and vibrational excitations of ordered, disordered and partially ordered solids as well as related liquids and gases have been studied using Raman and infrared spectroscopy together with extrinsic perturbations such as uniaxial stress.

Disordered Solids

(1) Five phases of As_2O_3 including the glassy, gaseous, and crystalline forms. -- Compounds which can be prepared in the crystalline, glassy, liquid, and gaseous states are of particular interest. Five of the six known preparable phases of one such compound, As_2O_3 , have been studied using Raman and IR spectroscopy.⁽¹⁻³⁾ Special attention was given to the structural features of the glassy and liquid forms and to the dynamics of the glass liquid transition. A new technique for accurately determining the glass transition temperature of a material has been developed. Also it has been shown that contrary to previous reports,⁴ no special temperature that characterizes layer disintegration in layer like amorphous solids exists.

Polarized Raman spectra of monoclinic As_2O_3 , claudetite, reveal the isomorphism of that material to the monoclinic forms of As_2S_3 and As_2Se_3 and provide detailed information on the structural remnants found in vitreous As_2O_3 . It has been shown that structural features of the vitreous form of a compound cannot be deduced by simply comparing the positions of the spectroscopic features of the vitreous and crystalline forms.⁵ However structural features of the vitreous can be ascertained by comparing both the

positions and polarization properties of spectral features in the ordered and disordered forms.

(2) Amorphous Selenium--Selenium is one of the few elemental materials that can be prepared in bulk amorphous form. The low temperature Raman and depolarization spectra of bulk amorphous Se have been studied in the range 13-300 cm^{-1} ⁽⁶⁾ Certain modes have been unambiguously identified as originating from Se_8 ring or polymeric chain vibrations. By exciting the spectra with both the 2 μm ABC YAG laser line ⁽⁷⁾ and the 7993 $\text{\AA}$ Kr^+ ion laser line temperature effects which had confused earlier workers ⁽⁸⁾ were eliminated. A study of the low frequency region was particularly revealing in that the Raman coupling coefficient was found to be frequency independent in the range 13-35 cm^{-1} . Because of the availability of neutron scattering measurements of the low frequency density of states of amorphous Se, we were able to make the first direct measurement of the Raman coupling coefficient. From the frequency independence of the coupling coefficient we established an upper bound of 8 $\text{\AA}$ for the correlation range in vitreous Se. That value is in excellent agreement with values deduced from x-ray diffraction studies. ⁹

(3) The Pseudo Binary Amorphous Alloys $(\text{GeS}_2)_{1-x}(\text{As}_2\text{S}_3)_x$ and $(\text{GeSe}_2)_{1-x}(\text{As}_2\text{Se}_3)_x$.-- Infrared and Raman spectroscopic studies of the above mentioned pseudobinary systems revealed unique coordination ^(10, 11) dependent mixed mode behavior not exhibited by crystalline alloys. Using a molecular model in conjunction with a valence force field calculation, the frequencies and symmetries of the dominant mixed and nonmixed modes of the alloy system were accurately calculated. There is clear evidence of

preferential heteropolar bonding in the Ge-Se-As-S alloy system and of the presence of well defined pyramidal and tetrahedral structural units in the glass.

Partially Ordered Solids

(1) Boron Nitride Microcrystals.--The properties of materials can be significantly altered by extrinsic perturbations such as doping, alloying, uniaxial and/or hydrostatic stress, etc. Thus the effects of extrinsic perturbations have been widely studied. In contrast, there has been little if any research on the effect of intrinsic perturbations on the properties of materials. Accordingly, we have undertaken an investigation of one of the most basic intrinsic perturbations namely, that of finite particle dimensions. The subject of our initial studies is BN.⁽¹²⁾ We find that this layer compound can be hardened if it is prepared in the form of microcrystallites.

Boron nitride is a member of the class of superhard materials which includes diamond and SiC among others. However boron nitride is the only member of that class which can be prepared in a turbostratic* graphite-like layer crystal form with crystallite sizes ranging from $40 \text{ \AA}$ to $4000 \text{ \AA}$. Naturally, the microscopic physical properties of any crystalline material are strongly influenced by the range of lattice order, i.e., by microcrystallite size.

To investigate the effect of crystallite size on the vibrational excitations of solids we have chemically prepared BN microcrystalline powders with typical particle dimensions as small as $40 \text{ \AA}$. To ascertain the parameters L_a and L_c which characterize

*A turbostratic layer compound is one for which the layers are parallel to one another but are randomly oriented about the optic axis orthogonal to the layer planes.

respectively the range of order within and orthogonal to the crystalline layer planes, the x-ray diffraction data shown in Fig. 1 were recorded. The spectrum XBN-1 corresponds to crystallites with $L_c \approx L_a \approx 1000 \text{ \AA}$ while increasing sample numbers correspond to decreasing crystallite size and $L_c \approx L_a \approx 40 \text{ \AA}$ for XBN-9.

In Fig. 2 is shown the effect of crystallite size on the Raman spectrum of the intralayer vibration of BN. Notice the marked change in linewidth and the shift to higher frequency with a decrease in crystallite size. Using a model which accounts for the quantum mechanical uncertainty in the momentum of a phonon created in a crystal of finite size we have calculated the shift and broadening of the intralayer mode as a function of L_c and L_a . This calculation agrees very well with our experimental results and indicates a superhard layer compound such as BN can be further hardened if it is prepared in microcrystallite form.

(2) Electronic Excitations in Semiconducting and Metallic Ge Doped With Donors or Acceptors.—Our studies of the metal nonmetal transition in doped germanium¹³ have yielded new results. The electronic Raman spectra of Ge(Ga) (Ga is an acceptor) reveal the development of continuum states at much lower impurity concentrations than Ge(As).¹⁴ These results have been explained in terms of wavefunction overlap that manifests itself at lower concentrations for weakly bound acceptor eigenstates. Moreover, the temperature dependence of electronic single particle excitations has been studied and the electron velocity distribution determined.¹⁵

A Piezo-Raman spectroscopic study of the valley orbit transition in Ge(As) has been carried out in great detail for uniaxial stress along the [111] and [110] directions.¹⁶

The group theoretically deduced electronic Raman selection rules have been experimentally verified. The shear deformation potential for Ge has been determined to be $\Xi_u = 17.6 \pm .5$ eV.¹⁷ The intensity of the stress split components has been calculated using stress dependent wavefunctions and is in excellent agreement with experiment.¹⁷

Ordered Solids

(1) Brillouin Scattering from Amorphous and Crystalline Solids:--During the past year we have completed construction of a Brillouin scattering apparatus. The apparatus has been calibrated and checked by recording the spectra of recognized standards such as toluene. The spectra of toluene which we have obtained are of excellent quality, an indication that the Brillouin apparatus is performing properly and can now be applied to the study of low frequency excitations in solids.

(2) Luminescence Rejection. In many light scattering measurements, signals of interest are obscured or swamped by an intense luminescence background. Expensive and sophisticated methods for selective rejection of luminescence have been tried and are, in our opinion, singularly unsuccessful.¹³ We have developed a very simple and inexpensive ($\approx \$100$) method for achieving reduction in luminescence background signals by factors in excess of 10,000 while simultaneously suffering no noticeable loss in Raman intensity.⁽¹⁹⁾ A very high speed (up to 0.4 MHz) mechanical chopper is used to modulate the incident laser beam in a Raman experiment. Since the Raman response time is $\approx 10^{-14}$ sec while the luminescence response time is $> 10^{-6}$ sec the unwanted luminescence signals are virtually unmodulated and can be rejected by a lock

in amplifier tuned to the chopping frequency. The above described system has been successfully employed to record the Raman spectrum of ruby, an intensely fluorescing material.¹⁹

The principal investigator has devoted two-thirds of his time since December 1, 1974 to the research funded under Contract AT(11-1)2126 Mod.2-1 and will continue to devote two-thirds of his time to that project.

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FIGURE CAPTIONS

- Fig. 1 The x-ray diffraction spectra of several BN microcrystals. Crystallite size decreases from about 1000 Å for XBN-1 to 40 Å for XBN-9.
- Fig. 2 Crystallite size dependence of the Raman spectra of the intralayer vibrational mode of turbostratic BN. The sample designation is the same as that used in Fig. 1.

INTENSITY (ARBITRARY UNITS)

Fig. 1

Fig. 2