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FORMATION AND RAMAN SCATTERING OF AMORPHOUS IODINE*

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Evaporation of iodine onto a liquid He cooled substrate has resulted in the formation of amorphous iodine. Raman scattering measurements indicate that amorphous iodine is a one-fold coordinated semiconductor. The spectra surprisingly indicate the lack of quasi-molecular character in the depolarization ratio. The intramolecular I_2 band is substantially broadened indicating considerable disorder beyond the first coordination sphere and appreciable intermolecular coupling.

I. Introduction

In contrast to amorphous metals, which have high coordination numbers, noncrystalline semiconductors are observed to have values of $n_1 \leq 6$. While a considerable number of studies have been performed on systems with $n_1 = 2,3$ or 4, no experimental or theoretical studies of a minimum coordination system with $n_1 = 1$ have been performed. For such systems, which are composed of diatomic molecules, the intrinsic absence of bond angle fluctuations present for $n_1 \geq 2$, implies that disorder is associated with fluctuations beyond the first coordination sphere. This is shown schematically in Fig. (1), where fluctuations in bond angle θ, for $n_1 \geq 2$, yield local variations in the electronic and vibrational excitations of the amorphous network. Implicit is the assumption that variations in the first neighbor distance are relatively small for all n_1. In contrast to higher coordinated semiconductors, a one-fold coordinated system with dominant first neighbor bonds lacks direct linkages of approximately equal strength in forming the amorphous network. A system of minimum coordination is thus expected to require modification of topological and localization considerations employed for higher n_1.

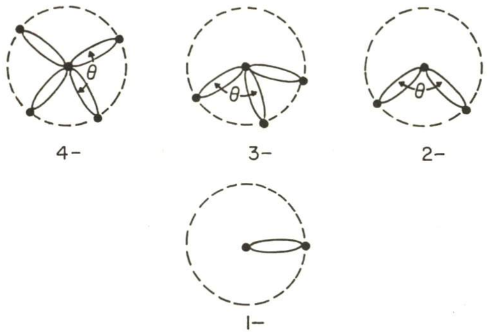

Fig. 1 Schematic of the nearest neighbor bonding in elemental amorphous semiconductors within the first coordination sphere: Fluctuations in bond angle, θ, are present for $n_1 \geq 2$

A candidate for a one-fold coordinated amorphous semiconductor is iodine. In its low pressure, orthorhombic phase, iodine is a layer like semiconductor in which both molecular as well as semiconductor behavior is observed [1,2]. The coupling between I_2 molecules has been considered in a number of studies in terms of directional p-orbital overlap [3] or alternatively as being delocalized in character [4]. The Raman scattering results presented here and discussed in more detail elsewhere [5], suggest that the latter picture of delocalized metallic-like bonding is more appropriate to both a-I and c-I.

II. Experiment

Amorphous iodine was prepared in thin film form by evaporation onto polished Si substrates cooled by liquid He to a temperature estimated to be 10 ± 5 K. Iodine vapor from a room temperature source was transferred to an evacuated prechamber. The vapor from the prechamber was directed through a 4 mm diameter nozzle onto the substrate. The process was repeated four times to form a film ~0.5 μ thick, as estimated by interference fringes during deposition. At higher substrate temperatures, ~80 K, thin films were found to generally be either crystalline or a mixture of amorphous and microcrystalline in nature for a variety of substrates and thicknesses. The amorphous component of the films deposited at 80 K was identified by appreciable low frequency scattering, while films which yielded a broadened high frequency mode with little low frequency scattering suggested possible microcrystalline material. It was observed that under apparent impurity stabilization, a-I could also be formed at 80 K with a reduction in density suggested [5]. The Raman spectra were obtained using a Spex triple monochromator and 7525 A Kr laser excitation. From the variation of the Stokes intensity with temperature, it was estimated that the sample was at ~30 K during laser illumination.

III. Results and Discussion

The Raman components I_{VH} and $I_{H'H}$ are shown in Fig. (2) for a-I deposited at 10 K. The presence of a continuum of relatively strong low frequency scattering indicates that the material is amorphous. In contrast to what would be predicted for a diatomic, molecular noncrystalline system, the spectra indicate little direct evidence for quasi-molecular character. In particular, no sharp features are observed in the H'H spectrum, which is qualitatively similar to that of the VH result. In addition, the magnitude of the depolarization ratio, corrected for the estimated refraction angle of ~13°, yields a relatively large value of 0.41 for its minimum at 181 cm^{-1}. A weak variation of the depolarization ratio for the high frequency band of Fig. (1) indicates quite weak quasi-molecular character. This result is rather surprising, given the molecular character of c-I and the suggested local intermolecular coupling via p-orbital overlap, which in a-I is expected to be reduced and as such, would predict molecular character in a-I.

The lack of quasi-molecular character in the spectra of a-I implies that the polarizability correlations [6,7] are fairly small and therefore the Raman spectra will indicate the approximate form of the phonon density of states. The presence of frequency dependent coupling parameters, which modify the relative peak intensities, is noted by the large integrated intensity of the higher frequency band. In contrast, the c-I integrated intensity ratio for the high to low frequency areas of the phonon density of states is predicted to be 0.2. The spectra of Fig. (2) indicate a phonon gap between ~100 cm^{-1}

to 150 cm^{-1} which parallels the corresponding gap in the phonon spectrum of c-I [8]. In the latter, this gap corresponds to a separation of high frequency, intramolecular stretching modes and lower frequency intermolecular optic and acoustic modes. This gap is also found to be preserved in liquid I [9].

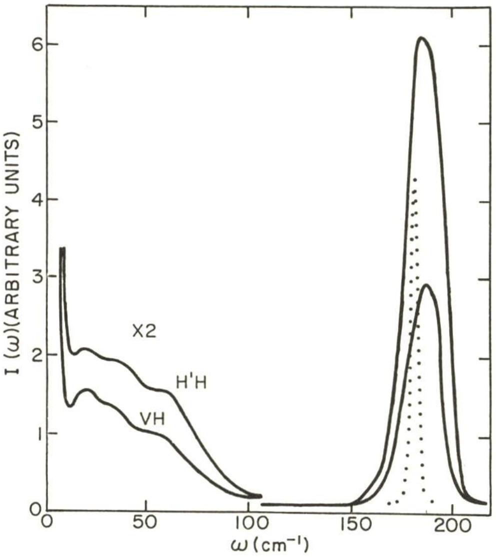

Fig. 2 First order Raman scattering in a-I at 30 K for a film deposited at $T_s \simeq 10$ K (solid curves) and the second order Raman spectrum at 80 K of c-I deposited at $T_s \simeq 140$ K (dotted curve). The frequency scale of c-I has been halved for comparison

In Fig. (2) the approximate form of the phonon density of states for c-I for the intramolecular band is indicated by the dotted curve. This represents a second order scattering spectrum whose frequency has been halved for comparison. This interpretation in terms of an approximate density of states assumes dominant overtone scattering for the second order scattering [8]. As is clear from Fig. (2) there is a quite significant increase in full width at half maximum of the a-I spectrum relative to c-I. The factor of 5.4 increase in width is substantially larger than that observed in other elemental or compound semiconductors and implies appreciable disorder in a-I beyond the first coordination sphere. This may arise from variations in intermolecular spacings or from fluctuations in the orientational distribution of I_2 molecules. That the system is concluded to be a one-fold coordinated semiconductor is reasonable, given the similarity of the high frequency peaks of the c-I and a-I spectra, though this is also physically most plausable given the improbability of forming other I clusters. Larger clusters, such as I_3 units would, in addition, result in a modification of the c-I spectrum. The small shift of the high frequency peak in the a-I spectra relative to c-I suggests that intramolecular coupling is not substantially modified and by implication the average intermolecular coupling has also not significantly decreased. Measurements in liquid I of lower density and on impurity stabilized a-I suggest that the average local density of I_2 molecules has not been substantially modified in the 10 K deposited a-I film [5].

The low frequency features of a-I in Fig. (2), with the exception of the peak at 20 cm^{-1}, also have corresponding peaks in the c-I phonon density of states. This is further consistent with a small change in average intra and intermolecular coupling. The pure polarized spectrum obtained from $I_{HH}-4/3I_{VH}$ is found to be relatively small for the low frequency band and is consistent with a local bond distortion model in which stretching modes dominate the polarizability fluctuations [10]. Below ~30 cm^{-1} the $I_{HH}-4/3I_{VH}$ spectrum essentially vanishes, indicating that the low frequency scattering is depolarized. This is reasonable given the character of the less localized acoustic-like low frequency modes which weakly modulate the

the susceptibility. The lowest frequency peak may be shown by an analysis [5] of possible frequency dependent coupling parameter variations to clearly not arise from a "Bose peak", but rather represents new low frequency states not present in c-I. The presence of a peak in the density of states at 21 ± 4 cm^{-1} further implies that the frequency range of Debye-like behavior in a-I must be rather limited.

The present results in a-I deposited at low temperature as well as those on films stabilized at 80 K [5] and on liquid I [9] suggest that the dominant bonding between I_2 molecules is via delocalized metallic-like bonding. This may be seen here by the absence of quasi-molecular character under a situation of appreciable intermolecular disorder. Were the bonding to be dominated by local directional p orbital overlap effects, such disorder would be expected to result in a more molecular character for a-I. The absence of any substantial molecular character thus suggests an alternative picture for intermolecular coupling that implies delocalized bonding. Estimates [5] of the optical absorption coefficient for a-I and c-I indicate that the amorphous phase is not metallic, however, but is semiconducting, with a somewhat larger (~2x) absorption coefficient at the laser excitation wavelength of 7525 A than that of c-I.

Similarities in the vibrational spectra of a-I and c-I suggest related local structures. This would imply, as a first approximation, that the structure of a-I has a possible local quasi-two dimensional character. The appreciable disorder in a-I implies, however, that were such local character present, it would correspond to highly distorted local layers. Clearly further work, including diffraction studies are required in a-I to obtain constraints on the possible range of structures in low temperature deposited films. As in other higher atomic number amorphous systems, the trend toward delocalized metallic-like bonding results in a loss of correlations and a general trend toward appreciable disorder and second or higher coordination sphere effects.

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