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TECHNICAL PROGRESS REPORT

ABSTRACT

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

Disordered Solids

(1) Irreversible Photostructural and Thermostructural Transformations of Amorphous As_2S_3 Films.--A detailed understanding of the photostructural and thermostructural transformation exhibited by amorphous As_2S_3 films is of fundamental interest and is also prerequisite to efficient film design. Therefore, we have carefully examined the Raman and infrared spectra of the As_2S_3 vapors from which the film is prepared.⁽¹⁾ We have also studied spectra of the film prior to and after thermal annealing (or equivalently photon annealing). We find the following results: (1) The vapor above As_2S_3 liquid is quite complex and contains many molecular species probably including but not limited to As_4S_4 , As_4S_6 , As_4 , and S_2 . (2) The molecular glass formed on deposition of the vapor also contains several different molecular species not just As_4S_6 , as suggested by de Neufville et al.⁽²⁾ Those species do indeed cross-link when the film is exposed to light or heat. (3) During deposition there is a transformation of some of the molecules of the vapor to other distinct molecular forms that are present in the glass. A structural transformation model based solely on As_4S_6 molecules⁽²⁾ is inappropriate.

(2) Structural Correlation Ranges in Disordered Solids.--A key parameter for characterizing the structure of a disordered solid is the structural correlation range (SCR), the length over which atomic positions are correlated. We have studied the low frequency Raman and Brillouin spectra of several amorphous semiconducting alloys, compounds, and homopolar materials composed of Ge, As, S, and/or Se.^{(3), (4)} From the light scattering spectra the corresponding SCR's have been determined. Our results compare favorably with values inferred from X-ray and normal Raman studies (see below).

(3) Evidence for Large Atomic Clusters in Amorphous Ge-Se-As-S Alloys.--The optic mode vibrational excitations of bulk chalcogenide amorphous semiconducting glasses have traditionally and, on the whole, successfully been attributed to excitations of small local atomic clusters such as the symmetric AsS_3 pyramidal unit in As_2S_3 ⁽⁵⁾ or the GeSe_4 tetrahedral unit in GeSe_2 .⁽⁶⁾ By studying the Raman and depolarization spectra of GeSe_2 alloyed with either Se or As_2S_3 , we have identified for the first time a feature that is definitively attributed to vibrational excitations of a large symmetric atomic cluster.⁽⁷⁾ That cluster consists of a ring of six Ge atoms interconnected by Se atoms. The maximum diameter of such a ring is $\approx 7 \text{ \AA}$ and is equal (within experimental error) to the structural correlation range of GeSe_2 glass, $8 \pm 1 \text{ \AA}$,⁽³⁾ deduced as described above. Thus we have not only reported the first experimental determinations of the SCR of an amorphous solid but we have also identified the structural entity with which the correlation range is associated.

Partially Ordered Solids

(1) Graphite Intercalation Compounds.--Crystal compounds of graphite exhibit enhanced anisotropy and in some cases basal plane conductivities approaching that of copper.⁽⁸⁾ To ascertain the effect of intercalation on the vibrational excitations and on electron phonon coupling, Raman spectra of vibrational excitations in graphite intercalated with acceptor or donor compounds have been studied.⁽⁹⁾ Stage 1, 2, and 3 cesium donor compounds prepared from highly oriented pyrolytic graphite (HOPG) were examined as were stage 1 and 2 HOPG potassium donor compounds and a polycrystalline powder potassium intercalate of mixed stage. The acceptor compounds studied, AlCl_3 , CrO_3 , and SbF_5 , were prepared from polycrystalline powder graphite with approximate stage 2, 1, and 3, respectively. Second stage cesium and potassium intercalates exhibit a single Raman band unshifted from the E_{2g} intralayer mode of HOPG which occurs at 1580 cm^{-1} . In contrast, the third stage cesium intercalate produces a doublet spectrum with one component upshifted from and the other at the same position as the HOPG intralayer mode. The spectra of SbF_5 and AlCl_3 compounds are quite similar and consist of a doublet both components of which are upshifted from the intralayer mode of pristine graphite. The CrO_3 spectrum consists of an asymmetric band slightly upshifted from the intralayer mode but with a high frequency tail. The above described observations for stage 2 and higher stage donor and acceptor compounds are explained by an analysis which considers (a) the nearest layer configurations which a given carbon layer can experience in

a given stage of intercalation, (b) the change in C-C bond distance with intercalation, and (c) the effect of intercalation on the carbon interlayer interaction. The spectra of stage 1 cesium and potassium intercalates are almost identical and each contains two anomalously shaped bands, one near to but down shifted from the interlayer mode of HOPG and one at $\approx 560 \text{ cm}^{-1}$, both being superposed on a continuum background. These bands are attributed to Breit-Wigner or Fano resonances between an electronic Raman scattering continuum and the E_{2g} intralayer mode and an out of plane intralayer vibration, respectively. The parameters Γ , q , and $\bar{\nu}$ governing the Breit-Wigner resonance are determined by fitting the observed line shapes of each of the two bands in the cesium and potassium intercalate spectra. Several strong Raman lines in the frequency range from 0-1500 cm^{-1} which are detected in the spectrum of the CrO_3 interlate have been identified as internal modes of the CrO_3 molecule. This identification is based on a comparison of the intercalate spectrum with the spectrum of pure CrO_3 . Similarly, the spectrum of anhydrous AlCl_3 has been recorded and used to identify two weak features in the spectrum of the AlCl_3 crystal compound as internal modes of the AlCl_3 molecule.

(2) Piezo Raman Spectroscopic Studies of Ge(As).--Electronic Raman scattering from the stress-split valley-orbit transition in Ge(As) has been studied for uniaxial stress along both the [111] and [110] directions.⁽¹⁰⁾ Each of the observed spectral components is shown to obey the group theoretically derived selection rules. A detailed quantitative comparison of the experimental positions of the spectral components is made with the theoretical predictions of Price.⁽¹¹⁾ Raman shifts associated with $1s \{A_1\} \longrightarrow 1s (\Gamma_i)$ transitions ($\Gamma_i \neq A_1$) can be accurately calculated using this theory. A discrepancy between theoretical predictions and the experimental results for the $1s \{A_1\} \longrightarrow 1s (A_1)$ transitions is attributed to stress-induced hybridization between the $1s (A_1)$ and $2s \{A_1\}$ states. After including hybridization effects the agreement between theoretical predictions and the experimental spectral positions is excellent. The shear deformation potential, Ξ_u , for the $1s$ manifold of impurity states was determined to be $17.8 \pm .5 \text{ eV}$. The experimentally determined intensities of the observed electronic Raman lines have been compared with theoretical calculations for the stress-dependent Raman cross section of the valley-orbit transition.⁽¹²⁾

Crystalline Solids

(1) Second Order Raman Spectrum of Graphite (2 Phonon Bound States).--Several recent calculations of the phonon dispersion curves of graphite have been reported and show serious disagreements, especially in the optic mode region which is inaccessible to neutron scattering studies. To establish the proper form of the dispersion curves, first and second order Raman spectra of single crystal graphite and highly oriented pyrolytic graphite have been obtained.⁽¹³⁾ The second order Raman spectra exhibit a step rise at 2432 cm^{-1} , a strong peak at 2739 cm^{-1} with a shoulder at 2698 cm^{-1} and a sharp peak at 3248 cm^{-1} . The latter feature is most noteworthy because (a) its half-width is approximately one-half of that of the first order line at 1582 cm^{-1} , and (b) its position indicates that the maximum phonon energy of graphite is not at the zone-center. Our results confirm the model of Nicklow et al.⁽¹⁴⁾ for the phonon dispersion curves of graphite. The 3248 cm^{-1} line has several features characteristic of a 2-phonon bound state⁽¹⁵⁾ but may in fact be just a manifestation of the dispersion curves themselves.

(2) Magnon Phonon Interactions in NiF_2 .--We have obtained preliminary but high quality room temperature Brillouin spectra of NiF_2 and have verified the group theoretical selection rules for the transverse and longitudinal phonons. The observed spectra are quite weak in part because a triple pass Fabry-Perot interferometer, which has reduced transmission but high spectral purity, was required to obtain them.

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