Experimental Evidence for an Inorganic Molecular Glass

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Inelastic neutron-scattering experiments have been performed for the first time on glassy phosphorus-selenium alloys. The effective density of vibrational states so obtained is highly structured in the case of glassy $P_{0.67}Se_{0.33}$ and provides evidence for the existence of molecular clusters in the structure based predominantly on P_4Se_3 units, i.e., a "zero-dimensional" glass.

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The atomic-scale structure of glasses, particularly concerning medium- (or intermediate-) range order, is still a very contentious issue. One useful way of approaching this problem for the case of inorganic glasses is in terms of the local network dimensionality.[1] Thus, a "zero-dimensional" (0D) structure corresponds to a molecular glass whose structure is (ideally) composed entirely of discrete molecular species.[2] The interest in such materials lies in the fact that for these the local short-range structure is well defined and so its influence on the medium-range order can be assessed. However, until now there has been no direct experimental evidence for the existence of such stable 0D structures in the bulk glassy phase for inorganic materials. There is evidence, e.g., from photoemission,[3] that, for example, evaporated thin films of As_xS_{1-x} are composed primarily of As_4S_4 molecular clusters; however, these films are extremely unstable and, upon annealing or exposure to light, polymerize readily to form a cross-linked network very similar to that of the bulk glass. In addition, sharp peaks have been observed in the Raman spectra of certain inorganic bulk glasses, for example B_2O_3 (Ref. 4) and $GeSe_2$ (Ref. 5), perhaps indicative of decoupled molecular modes; however, the vibrational densities of states (VDOS) for B_2O_3 (Ref. 6) and $GeSe_2$ (Ref. 7) do *not* exhibit correspondingly sharp intense features, indicating that molecular characteristics, if responsible, are not a dominant structural motif.

It is interesting, therefore, that recently Price and coworkers[8,9] have suggested, on the basis of (elastic) neutron-scattering, extended x-ray absorption fine structure, and Raman scattering results on selenium-rich phosphorus selenide glasses, that the system P_xSe_{1-x} might be a possible candidate for such 0D amorphous structures. With this in mind, we have undertaken the first inelastic neutron-scattering studies of P_xSe_{1-x} glasses, in particular, investigating the previously unstudied *phosphorus*-rich compositions. (In addition, elastic neutron diffraction experiments have been carried out on the same compositions.[10]) The motivation behind such studies has been to obtain information on the VDOS, unaffected by the matrix-element effects which occur in Raman scattering. A signature of vibrationally decoupled molecular clusters comprising a molecular (0D) glass is expected to be a vibrational spectrum exhibiting characteristically narrow peaks corresponding to the individual vibrational modes of the clusters, unbroadened by coupling of these modes to the rest of the structure.

The P_xSe_{1-x} system forms glasses over a wide range of compositions, although two distinct regions can be distinguished[8,11]: For Se-rich compositions, glasses can be produced for $0 < x < 0.52$, and in addition, P-rich compositions can be rendered glassy for $0.63 < x < 0.85$. Glassy samples with compositions corresponding to $x = 0.29$ and 0.40 from the first glass-forming region and $x = 0.67$ from the second were prepared by direct reaction of the elements—details of the preparation procedure are given elsewhere.[10] Powdered samples of the glasses with a volume $4 \times 100 \times 25$ mm^3 were sandwiched between thin Al plates in a flat-plate sample holder. The inelastic neutron-scattering measurements were performed at the high-flux reactor at the Institut Laue-Langevin, Grenoble, with the double-monochromator thermal-neutron time-of-flight spectrometer IN4. An incident energy of $E = 67$ meV (corresponding to a neutron wavelength of 1.1 Å) was used; counting times were typically ~ 12 h.

The data were corrected for background and absorption effects with standard procedures,[12] although Monte Carlo simulations for multiple-scattering corrections were not performed. Beyond the region of the elastic peak, the data were smoothed with a cubic spline fit, and in order to obtain cuts through the dynamical structure factor $S(Q,E)$ at constant Q, spline functions were fitted to the data at constant E. In this way, values of $S(Q,E)$ were obtained over a Q range of $0.7 < Q < 8.0$ Å^{-1} (at $E = 0$) and a range of energy transfers $0 < E < 55$ meV. [It should be noted that because the incoherent scattering is $< 4\%$ for both P and Se, $S(Q,E)$ is approximately equal to the coherent scattering function $S_c(Q,E)$.] The data were subsequently normalized by comparison of the calculated $S(Q) = \int_{\infty}^{\infty} S_c(Q,E)dE$ with that obtained experimentally.[10]

Finally, an estimate for the average one-phonon density of vibrational states $G(E)$ was calculated from[12]

$$G(E)=\int_{Q_1}^{Q_2}\frac{G(Q,E)}{Q_2-Q_1}dQ, \tag{1}$$

where the generalized density of states $G(Q,E)$ was obtained with the expression[12]

$$S_{c,1}(Q,E)=e^{-2w}\frac{-\hbar^2Q^2}{2\bar{m}E}\langle n_j+1\rangle G(Q,E), \tag{2}$$

where $\langle n_j+1\rangle=[1-\exp(-\hbar\omega_j/kT)]^{-1}$, the average mass is defined as $\bar{m}^{-1}=\sum m_i^{-1}/N$ and $e^{-2\bar{w}}$ is the Debye-Waller factor, obtained by a procedure described elsewhere.[10] It should be pointed out, however, that $G(E)$ is not identical to the true density of vibrational states $\rho(E)$ because of the differences in the masses and scattering lengths of P and Se, and because the incoherent approximation is not valid. However, the essential features of the density of states are expected to be retained. It should also be noted that because of the relatively poor resolution near the elastic line of the IN4 spectrometer, the data are only reliable for energy transfer $\gtrsim 10$ meV.

The experimental density of vibrational states for the phosphorus-rich glass, $P_{0.67}Se_{0.33}$, is shown in Fig. 1. Inspection of the raw data indicates that all the major features appear as in the smoothed density of states, indicating that the smoothing procedure has not introduced any spurious peaks into the spectrum. (It should also be pointed out that because of the difficulties in obtaining accurate subtractions in the vicinity of the elastic line, it is likely that the first peak in the inelastic spectra of Figs. 1 and 2, at $\simeq 14$ meV, is a artifact.) It is immediately apparent from Fig. 1 that the vibrational spectrum of glassy $P_{0.67}Se_{0.33}$ is remarkably rich in detail, and, moreover, that the observed peaks in the density of states are very narrow, bearing in mind that the material is a glass. (The resolution of IN4 is $\simeq$3-4 meV, comparable to the width of some of the peaks, indicating that these peak widths are probably resolution limited.) The densities of states for two Se-rich compositions, $P_{0.29}Se_{0.71}$ and $P_{0.4}Se_{0.6}$ are also shown for comparison in Fig. 2. These two vibrational spectra are rather similar to each other, but a comparison of Figs. 1 and 2 shows that $G(E)$ for $P_{0.67}Se_{0.33}$ is considerably more structured, particularly at higher energies.

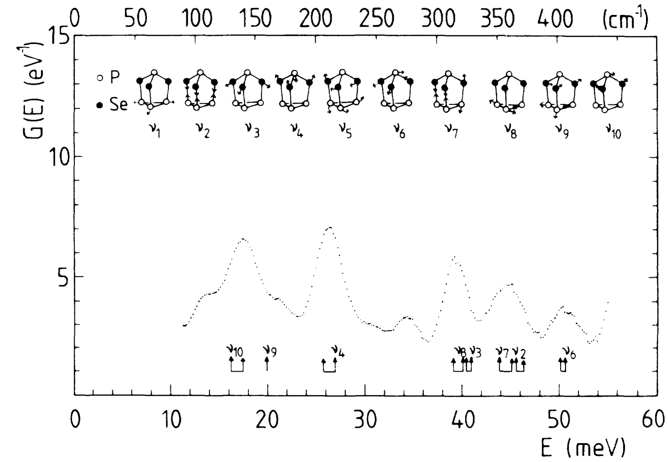

FIG. 1. Inelastic neutron VDOS for glassy $P_{0.67}Se_{0.33}$. Inset: Ten normal modes of the P_4Se_3 molecule, and the ranges in position of the Raman peaks for crystalline P_4Se_3, assigned in terms of these modes (Ref. 13), are also shown.

The richness of the vibrational density of states for g-$P_{0.67}Se_{0.33}$, taken together with the narrowness of the peaks therein, is strongly suggestive of a molecular character to the structure, indicating that this might be a 0D glass, rather than a network material as it appears to be in the case for the chemically related system As_xSe_{1-x}.

Several P_4Se_n molecularlike species are known from gas-phase and single-crystal studies,[14] although the only appreciably stable P-rich molecular species appears to be P_4Se_3. Indeed, the stability of this molecule is such that its composition lies at the boundary between the two glass-forming regions in the P-Se system, and only crystalline material results on quenching P-Se melts with compositions near $x=0.57$ (see later). It is therefore natural to ascertain whether the vibrational characteristics of the molecular specie P_4Se_3 can account for the VDOS shown in Fig. 1. This molecule has a highly symmetric cagelike structure with C_{3v} symmetry, with three basal phosphorus atoms (P_b) in a highly strained threefold ring, each connected to a Se atom and thence to an apical phosphorus atom (P_a) (see inset in Fig. 1). A number of Raman (and ir) spectroscopic studies have been performed on P_4Se_3 in both the crystalline and liquid states.[8,13,15-17] Two crystalline phases of P_4Se_3 exist, a low-temperature form (α) and a plastic phase (β) stable above 355 K,[18] and differences in the Raman peak positions between the two phases are discernible in the published data, particularly for the low-frequency

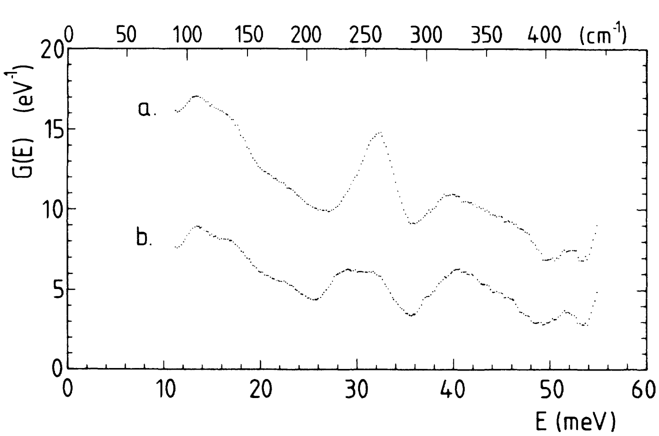

FIG. 2. VDOS for (curve *a*) glassy $P_{0.29}Se_{0.71}$ and (curve *b*) glassy $P_{0.4}Se_{0.6}$. The data sets have been displaced vertically for clarity.

modes. Moreover, there are appreciable differences in the reported peak positions for α-P_4Se_3 itself, the phase most studied, a problem compounded by the crystal-field and Davydov splittings prevalent particularly at low temperatures.[17,18] The range of these reported Raman frequencies is given in Table I. In addition, some theoretical vibrational analyses of P_4Se_3 have been performed,[16,19] although the agreement with experimental mode frequencies is often relatively poor, perhaps casting doubt on some of the mode assignments[13] given in the table and Fig. 1.

It can be seen that of the ten vibrational modes of the P_4Se_3 molecules, six can be identified closely with peaks in the VDOS for g-$P_{0.67}Se_{0.33}$ (Fig. 1 and Table I). Of the remaining four, the one at highest frequency (ν_1) could not be measured in this experiment due to the limited energy transfer possible under the conditions employed and one (ν_5) is neither Raman nor ir-active and so its experimental value is unknown; the other two correspond to vibrational modes with very similar frequencies, viz., (ν_3, ν_8) and (ν_2, ν_7), and it is expected that the poorer resolution of the inelastic neutron-scattering experiment (25–30 cm^{-1}) compared with that of Raman scattering would mean that they would be essentially unresolvable in these experiments. It is very interesting to note, however, that a recent Raman study[20] of g-$P_{0.67}Se_{0.33}$ reports peak frequencies essentially identical to those found here, and that the dominant Raman band at $\sim$360 cm^{-1} is resolved into two components (ν_2, ν_7). The observation of a clearly defined peak in the VDOS at $\sim$360 cm^{-1} is very significant since the assigned modes (ν_2, ν_7) are the only ones (in addition to ν_5, ν_9) which are completely representative of cage vibrations; all other modes involve vibrations of either apical or basal atoms only (see Fig. 1), and could therefore also appear in a network structure.

TABLE I. Experimental and theoretical values for the vibrational frequencies of molecular P_4Se_3 and glassy $P_{0.67}Se_{0.33}$.

Mode (character)	Theoretical frequency[a] (cm^{-1})	Raman frequency[b] (cm^{-1})	Neutron VDOS[c] (cm^{-1})
ν_{10} (E)	117	130–140	112[d] 140
ν_5 (A_2)	127	...	
ν_9 (E)	201	160	163
ν_4 (A_1)	187	207–217	211
ν_8 (E)	353	315–323	317
ν_3 (A_1)	297	326–330	
ν_7 (E)	402	352–363	360
ν_2 (A_1)	356	367–373	
ν_6 (E)	415	404–407	408
ν_1 (A_1)	470	485–486	

[a] P_4Se_3 (Ref. 16).

[b] Crystalline $\alpha(\beta)$-P_4Se_3 (Refs. 8 and 13, 15–17).

[c] Glassy $P_{0.67}Se_{0.33}$ (this work).

[d] Possibly an artifact of data reduction procedure.

An additional peak is observed in the VDOS of g-$P_{0.67}Se_{0.33}$ which is *not* accounted for by the vibrational modes of P_4Se_3 molecules, namely that at 278 cm^{-1}. It is interesting to note that this frequency lies in the region $\simeq$220–320 cm^{-1}, where no vibrational modes for P_4Se_3 are predicted or observed.[13] However, examination of the VDOS for amorphous elemental phosphorus indicates that a dominant peak appears at $\simeq$280 cm^{-1}.[21] A vibrational analysis for the Hittorf crystalline modification of phosphorus has shown[22] that modes in this frequency range arise from localized rotational vibrations of groups of atoms associated with the P_8 and P_9 clusters present in the structure of this polymorph, indicating that such clusters could be present in the structure of a-P too. We propose, therefore, that the observation of the peak at $\simeq$278 cm^{-1} in the VDOS of g-$P_{0.67}Se_{0.33}$ may be a signature of phosphorus-related clusters in the structure. Such clusters may arise through phase separation, but we believe instead that they arise naturally in the P-Se clusters believed to be present in this 0D glass. In fact, in order to maintain stoichiometry, an extra two P atoms per P_4Se_3 molecule need to be incorporated into the structure, and a suggested configuration for such P inclusions is indicated in Fig. 3. In this case, a strained bond between two basal P_b atoms is broken and new bonds made with the inserted P atoms. It is noteworthy that the configuration in Fig. 3 is very similar to that of the P_8 cluster found in Hittorf (and amorphous) P,[22] and the vibrational characteristics would therefore be expected also to be very similar. It is proposed, therefore, that such phosphorus clusters are the origin of the 278-cm^{-1} peak in the VDOS of g-$P_{0.67}Se_{0.33}$. The other vibrational modes of the P clusters have similar frequencies to those of the P_4Se_3 molecule,[8,13,15–17] in particular at $\simeq$370 cm^{-1}, and this may explain why the peak in the VDOS at this energy is somewhat broader than the others. It should be noted that the insertion of extra P atoms in configurations such as that shown in Fig. 3 essentially preserves the cagelike molecular nature of the P_4Se_3 moieties, and therefore the vibrational modes involving the apical P atoms and the Se atoms would be very little

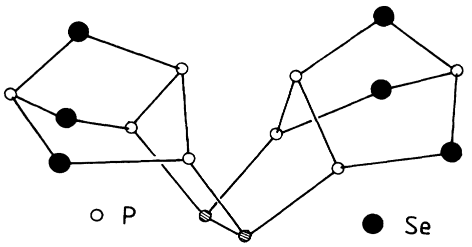

FIG. 3. Suggested cross-linking configuration between two P_4Se_3 molecules involving a cagelike phosphorus cluster. The inserted P atoms are shown as the hatched circles.

affected. The vibrational spectrum of the whole unit can be assumed, to a first approximation, to consist of a superposition of vibrational modes characteristic of P_4Se_3 and P clusters; theoretical calculations are planned to confirm this point.

It is worth remarking that a peak at a frequency of $\simeq 254$ cm^{-1}, characteristic of the optic mode of *a*-Se,[23] does not appear at all in the VDOS of *g*-$P_{0.67}Se_{0.33}$ (Fig. 1), while its contribution becomes increasingly important for Se-rich glasses (see Fig. 2). This observation is in accord with the conclusions of Price *et al.*[8] from Raman scattering experiments that the structure of Se-rich P_xSe_{1-x} glasses consists of a matrix of Se, possibly containing remnants of Se-rich P_4Se_n molecular entities. However, contributions of modes involving trigonally bonded P-Se_3 units, viz., ν_3, ν_4, ν_6, and ν_{10}, are still discernible in the VDOS of *g*-$P_{0.4}Se_{0.6}$, and are probably signatures of P atoms in network, rather than cluster, configurations.

Finally, we offer a suggestion for the reason why, for P_xSe_{1-x} materials, the Se-rich glass-forming region ends at $x=0.52$ while the P region starts at $x=0.63$.[8,11] We have already remarked that between these two compositions crystalline P_4Se_3 forms on quenching the melt. We suppose that, for compositions very close to that of P_4Se_3, crystallization is favored because there are no influences which restrict the effectively free rotation of the very symmetric P_4Se_3 molecules, with the result that the lowest-energy state, viz., the crystal, will always be reached on cooling the melt. In order to form a glass the rotational freedom needs to be appreciably restricted so that the rotational disorder characteristic of the melt is quenched in, and this can be achieved either by some form of cross linking of the molecules or by a process of phase separation in which P-rich or Se-rich glassy regions separate isolated P_4Se_3 (or other) clusters. The minimum degree of cross linking that can be envisaged involves the breaking of one strained basal P_b-P_b bond in each of a neighboring pair of P_4Se_3 molecules and the subsequent insertion of and rebonding with a pair of either Se atoms (on the Se-rich side) or P atoms (on the P-rich side)—see Fig. 3. If this pairwise molecular cross linking is deemed to be sufficient to quench in rotational disorder, we would predict therefore that the limits to the two glass-forming regions correspond to $x=0.5$ and $x=0.63$, respectively, values which are very close to those observed experimentally.[11]

In conclusion, we have presented evidence from inelastic neutron-scattering experiments for the first unambiguous observation of a stable inorganic molecular (zero dimensional) glass. This material, $P_{0.67}Se_{0.33}$, exhibits a vibrational density of states consisting of a series of narrow peaks which can be completely understood in terms of the vibrational modes of P_4Se_3—related molecular clusters together with a minor component of clustered (cagelike) phosphorus atoms. Further confirmation for the presence of molecular clusters in the glass could come from examination of the Q dependence of the inelastic scattering intensity. However, the present data have insufficient signal to noise to allow this behavior to be investigated; further experiments are planned to study this aspect further. Structural simulation studies are currently in progress with the aim of understanding the medium-range order in terms of the molecular short-range order found in these glasses.

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