

Observation of Discrete Molecular Structures in Glassy P_xSe_{1-x} by Raman SpectroscopyR. T. Phillips, D. Wolverson, M. S. Burdis, and Y. Fang^(a)*Department of Physics, University of Exeter, Exeter EX4 4QL, Great Britain*

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We report conclusive evidence for the existence of molecular local ordering in four phosphorus-selenium glasses. The compositions were chosen to span the P-rich glass-forming region and were P_2Se , P_3Se , P_4Se , and $P_{0.84}Se_{0.16}$. Raman spectra show unequivocally the existence in each glass of well-defined P_4Se_3 cage molecules. All nine Raman-active internal modes of this molecule have been observed, with a clear trend of reduction of their intensity as the P content is increased. We find that these materials behave as a matrix-supported assembly of P_4Se_3 molecules.

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The bonding connectivity of inorganic glasses has been a central feature of all models of the structure of covalent glasses. The development from the initial picture of a continuous random network of bonds to more elaborate models involving extensive short- or intermediate-range molecular order¹ has been hampered by the difficulties of obtaining real-space structural information. Most probes of electronic or vibrational properties have only partially resolved the questions concerning the presence of well-defined structural units. For example, the observation of sharp Raman lines in the spectrum of glassy B_2O_3 (Ref. 2) appears to be associated with matrix-element enhancement rather than with sharp features in the vibrational density of states (VDOS).³ We report here the first identification, by Raman spectroscopy, of the *full* vibrational signature of a distinct molecular species in an inorganic glassy semiconductor. We show that for a range of compositions rich in phosphorus the P_xSe_{1-x} glasses (*g*- P_xSe_{1-x}) retain this molecular component in their microstructure, and we assess the possible nature of network connectivity in the light of these results.

We have concentrated our attention on *g*- P_xSe_{1-x} because detailed studies of elastic neutron scattering and extended x-ray-absorption fine structure of glasses in the P_xSe_{1-x} system have already shown evidence for the existence of structural units based on the stable P_4Se_3 cage structure,⁴ and because inelastic neutron scattering measurements have revealed a VDOS similar to that of crystalline P_4Se_3 .⁵ Furthermore, we have recently shown that the radiative recombination in *g*- P_2Se (Ref. 6) and related glasses⁷ is strongly suggestive of there being a well-defined structural element associated with the recombination which persists through a wide range of compositions.

We have prepared the glasses by reacting mixtures of appropriate composition of 99.999% red *a*-P (MCP Electronic Materials, Ltd.) and 99.999% *a*-Se pellets (Koch-Light) in a sealed, evacuated quartz ampoule in a rocking furnace at temperatures in the range 560–600 °C chosen in accordance with the P-Se phase diagram.⁸

The synthesis ampoules were removed from the furnace and then air quenched to given optically clear, glassy specimens. In addition to the Raman study, some specimens have also been examined by photoluminescence, x-ray diffraction, and transmission electron microscopy. Though these glasses readily crystallize in an electron beam, the two diffraction techniques confirm the macroscopically amorphous nature of the materials. To avoid possible contamination of the specimens introduced during polishing, we have worked with pieces broken from the synthesis tubes, and have taken advantage of the resulting large conchoidal fracture surfaces in order to reduce Rayleigh scattering. The specimens were excited by < 10 mW of cw dye-laser light, tuned to 6800 Å. This wavelength is only slightly attenuated in the glass, so the Raman measurement probes the bulk material. The light was only weakly focused (to a few hundred μm diameter) in order to eliminate possible heating effects. The experiment was repeated at low power levels (< 2 mW) of both 6800 and 6328 Å, and no changes were seen in the spectra. The specimens were held in helium gas and data taken at 295 and 10 K: Some slight improvement in resolution occurred on cooling but no new features appeared. The scattered light was dispersed by a Spex spectrometer and detected with an Astromed silicon charge-coupled device.

Curves *a*–*d* of Fig. 1 show Raman-Stokes spectra for the four glasses, covering the frequency range of seven out of the nine Raman-active modes of the P_4Se_3 molecule. The polarization of exciting and scattered light were both horizontal (*HH*) though little change was seen when vertically polarized scattered light was selected. The first striking aspect of these spectra is the wealth of detail present: Relatively sharp Raman lines have been found in amorphous materials before, but we are not aware of a previous example showing *all* the Raman-active internal modes of a medium-sized molecule in an inorganic glass. Here we have glassy materials supporting a spectrum of sharp vibrational modes, showing broadening due to disorder at the level of < 1 meV FWHM. Of particular significance is the resolution

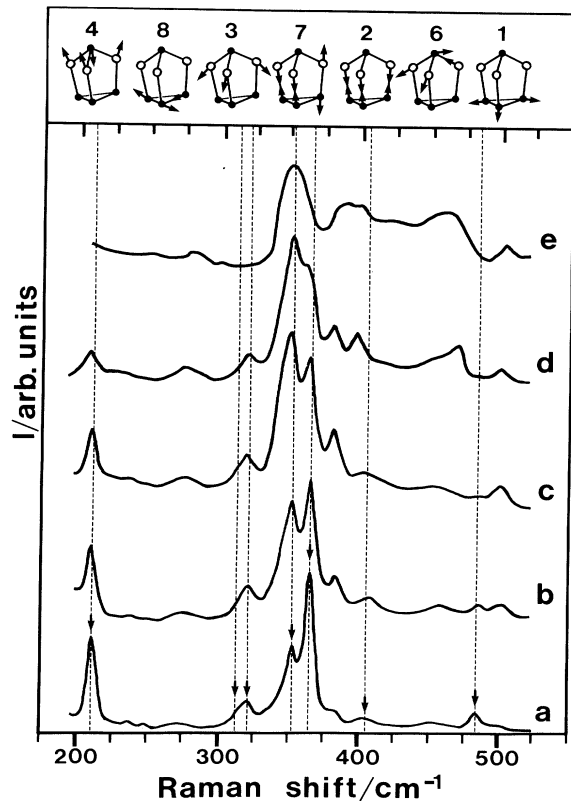


FIG. 1. Raman spectra obtained at room temperature with excitation wavelength 6800 Å for curve *a*, *g*-P₂Se; *b*, *g*-P₃Se; *c*, *g*-P₄Se; *d*, *g*-P_{0.84}Se_{0.16}; and *e*, *a*-P. The eigenvectors of the modes of the P₄Se₃ cage are shown with assignments to the modes of the glasses.

afforded by the Raman technique, which separates the modes ν_2 and ν_7 , and resolves ν_8 as a distinct shoulder on the larger peak at ν_3 . The cage modes are indicated by arrows on curve *a* of Fig. 1, and the modes ascribed to vibrations of the matrix are readily seen by comparison of the spectra of the alloys with that of *a*-P (Fig. 1, curve *e*). The two remaining Raman-active modes expected for the cage molecule are shown in Fig. 2, curves *a*-*d*, obtained at higher dispersion than for the previous data. Because of the optical effects resulting from the conchoidal nature of the samples' surfaces, no significance should be attached to the relative intensities of the bands shown in Fig. 2. We assign ν_9 to 174 cm⁻¹ and ν_{10} to 133 cm⁻¹. The value for the frequency of mode 9 is rather high in comparison with that found in the crystal,⁹ but we prefer to assign this mode to the sharp feature shown in Fig. 2 rather than to the broad band at lower wave number which we have also included in the figure and which we believe *not* to be a cage mode. Table I summarizes our assignments of all the clearly observed modes and gives details taken from a previous Raman study of crystalline P₄Se₃ for reference. We attribute to the matrix, rich in P, those modes not associat-

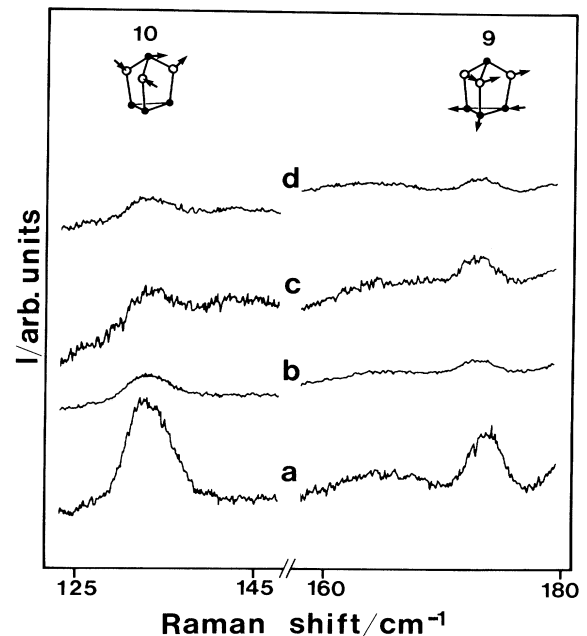


FIG. 2. Raman spectra obtained under the same conditions as for Fig. 1, but at higher dispersion, for curve *a*, *g*-P₂Se; *b*, *g*-P₃Se; *c*, *g*-P₄Se; and *d*, *g*-P_{0.84}Se_{0.16}. The peaks at 133 and 174 cm⁻¹ are assigned to the modes of the P₄Se₃ cage illustrated.

ed with the internal modes of P₄Se₃. This matrix is required to maintain the stoichiometry, and supports the P₄Se₃ molecules. As the P content of the glass is increased, the proportion of matrix necessarily increases relative to that of the discrete molecules, and this is reflected in the strength of scattering involving the internal molecular modes. For the highest P content the weaker cage modes are barely detectable, and several new features have begun to dominate the spectrum. The likely origin of these modes is best demonstrated by comparison with the Raman spectrum of red *a*-P, which has been extensively studied.¹⁰⁻¹² Because of some incon-

TABLE I. Modes of P₄Se₃ cage structures observed by Raman scattering in the *a*-P₄Se₃ crystalline phase (Ref. 9) and in P_xSe_{1-x} (this work) at room temperature.

| Symmetry | Mode | <i>a</i> -P ₄ Se ₃ (cm ⁻¹) | <i>a</i> -P _x Se _{1-x} (cm ⁻¹) |
|-----------------------|------|---|---|
| <i>A</i> ₁ | 1 | 485 | 487 |
| | 2 | 360 | 365 |
| | 3 | 320 | 324 |
| | 4 | 207 | 214 |
| <i>E</i> | 6 | 404 | 408 |
| | 7 | 344 | 353 |
| | 8 | 315 | 315 |
| | 9 | 160 | 174 |
| | 10 | 132 | 133 |

sistencies in the published data on this material, we have included our own spectrum. In common with some of the earlier work it shows not only the broad, strong features near 360 cm^{-1} but also a relatively sharp peak at 500 cm^{-1} . The development of this peak in the glassy alloys is particularly clear, as is the decline in the highest mode of the cage structure (ν_1).

In order to understand the vibrational properties of the $\text{P}_x\text{Se}_{1-x}$ glasses, close reference must be made to the α -crystalline form of P_4Se_3 . This material was originally described by Keulen and Vos¹³ as a molecular solid, and much of the analysis of both the crystal and the vibrational structure has paralleled that for crystalline P_4S_3 . We are using the results of a symmetry analysis of the isolated molecule of C_{3v} symmetry, which indicates that the ten internal normal modes split into four A_1 , one A_2 , and five E representations, of which the A_2 is expected to be inactive in Raman scattering. Investigation of the α -crystalline form by Burns¹⁴ has led to a description which emphasizes the close proximity of the molecular units assembled into the crystal structure. Within the cages, the average basal-plane P-P distance is 2.226 \AA , the P-Se distance is 2.241 \AA , and the Se-Se distance is 3.422 \AA . Burns, Rollo, and Clark¹⁵ have pointed out that intercage Se-Se distances range from 3.625 to 3.798 \AA which indicates a stronger Se-Se interaction than van der Waals bonding. The importance of this for the interpretation of the Raman spectra of $\text{P}_x\text{Se}_{1-x}$ is that since we are making comparison with the normal modes of P_4Se_3 cages *already bonded* into a 3D structure the changes in the normal modes which arise when cages are allowed to interact are already partially accounted for. This becomes apparent when comparison is made between the observed bands in $g\text{-P}_x\text{Se}_{1-x}$ and $\alpha\text{-P}_4\text{Se}_3$. For the most prominent mode in the crystal, near 365 cm^{-1} , the width of the Davydov-split band is 8 cm^{-1} at 20 K compared to 12 cm^{-1} FWHM in, for example, $g\text{-P}_2\text{Se}$ at 10 K . The lack of significant improvement in the resolution of the Raman spectrum of the glass on cooling to 10 K indicates that the modes show broadening amounting to no more than 5 cm^{-1} ($\approx 0.6\text{ meV}$) due to the variety of sites occupied by the cage units.

For the four compositions of the glass which we have studied, the ν_2 band remains at the same frequency to within experimental error ($\pm 2\text{ cm}^{-1}$). This probably indicates that intercage coupling changes only weakly in the range of compositions which we have studied, which extends from two matrix P atoms per cage to thirteen for the idealized case of all Se atoms being in cages. It is difficult to rule out completely some form of microscopic segregation of the cages, but it is not necessary to invoke this to explain our results. Similar considerations apply to the modes involving only the basal P atoms (1 and 8). Detailed comparison of the intensity ratio of mode 1 to mode 2 for the glasses and crystal is difficult, but it appears that the symmetric basal vibration (mode 1) is not significantly diminished in the glasses in comparison with

the crystal. The clear detection of this mode and mode 8—particularly in $g\text{-P}_2\text{Se}$ —indicates that most of the strained basal triangles of P atoms survive incorporation into the glass. We therefore believe that the superior resolution of the Raman data eliminates the model suggested by Verrall and Elliott⁵ of pairs of cages cross-linked at their bases by P atoms. This configuration may occur, but not in sufficient density to remove the 487-cm^{-1} band. Calculations by Lister and Jones¹⁶ using a local-density-functional method, confirm that the observed mode structure would be lost if the cages aggregate covalently into larger units. We are therefore led to the conclusion that P_4Se_3 cages behave as matrix-supported molecules. Detailed modeling is hampered by the lack of information concerning the relative Raman scattering strengths in the cages and in the phosphorus matrix. We know that in our experiment the Raman signal from cages might be slightly resonantly enhanced,¹⁵ but since the VDOS measurements of Verrall and Elliott⁵ also show broad features in the correct regions of the spectrum, their data are consistent with there being only relatively weak enhancement of Raman sensitivity to features in the VDOS. This contrasts markedly with the case of B_2O_3 ,³ and allows us to proceed to describe the matrix on the basis of the newly resolved VDOS features which we have identified.

It is now possible to attempt assignment of the remaining features in the Raman spectra. Figure 1 shows clearly the coincidence with vibrations of red $a\text{-P}$ of some of the peaks not associated with the cages; this strongly supports a model of distribution of P_4Se_3 cages in a matrix of $a\text{-P}$. This model also suggests an interpretation of the position of the upper limit to the P-rich glass-forming region. We suppose that the glass comprises P_4Se_3 cages interacting much as in the crystal, the stability of the glass deriving from the strength of this interaction. The disruption of regular packing induced by the presence of excess P atoms suppresses the tendency to crystallize which becomes dominant at low P concentration near to stoichiometric P_4Se_3 . The observed upper limit for glass formation in $\text{P}_x\text{Se}_{1-x}$ is near $x=0.85$, corresponding to a concentration of matrix P atoms of ≈ 13 per cage. If the cages are not clustered, this is of the same order as the number of P atoms required to produce a crust of matrix around each roughly spherical cage. The upper limit of the glass-forming region within this model reflects the loss of intercage interaction in glasses of high P content. The detection of vibrational modes of the matrix which are clearly closely related to those of bulk $a\text{-P}$ indicates either that even relatively thin "shell" structures of the matrix are capable of yielding bulklike modes or alternatively that some degree of microscopic aggregation occurs. The evolution of certain features in the spectra attributed to the matrix—for example, the decline of the modes at 230 and 240 cm^{-1} as the P content is increased, and the simultaneous increase in those at 475 and 500 cm^{-1} —may suggest that the

matrix itself evolves from a tenuous shell-like form at low excess P to a more three-dimensional network at the higher P compositions.

In conclusion, we have shown that the glassy semiconductors P_2Se , P_3Se , P_4Se , and $P_{0.84}Se_{0.16}$ show remarkably well-resolved structure in their Raman spectra. We have shown that this system exemplifies the transition from a quasi-zero-dimensional molecular glass (P_2Se), with a high concentration of P_4Se_3 cage molecules and a barely formed supporting matrix of P atoms, to weakly interacting cages isolated in a P-rich matrix. The close correspondence between the frequencies of the modes observed in the glass and in the crystalline phase α - P_4Se_3 shows unambiguously that the cage molecules of the latter form an important feature in the structure of the glasses of different macroscopic stoichiometry.

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