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1989 J. Phys.: Condens. Matter 1 10361

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***Ab initio* calculations on topological defects in amorphous phosphorus**

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Received 17 April 1989

Abstract. The structure and dynamic properties of over-coordinated P_4 and under-coordinated P_2 defects in a-phosphorus are explored using local density functional methods applied to large clusters of phosphorus atoms. The energy levels of the states associated with these defects are found and the structural change on exciting an electron-hole pair are described. Our principal conclusions are that VAPs and IVAPs are stable when formed by shearing tubes present in Hittorf's phosphorus; the P_2 and P_4 defects give rise to vibratory modes around 330 cm^{-1} and 500 cm^{-1} respectively and that large Stokes shifts are to be expected since significant structural changes occur upon photoexcitation. This is especially so when an electron is promoted to a P_4 state from a P_2 state, but less so when it is excited from the valence band.

1. Introduction

The structure of red a-P prepared by heating white phosphorus above 250°C is uncertain. There are two main models based on different allotropes of crystalline phosphorus: Hittorf's and black P.

Hittorf's P crystallises in the monoclinic space group $P2_1/C$ and has a unit cell containing 84 atoms. Thurn and Krebs (1969), Olego *et al* (1984) and Fasol *et al* (1984) argue that this forms the basis of red a-P. Its structure consists of layers of pentagonal tubes. Each tube contains 8 and 9 atom cages joined by a pair of P atoms in a boat configuration as illustrated in figure 1. The tubes are stacked together, being bonded at only a few places so that each tube is joined to one lying above and almost perpendicular to it. Only one atom in 21 has bonds which couple tubes together. This bond is 2.18 \AA long and is the shortest P–P bond. The other P–P bond lengths range up to 2.303 \AA with bond angles around 102° . By comparing peaks in the radial distribution functions of red a-P and distances between atoms in a single tube in Hittorf's phosphorus, Thurn and Krebs (1969) concluded that these tubes form a major structural component of the amorphous phase. The vibration modes of the crystal fall into three bands, the lowest of which ranges from 0 to $\sim 160\text{ cm}^{-1}$ and whose normal coordinates consist of extended bending modes of tubes. There is a gap or pseudogap around 170 cm^{-1} and thereafter a band of modes up to $\sim 300\text{ cm}^{-1}$ due to localised bond bending. This vibration spectrum is quite different from black P which has no gap up to $\sim 300\text{ cm}^{-1}$. Moreover, the spectrum of a-P does indeed have a pronounced pseudogap around 170 cm^{-1} , which shows that its structure cannot be that of layered black-P. The optical gap of Hittorf's

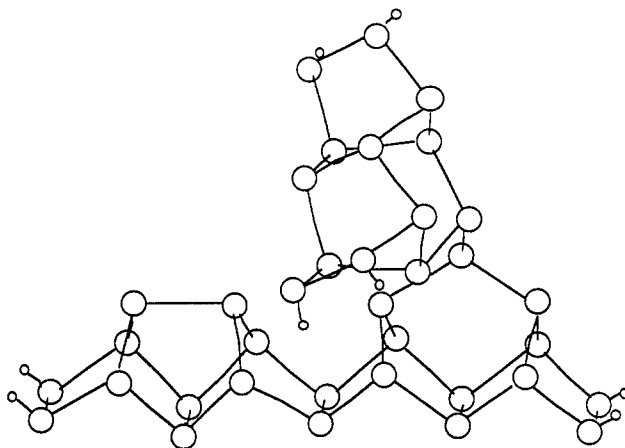


Figure 1. The 44-atom cluster $P_{36}H_8$ arranged as in Hittorf's phosphorus. The lower part of the cluster shows clearly the 8- and 9-atom cages. The upper part shows another tube almost perpendicular to the lower one.

P, ~ 1.9 eV (Fasol *et al* 1984), is quite close to that of red a-P. Other relevant P structures are the polyphosphides like NaP_{15} . These consist of pentagonal tubes of P atoms which are isolated and not joined together. Instead every 15th P atom is two-fold coordinated and close to a cation. Again they have a band gap close to that of red a-P.

The CRN model of a-P (Greaves *et al* 1979) is based on distortions of another allotrope of phosphorus, namely black P. This is a layered material with a double puckered layer of bonded P atoms. The layers are said to be joined with Van der Waals forces. The P–P intralayer length is 2.2 \AA and the bond angle is close to 102° . The smallest interlayer P–P length is 3.59 \AA . Beyeler and Veprek (1980), using a-P prepared by a different process (plasma chemical transport), found a well resolved third peak of the radial distribution function at 4.15 \AA , which they attributed to the third-neighbour distance in P_6 rings found in each double layer in black P. Thurn and Krebs (1969) were also able to resolve a third peak in the RDF of red a-P (prepared in the usual way) at 4.28 \AA and, as this separation is not found in Hittorf's P, attributed it to a different arrangement of tubes in the amorphous structure.

Black P has a small gap of only 0.3 eV, which can be understood (Takao *et al* 1981) as arising from the strong broadening of the highest occupied and lowest unoccupied states of a single layer, which are both composed of p orbitals perpendicular to the layers. This type of valence band casts doubt on whether or not the layers in black P are bonded together by Van der Waals forces. Such a broadening does not occur in Hittorf's P, which has a gap (1.9 eV) close to the polyphosphides and to red a-P. We consider that if red a-P did consist of large sections of layered material then the optical gap would be much smaller than that observed (2 eV). Furthermore the luminescence seen around 1 eV in both red a-P and Hittorf's phosphorus strongly suggests that this allotrope plays an important role in the structure of red a-P. This luminescence is then almost certainly linked to defects in both Hittorf's P and a random distribution of bonded tubes which we take as a model for ideal red a-P.

Mott *et al* (1975) and Street and Mott (1975) first proposed that the principal defects in chalcogenide glasses consisted of positively and negatively charged dangling bonds,

D^{+-} . Spin pairing is energetically favoured because of the strong relaxation energy resultant on charging the neutral defect (Anderson (1975). Kastner *et al* (1976) modified this model and suggested that the positively and negatively charged defects were over- and under-coordinated atoms, P_4 and P_2 respectively, and that dangling bonds were unstable relative to these. These valence alternation pairs (VAP) are attracted to one another by their coulomb attraction and hence the intimate pair (IVAP) is expected to be the most stable. Elliot and Davis (1979) considered this in greater detail specifically for group V materials. They argued that although the energy difference between the 3s and 3p levels was considerable, the extra bonding energy arising from sp^3 hybridisation would be sufficient to stabilise over-coordinated atoms.

More evidence comes from time-resolved photoluminescence experiments. Early workers (Fasol *et al* 1982, Fasol 1985) found two broad luminescent bands: the high-energy (HE) band at 1.4 eV which dominated after long (ms) time delays, and the low-energy (LE) band dominant at shorter times (ns). They assigned Stokes shifts of 0.5 eV and 0.85 eV respectively to these. There is also a zero delay band at ~ 1.4 eV. Depinna and Cavenett (1983) carried out ODMR experiments and interpreted the HE and LE bands as recombination between carriers trapped on different IVAPS (inter-IVAP) and recombination between carriers trapped on the same IVAP (intra-IVAP) respectively. This model can correctly account for the ordering of the energies of the two processes. However, further work showed this explanation to be untenable.

Sobiesierski and Phillips (1986, 1987) showed that, in the first 150 ns after excitation, the luminescent peak moves from higher energies: 1.4 eV at 10 ns to 1.15 eV at 150 ns. They showed that the luminescence profile could be well fitted by a single gaussian with a monotonically decreasing width at all times during this shift, and concluded that a single process was involved (i.e. this was still part of the LE band). By comparing work of Fasol (1985) with that of Sobiesierski and Phillips (1986), it is seen that the excitation energy dependence of the pl peak was the same for both the LE and HE bands, indicating that a common centre was involved. This had also been suggested by the ODMR experiments of Depinna and Cavenett (1983). However Sobiesierski and Phillips (1986) showed that the decay with time of the (shifting) LE band required a distribution of lifetimes, correcting some earlier measurements and interpretations.

The shift of the LE peak with delay after excitation could be due either to 'slow thermalisation' of excited carriers or to recombination at different defects. Picosecond photoluminescence work by Phillips *et al* (1987) showed that the energy dependence of the initial decay rate is inconsistent with a simple model of thermalisation due to Kastner (1980). If the shift is due to recombination at different defects, then at the shortest delays recombination is expected to occur at IVAPS where the luminescent energy would be greater due to the coulomb potential of the charged ground state, and for longer delays, at VAPS of progressively increasing separation. However, if the coulomb term is used to explain the shift of the LE band, it cannot also explain the energy difference between the HE and LE bands within the framework of Depinna and Cavenett's (1983) model. Thus, Phillips and Sobiesierski (1987) proposed that the LE band was due to recombination between carriers trapped on intrinsically charged under- and over-coordinated atoms of variable separation, with the coulomb term explaining the energy shift in the first 150 ns. The HE process was then ascribed to recombination between electrons trapped on P_4 sites and holes in valence band tail states. This model has a centre (P_4) common to both processes as required. The P_4 states must then form a broad band of electronic states just below the conduction band and the P_2 states a band just below mid-gap.

Theoretical calculations to determine the positions of the states in the gap have been carried out by Pollard and Joannopoulos (1979) and O'Reilly and Kelly (1981). Both

these calculations found that two-fold coordinated group V elements produce levels which are lower in the gap than those associated with over-coordinated atoms. However both calculations used an empirical tight-binding approach which gave results strongly dependent on the parametrisation. Also relaxation around the defect (expected to be important for deep level defects) was either carried out using a simple Keating potential or ignored completely so that the stability of the defects could not be investigated. Charge transfer effects, important for these charged defects, were also ignored.

Nemanich *et al* (1978) analysed the vibrational modes of topological defects in a-As using a Bethe lattice. They found, using force constants derived from a fit to the molecule As_4 , that the over-coordinated defect has a mode just above the highest frequency seen in crystalline As. There is evidence in the Raman spectrum of a mode of this frequency. This has been cited as evidence for the existence of over-coordinated defects. No mode localised on the under-coordinated As atom was found.

Here we present results of *ab initio* calculations on several defect structures containing under- and over-coordinated phosphorus atoms P_2 and P_4 respectively. This method allows us to take into account the effects of charge transfer between atoms and to move them in response to the forces acting on them. It allows us to determine accurately the structure of the defects as well as their vibrational properties.

We briefly describe the method used in § 2. In § 3 we apply the method to discuss the smallest possible cluster P_6H_8 for which a P_4 - P_2 defect can be constructed. It is remarkable that many of the expected properties of the defects are illustrated by this small cluster. In § 4 we consider larger clusters based on tubes of Hittorf's P. We investigate a defect suggested by Phillips and Sobiesierski (1987) and find it to be unstable. We then consider defects arising from the shearing of two tubes and show that they indeed give rise to stable P_2 - P_4 structures. We also analyse the structure of these in excited states, showing that considerable structural changes are likely on photo-excitation leading to large Stokes shifts. In § 5 we consider how the vibrational properties of such defects may be determined. Finally in § 6 we give our conclusions.

2. Method

The calculations presented here are from first principles (*ab initio*) in the sense that they contain no empirical parameters but take as input only atomic numbers and atomic masses. We use non-spin-polarised local density functional (LDF) theory (Hohenberg and Kohn 1964, Kohn and Sham 1965) with an approximation for exchange and correlation (Ceperley and Alder 1980, Perdew and Zunger 1981) in conjunction with a first-principles norm-conserving pseudopotential generated using a prescription proposed by Bachelet *et al* (1982). Our formalism is described in some detail in previous papers (Jones and Sayyash 1986, Jones 1988) and so we give only a brief account here.

We perform the calculations on clusters of P atoms containing defects. The clusters are terminated with H atoms which serve to tie up dangling bonds. These would otherwise give rise to levels in the gap which are difficult to distinguish from intrinsic defect states. Unfortunately these H atoms have bonding and anti-bonding levels which mix strongly with states at the top of the valence and bottom of the conduction band respectively and lead to a larger band gap than observed, even though LDF theory for a periodic solid is expected to give a smaller gap. However, as has been found with these calculations in the past, an incorrect band gap does not appear to affect other properties such as

bond lengths and angles, formation energies or vibrational frequencies, and the LDF approximation has always been very successful in determining these.

We employ two bases of Gaussian orbitals (centred on both the atoms and the middle of P–P bonds) with which we fit both the wavefunction and the charge density. The wavefunction on each phosphorus atom is fitted to four linear combinations (s , p_x , p_y , p_z) each of four gaussians and the charge density to four s gaussians on each atom. Each hydrogen atom has four linear combinations each of two gaussians for the wavefunction basis and three s gaussians are used to fit the charge density. Four wavefunction basis functions and one charge density basis function are placed on each bond centre. The approach is completely self-consistent, with charge being allowed to flow around the cluster in such a way as to minimise the total energy. Forces on each atom are calculated semi-analytically and a conjugate gradient method used to relax each cluster.

The particular problems we address are: whether or not P_4 and P_2 defects are stable; in which regions of the gap their energy levels lie; and whether or not the excited state structures are radically different from the ground state ones leading to large Stokes shifts. We also investigate whether the defects have localised vibrational modes.

Two problems associated with density functional theory arise in connection with these questions.

(i) Since density functional theory is rigorously correct for the ground state, or for certain excited states which have a conserved quantum number like L or S distinct from the ground state (Von Bath 1979), and not expected to be so for excited states in general, one can question whether LDF theory can be usefully employed to estimate Stokes shifts. Gunnarson *et al* (1977) investigated the structure and dynamic properties of excited states, namely nearby multiplets of C_2 , using both spin-polarised and non-spin-polarised local density functional theory with Slater exchange. They partially occupied the π_u and σ_g molecular levels to generate spin densities corresponding to Slater determinants of the correct symmetry. Specifically they used the configurations $\pi_u(\uparrow\uparrow\downarrow\downarrow)$, $\pi_u(\uparrow\uparrow\downarrow)\sigma_g(\uparrow)$, $\pi_u(\uparrow\uparrow\downarrow)\sigma_g(\downarrow)$, $\pi_u(\uparrow\uparrow)\sigma_g(\uparrow\downarrow)$. These determinants are trial wavefunctions for the multiplets $^1\Sigma_g^+$, $^3\Pi_u$, $^1\Pi_u$ and $^3\Sigma_g^-$ respectively. They found that the bond lengths and vibrational frequencies of each excited state were less than 0.1 Å above and 200 cm^{-1} below the experimental ones (errors of 4% and 12% respectively), with the trend on changing the multiplet correctly given. The non-spin-polarised theory gave the same results.

Experimentally, the binding energy of $^1\Sigma_g^+$ is slightly above that of $^3\Pi_u$, but the LDF theory reversed this ordering. In general the LDF energies are in poor agreement with experiment. Nevertheless, we conclude that the use of LDF theory in excited states can give realistic structures, and to explain large Stokes shifts we need only show that there is a substantial difference between the excited and ground state structures.

(ii) The second problem concerns the one-electron energy levels. These are not given correctly by LDF theory, and there is no formal justification for using them. However, even if the position of the defect levels is not given exactly, the level can still be identified by the form of the wavefunction associated with it (for example a state in the band gap whose wavefunction is localised and has p character is obviously a dangling bond state associated with an under-coordinated or P_2 atom). Also, it is possible to judge roughly where a level falls from a DFT calculation (e.g., it is possible to distinguish between deep and shallow levels), although the band gap is always incorrectly estimated. One should note however that the total energy of the cluster in its ground state is given correctly by density functional theory and thus formation energies should also be correctly given.

One feature of interest is the extent to which any given state is localised on or around a particular defect atom. There are several ways of describing this. We choose a prescription proposed by Mulliken which is especially easy to apply within the formalism of a localised basis set.

If the wavefunction of energy level λ is written as a linear combination of basis functions, $\varphi_i(\mathbf{r})$:

$$\Psi_\lambda(\mathbf{r}) = \sum_i c_i^\lambda \varphi_i(\mathbf{r})$$

then the charge density associated with this level may be written

$$n_\lambda(\mathbf{r}) = \sum_{i,j} c_i^\lambda c_j^\lambda \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}).$$

We then define the Mulliken population on site ' i ' associated with energy level λ to be

$$m_i^\lambda = c_i^\lambda \sum_j c_j^\lambda \int \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) d\mathbf{r}.$$

Clearly,

$$\sum_i m_i^\lambda = 1$$

as required by normalisation and, if the population is large on a particular atom or bond centre, then this implies that the wavefunction is large there. The Mulliken populations therefore serve as a measure of the localisation of the different states.

3. The 14-atom cluster P_6H_8

This small cluster illustrates many of the experimental results on red a-P surprisingly well, even though its predictions are quantitatively incorrect as would be expected.

The central six phosphorus atoms arranged as in a layer of black P have terminating H atoms (figure 2(a)). The relaxed bond lengths and angles are within a few % of black P although our cluster has an excitation energy of 4.1 eV. This last result is obtained by calculating the difference between the self-consistent total energies of the cluster in its electronic ground state and the state formed by promoting an electron to the first empty level. In this particular case, it is also equal to the difference between the highest filled and lowest unoccupied electronic energy levels of the cluster in its ground state. In the following, energies of all other one-electron levels are quoted relative to the top of the valence band (E_v) and the excessive size of the gap should be borne in mind when considering these—for example a level at $E_v + 1.7$ eV is just below mid-gap even though the experimental band gap in red a-P is only ~ 2 eV.

To create an IVAP (figure 2(b)), a PH_2 unit was pulled from the top P atom (figure 2(a)) and brought closer to the lower P atom. The whole cluster was then relaxed. We found the $\text{P}_4\text{-P}_2$ defect to be stable with a formation energy of 1.0 eV. There are now two states in what was previously the gap. The lower filled state ($E_v + 1.7$ eV) is localised around the P_2 atom (it had a Mulliken bond population of 70% on this atom). The lowest unoccupied state is localised on the P_4 atom and its neighbours. We then excited a electron from the P_2 level to the unoccupied P_4 one. The absorption energy (i.e. the difference in total self-consistent energies) is 2.7 eV. The system was then relaxed in this

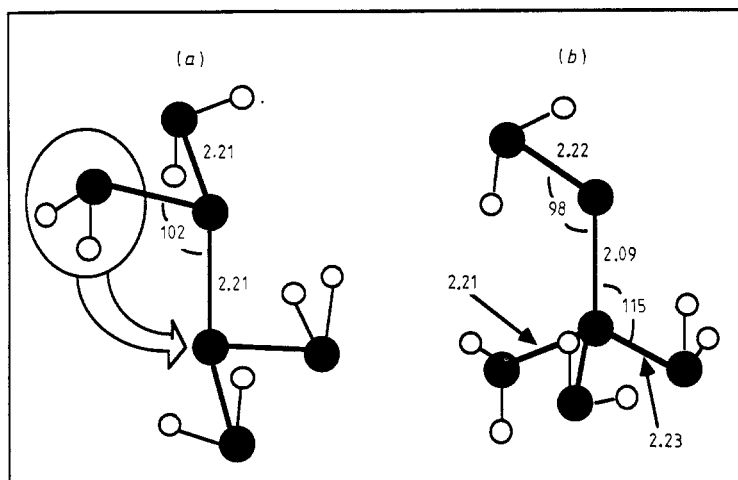


Figure 2. The cluster P_6H_8 . (a) shows the cluster arranged as in black phosphorus and how the IVAP shown in (b) may be produced by moving a PH_2 group.

excited state and this resulted in the P_4 - P_2 bond length increasing by 20% to 2.65 Å. The luminescent energy is then the difference in energy between this relaxed excited state and the electronic ground state with this structure and is 0.8 eV, thus giving a Stokes shift of 1.8 eV. Obviously this would be much reduced if the surrounding network prevented such a large relaxation.

4. Investigations on clusters derived from Hittorf's phosphorus

4.1. The perfect material

We constructed a 44-atom cluster $P_{36}H_8$ with the crystalline structure as shown in figure 1. As a program check, all the atoms were allowed to relax to minimise the total energy. We found the RMS difference between our equilibrium structure and that deduced by Thurn and Krebs (1969) to be 0.06 Å in bond length and 2° in bond angle (i.e. to within 3%—the usual accuracy in our approach). The band gap was 3.1 eV and a density of states (projected onto central atoms inside the cluster) is shown in figure 3.

4.2. The Phillips–Sobiesierski defect

Phillips and Sobiesierski (1987) suggested that one possible charged defect could be introduced by moving an atom as shown in figure 4, breaking one bond and forming another to create a VAP. We introduced this defect into two different clusters containing 30 and 50 atoms. However on relaxing these structures, the newly formed bond broke and the atoms relaxed back to their starting positions.

In carrying out this procedure, in order to have any chance of finding a stable defect, it was clearly important to ensure that the starting structure had sensible bond lengths and bond angles around the defect and also to make certain that the scheme adopted for relaxation should be representative of what would happen in the solid. For instance, in a solid, the surrounding network would provide constraints that would inhibit a fully

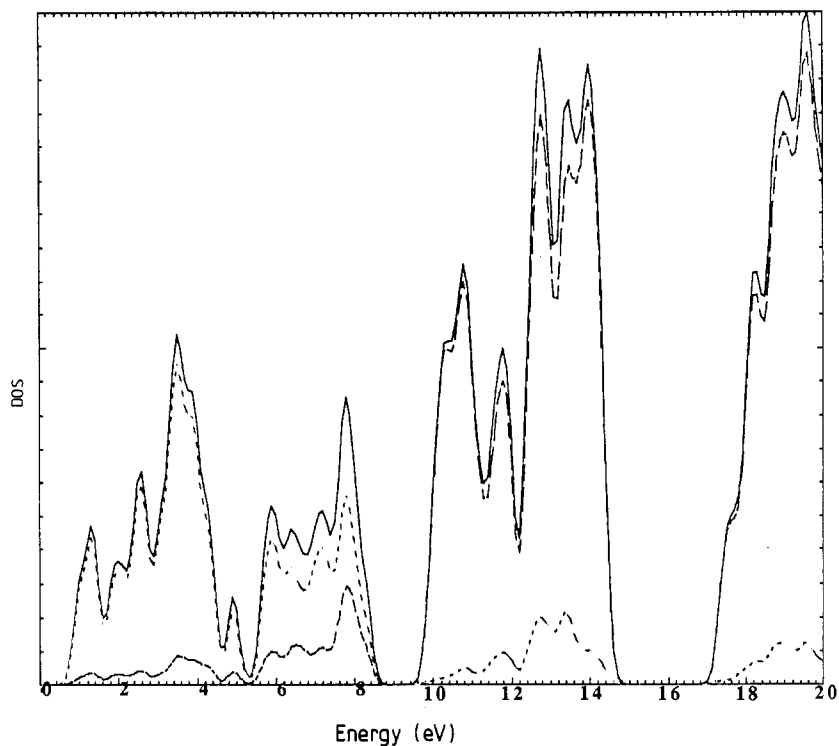


Figure 3. Electronic density of states of 44-atom cluster $P_{36}H_8$ arranged as in figure 1. The lower bands are mainly s-like whereas the upper valence bands are p-like. The gap, around 15 eV, is overestimated due to the hydrogen atom termination of the cluster. The dotted curve refers to s-like states, the broken curve to p-like states and the full curve to the total density of states.

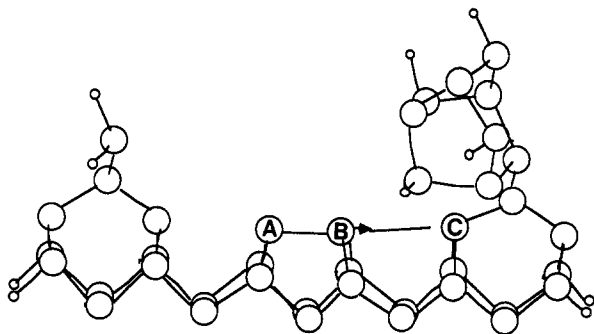


Figure 4. Formation of the Phillips-Sobiesierski defect. Atom B is displaced to the right as shown, breaking its bond with A and forming a new bond with C. The under- and over-coordinated atoms produced by this procedure are then A and C respectively.

comprehensive relaxation of the immediate neighbourhood of the defect, and these must be borne in mind when relaxing the cluster. For these reasons several different initial structures were used, one of which was relaxed with a valence force potential

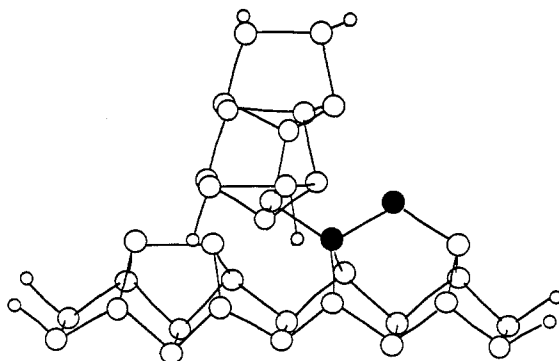


Figure 5. The 44-atom cluster $P_{36}H_8$ containing an IVAP formed by shearing the two tubes shown in figure 1. The over- and under-coordinated atoms are shaded.

which tried to make the bonds formed by the over-coordinated atom tetrahedrally distributed. Also in carrying out the structural relaxation, several schemes were carried out:

- (i) all the atoms in the cluster were relaxed simultaneously;
- (ii) only atoms B and C in figure 4 were relaxed, keeping the rest of the structure unchanged;
- (iii) all atoms in the cluster apart from B and C were first relaxed. This allowed the cluster to become accustomed to the presence of the defect to make the formation of a stable defect most probable. Having carried out this procedure, atoms B and C were then relaxed.

In all of the above procedures the newly formed bond between atoms B and C broke and reformed between atoms A and B. We therefore conclude that this defect is not stable and so cannot explain the luminescence properties of red a-P.

4.3. An IVAP created by shearing two connected tubes

Another way to introduce topological defects is to shear two bonded tubes present in Hittorf's phosphorus and then rejoin them at a different location. At the point where the tubes were separated a dangling bond (under-coordinated atom) is created and where they are joined back together an over-coordinated atom can be formed. By shearing the tubes through progressively greater distances it is possible to create VAPs of greater separation. In this way, stable defects could be formed.

This procedure was carried out using the 44-atom cluster shown in figure 1, producing an IVAP and a VAP (with a distance between the defect atoms of 3.7 Å).

First we consider the IVAP (figure 5). This was constructed as described above and then all 44 atoms were allowed to relax so as to minimise the energy. The formation energy of this IVAP relative to the perfect structure calculated above was 2.0 eV (the formation energy of this defect in bulk Hittorf's phosphorus would of course be larger due to the energy involved in causing longer-ranged deformations of the structure). This energy shows that they could not be formed thermally in large numbers. However, they could be thermally stable as the barrier to the movement of the tubes required for them to anneal out is likely to be considerable. The bond lengths surrounding the P_4 atom

ranged from 2.20 Å (which joins the P₂ atom) to 2.46 Å. The other longer bonds imply a lower chemical binding. The short bond is to be expected due to the Coulomb attraction between the atoms. The bond angles ranged from 96° to 111°. The bonds connecting the P₂ atom were each close to 2.2 Å and their angle was 104°.

A doubly occupied electronic level was introduced near mid-gap ($E_v + 1.3$ eV) whose wavefunction was substantially localised on the P₂ atom (it had a Mulliken population of 67% localised on this atom). A state localised on the P₄ atom was also produced (it had a population of 13% on the P₄ atom itself and 27% on its neighbours). However, the associated level was located *above* the lowest lying level of the conduction band, suggesting that in a-P the P₄ band would overlap with conduction band tail states.

An electron was then transferred from the highest occupied state to the lowest unoccupied state (i.e. not the P₄ state), whilst keeping the same structure. The difference between total energies, according to the Franck–Condon principle, is the optical excitation energy and equalled 2.3 eV. The structure was then allowed to relax in this excited state electronic configuration. A large structural change occurred: the bond joining the P₄ and P₂ atoms broke producing a three-fold coordinated atom and a P atom with only one bond (of length 2.24 Å—a typical P–P length). Two levels were produced in the gap: one exactly where the original P₂ level fell, the other just below the conduction band. Both were dangling bond states localised on the P₁ atom (with populations of 83% and 63% respectively).

The promoted electron was then transferred back to its ground state level, again keeping the same structure. The energy was re-evaluated and from the difference of total energies we found the luminescence energy to be 1.1 eV. Thus we have found a large Stokes shift. On allowing the structure to relax once more with the ground state electronic configuration, the broken bond reformed and the ground state structure of the IVAP was recovered. This shows that defects are neither created or destroyed in this excitation–luminescence cycle. A modest fatigue of photoluminescence is observed in a-P but this must be associated with a different defect.

A similar sequence of calculations was carried out but, instead of considering recombination with a hole trapped at a P₂ site, we promoted the electron from the valence band. This should correspond to the HE process according to the model proposed by Phillips and Sobiesierski (1987). On allowing this excited state structure to relax, no bonds broke and only a modest relaxation occurred, presumably because the wavefunction of the hole is much less localised than previously. We found a Stokes shift of ~0.5 eV—far smaller than that obtained for the previous process. This is consistent with the experimental ordering of the HE and LE processes within the framework of the model proposed by Phillips and Sobiesierski.

4.4. A VAP created by shearing tubes

A VAP could also be created by displacing the two tubes by a greater amount leading to a separation between P₄ and P₂ atoms of 3.7 Å. This gave a larger formation energy of 2.3 eV. The P₂ level occurred at $E_v + 1.4$ eV—almost exactly the same as for the IVAP above. This state had a 61% population on the P₂ atom. The P₄ level was again close to the conduction band. However, this time the level fell in the gap (0.2 eV below the conduction band) and had populations of 17% on the P₄ atom itself and 44% on the four nearest-neighbour atoms. Comparing the position of these levels with those of the IVAP, it is seen that the level associated with the P₂ atom changes by only 0.1 eV, whereas that associated with the P₄ atom changes by ~0.5 eV. This suggests that, in the solid, the P₄

levels would form a broad band overlapping the conduction band, whereas the P_2 levels would form a narrow defect band around mid-gap.

The optical excitation energy is 2.6 eV and relaxing the excited state structure again led to the dissociation of the P_4 structure, with the bond we formed in joining up the two sheared tubes breaking. We therefore ended up with a pair of P_2 defects.

5. Vibrational properties

5.1. Determination of interatomic potential

We now consider the vibrational properties of phosphorus and how these may be determined from first principles. We address the question as to whether or not under- or over-coordinated atoms give rise to observable localised vibrational modes (LVMS).

In order to determine the vibrational frequencies of any mode it is first necessary to determine the interactions between atoms, bearing in mind that the interactions around a defect may be considerably different from those in the perfect material. It is therefore necessary to determine two potentials—firstly, the interaction between P atoms in the normal three-fold coordinated configuration and then the changes in this due to changes in bonding.

The interatomic potential for Hittorf's phosphorus was obtained by evaluating second derivatives of the total energy of the relaxed 44-atom cluster (described in § 4) with respect to displacements of four central atoms:

$$\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 E_{\text{TOT}}}{\partial R_{i\alpha} \partial R_{j\beta}} \quad (i, j = 1, 4 \quad \alpha, \beta = x, y, z).$$

These four atoms had four intervening P atoms between themselves and the terminating H atoms and we therefore consider that the derivatives obtained would not be influenced by the termination. These 144 derivatives were then fitted to a five parameter valence force potential (Musgrave and Pople 1962) using a least-squares fitting procedure. That is to say, we wrote

$$E_{\text{TOT}} = \sum_{i=1}^{\text{no. of atoms}} V_i^{\text{pure}}$$

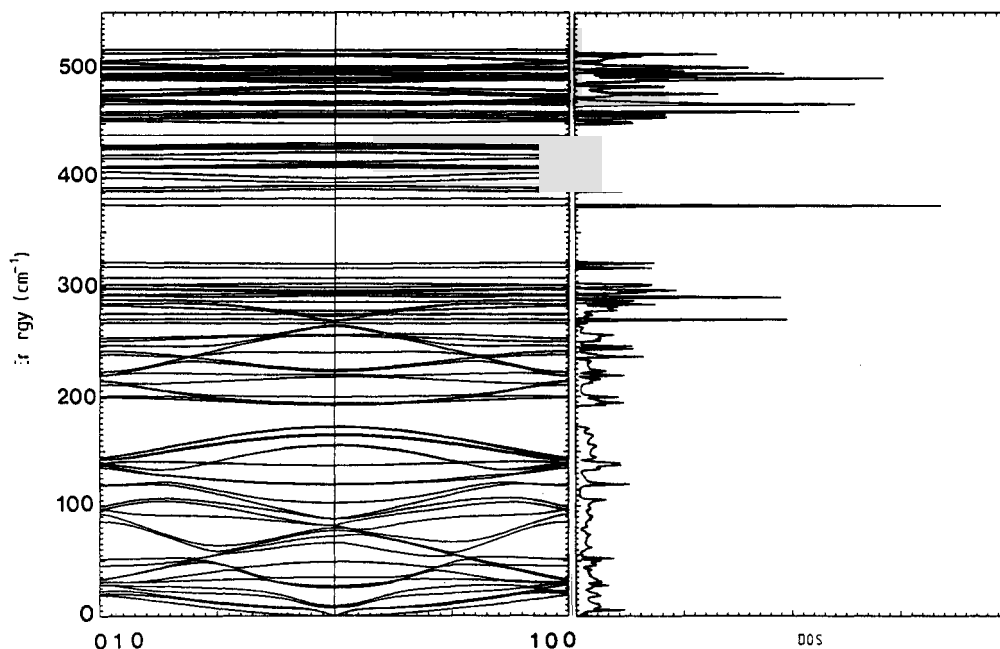
where

$$\begin{aligned} V_i^{\text{pure}} = & \frac{1}{4} \sum_{j=1}^n f_r (\Delta r_{ij})^2 + \frac{1}{2} f_{\theta} r_0^2 \sum_{j=1}^{n-1} \sum_{k=j+1}^n (\Delta \theta_{jik})^2 + f_n \sum_{j=1}^{n-1} \sum_{k=j+1}^n \Delta r_{ij} \Delta r_{ik} \\ & + r_0 f_{r\theta} \sum_{j=1}^{n-1} \sum_{k=j+1}^n (\Delta r_{ij} + \Delta r_{ik}) \Delta \theta_{jik} \\ & + r_0^2 f_{\theta\theta} \sum_{j=1}^{n-2} \sum_{k=j+1}^{n-1} \sum_{l=k+1}^n (\Delta \theta_{jik} \Delta \theta_{kil} + \Delta \theta_{kil} \Delta \theta_{lij} + \Delta \theta_{lij} \Delta \theta_{jik}). \end{aligned}$$

where $\Delta r_{ij} = r_{ij} - r_{ij}^0$ is the distortion of bond joining atoms i and j , and $\Delta \theta_{jik} = \theta_{jik} - \theta_{jik}^0$ is the distortion of the angle jik from equilibrium, and r_0 is an equilibrium bond length—we set $r_0 = 2.23 \text{ \AA}$.

Table 1. Valence force parameters for phosphorus (in eV \AA^{-2}).

$f_r = 11.7007$	$f_\theta = 1.1115$	$f_{rr} = 0.4131$
$f_{r\theta} = 0.5130$	$f_{\theta\theta} = -0.0069$	

**Figure 6.** Calculated phonon dispersion relation and density of states for Hittorf's phosphorus.

The five fitting parameters $f_r, f_\theta, f_{rr}, f_{r\theta}, f_{\theta\theta}$ are given in table 1.

Having obtained this potential, it is straightforward to find the vibrational properties of phosphorus by setting up the dynamical matrix and diagonalising it in the usual way.

To test the potential, we constructed half of the unit cell of Hittorf's phosphorus. The full unit cell of 84 atoms consists of two parts which are not chemically bonded and interact only via Van der Waals interactions. We did not attempt to fit a potential describing these interactions. The omission of these weak interactions obviously means that any low-frequency modes in our calculation are unreliable, but the higher-energy modes which are localised within a given tube should be correctly given. The dispersion relation for this unit cell was calculated and integrated over the Brillouin zone using the tetrahedron method to determine the phonon density of states (figure 6).

It is seen that our calculation reproduces two pronounced experimental features of the spectrum—we obtain the gap between 322 cm^{-1} and 374 cm^{-1} found in both Hittorf's P and orthorhombic black P, and the pseudogap found in Hittorf's P and red a-P but not black-P around 170 cm^{-1} .

A previous calculation of this density of states by Fasol *et al* (1982) produced very similar results although they used force constants that had been fitted for black

phosphorus (Kaneta *et al* 1982). The main differences between their spectra and ours is the lack of dispersion in our optic branches and our slightly higher frequencies. However, the advantage of our method is that we can calculate a modified potential due to defects. We now describe how this was done.

To determine frequencies associated with the defect, the second derivatives of the total energy of the IVAP cluster discussed in § 4 with respect to displacements of the under- and over-coordinated atoms and their nearest neighbours were determined. These were then inserted in the appropriate places in the dynamical matrix before diagonalising it, replacing the derivatives produced by the valence force potential described above. In this way, the changed interactions between the atoms in the defect's vicinity are taken into account.

Alternatively, the changes in bond strengths around the defect can be obtained by fitting the double derivatives to a valence force potential which allows a local variation of the force constants in this region. To this end we wrote

$$E_{\text{TOT}} = \sum_{i=1}^{\text{no. of atoms}} V_i^{\text{pure}} + \Delta V^{\text{def}}$$

where V_i^{pure} is defined above (the potential associated with the perfect material) and ΔV^{def} is the correction to the potential due to changes in bonding around the defect. We determined the second derivatives of energy between six atoms of the cluster in § 4. These were chosen to be the P_2 and P_4 atoms themselves and the neighbours of each. The contribution to these that would arise from the original potential (i.e. for the perfect material) was subtracted and the remainder ΔV^{def} fitted to

$$\Delta V^{\text{def}} = \Delta V(P_4) + \Delta V(P_2) + \Delta V(P_2 - P_4)$$

where $\Delta V(P_4)$ and $\Delta V(P_2)$ have the form of V_i^{pure} and merely represent the changes in the force constants associated with distortions of bond lengths and angles next to the under and over-coordinated atoms.

We therefore introduce force constants $\Delta f_r(P_4)$, $\Delta f_\theta(P_4)$, $\Delta f_{rr}(P_4)$, $\Delta f_{r\theta}(P_4)$, $\Delta f_{\theta\theta}(P_4)$, with similar parameters relating to the P_2 atom. However, the following changes were made.

(i) In the bond stretching term, the prefactor of $\frac{1}{4}$ (introduced to avoid double counting) becomes $\frac{1}{2}$.

(ii) In the bond-stretching term, the bond joining the P_2 and P_4 atoms is excluded from the summation over nearest neighbours—this special bond is allowed to have an independent stretching force constant through the term

$$\Delta V(P_2 - P_4) + \frac{1}{2}(\Delta f_r^{24})(r_{24} - r_{24}^0)^2.$$

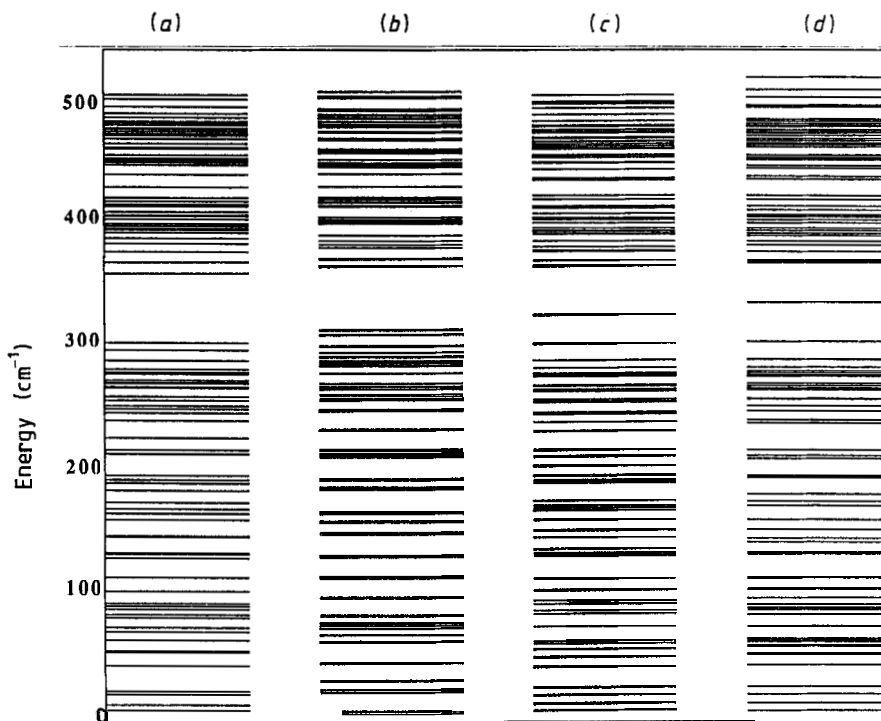
The three remaining bonds associated with the P_4 atom are allowed to have different strengths,

$$\Delta f_r^\alpha(P_4), \Delta f_r^\beta(P_4) \text{ and } \Delta f_r^\gamma(P_4).$$

(iii) As there is only one angle associated with a two-fold coordinated atom, the term $\Delta f_{\theta\theta}(P_2)$ was omitted from $\Delta V(P_2)$.

Table 2. Changes in valence force parameters near an IVAP (in eV Å⁻²).

$\Delta f_r^\alpha(\text{P}_4) = -5.1120$	$\Delta f_r^\beta(\text{P}_4) = -4.6411$	$\Delta f_r^\gamma(\text{P}_4) = 0.0668$
$\Delta f_\theta(\text{P}_4) = -0.8322$	$\Delta f_{rr}(\text{P}_4) = 0.3637$	$\Delta f_{r\theta}(\text{P}_4) = -0.4955$
$\Delta f_{\theta\theta}(\text{P}_4) = -0.0582$	$\Delta f_r(\text{P}_2) = 0.7567$	$\Delta f_\theta(\text{P}_2) = 0.2515$
$\Delta f_{rr}(\text{P}_2) = 1.2569$	$\Delta f_{r\theta}(\text{P}_2) = 0.4598$	$\Delta f_r^{24} = -1.1702$

**Figure 7.** Vibrational levels for (a) The 42-atom unit cell of Hittorf's phosphorus at Γ , (b) the 44-atom cluster arranged as in Hittorf's phosphorus, (c) the 44-atom cluster with an IVAP and modified force constants around the defect, (d) the 44-atom cluster with an IVAP assuming unchanged force constants around the defect.

The twelve fitting parameters are given in table 2. The weakening of the force constants around the P_4 atom is particularly noticeable.

5.2. Vibrational modes of the IVAP

Having determined the potential in this manner, we applied it to the case of the IVAP discussed in § 4. There are two possible ways of proceeding—one could place a defect in a large cluster or in a large unit cell (supercell). We chose the former for simplicity, terminating the cluster with H atoms. These atoms vibrate at a far higher frequency than P atoms (on account of their smaller mass) and so have a negligible influence on the P modes. Modes associated with the P_2 and P_4 atoms were unaffected when the mass of the H atom was changed to either 0.1 or 100 times its correct value (corresponding to free and fixed boundary conditions respectively). The results are shown in figure 7.

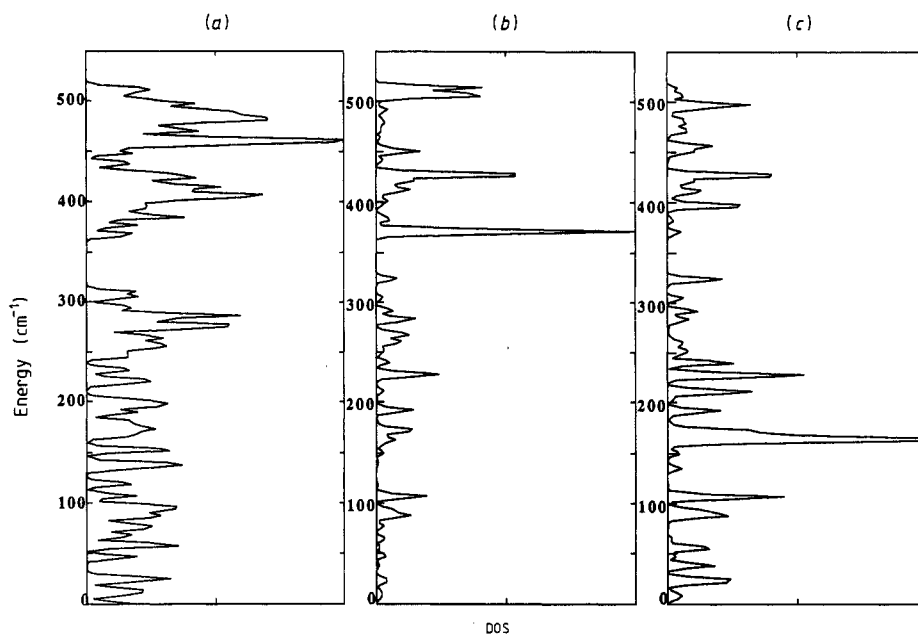


Figure 8. Vibronic density of states for the 44-atom cluster. (a) refers to the cluster arranged as in Hittorf's phosphorus; (b) and (c) refer to the cluster containing an IVAP with the density of states projected onto the over- and under-coordinated atoms respectively.

The first two columns of the figure show that the differences involved between frequencies found from a cluster or unit cell approach are minimal. This is because, for the frequency range of interest, the dispersion curves for Hittorf's phosphorus are so flat that the gamma point frequencies are representative of the whole Brillouin zone.

The third and fourth columns show the modes associated with the IVAP. The differences between them correspond to the effect of allowing 'local force constants' around the defect—neglected by earlier workers (Nemanich *et al* 1978). A density of states was constructed by convoluting the levels with a gaussian. A local density of states was formed according to the prescription

$$\rho(E, i) = \sum_{\lambda} |a_i^{\lambda}|^2 g(E - E_{\lambda})$$

where λ labels the vibrational mode, a_i^{λ} is the amplitude of vibration of atom i in mode λ and $g(E - E_{\lambda})$ is a gaussian centred on $E = E_{\lambda}$ of width 2.0 cm^{-1} .

The resulting densities of states are shown in figure 8. It is seen that modes localised on the P_2 atom occur at 163 cm^{-1} and 324 cm^{-1} . The first of these would not be seen experimentally as it would be completely hidden by the excitations of the rest of the network. The mode at 324 cm^{-1} does in fact fall into the vibronic gap in Hittorf's phosphorus. Modes associated with the over-coordinated atom occur at 371 cm^{-1} , 427 cm^{-1} and $\sim 510 \text{ cm}^{-1}$. A peak in the Raman spectrum is however seen beyond the one-phonon excitation spectrum in both amorphous arsenic and phosphorus that is not found in the crystalline states. This must be due to some other defect—a double bond would be expected to give a higher vibrational frequency for example.

It may appear surprising that the over-coordinated atom doesn't give rise to a mode substantially split off from the bulk excitations as reported previously (Nemanich *et al* 1978). However, this arises from the weakening of the force constants associated with its four bonds which was neglected by earlier workers. If this weakening is not taken into account, then a split off mode is produced as shown in the fourth column of figure 8.

6. Conclusions

The *ab initio* cluster calculations described here have reproduced the experimental structure of Hittorf's phosphorus to within 3%. The calculated phonon spectrum possesses gaps around 170 cm^{-1} and 350 cm^{-1} and beyond 516 cm^{-1} . These agree with the results of Raman measurements except that our highest mode is 20 cm^{-1} too high. The calculated electronic energy gap is 50% too large but is typical of cluster calculations where surfaces have been saturated by hydrogen.

Stable pairs of over- and under-coordinated atoms, P_4 and P_2 respectively, could not be formed by distorting atoms within a tube as had been previously suggested. They could however be created by shearing tubes. This suggests that plastically deformed Hittorf's phosphorus might contain these defects.

The IVAP and VAP have formation energies 2.0–2.3 eV which are too large for them to be present in appreciable equilibrium densities. However, their mode of preparation (by the displacement of rigid tubes) suggests that once they are formed, the barrier to annihilation involving the motion of a large number of atoms would be considerable.

The P_2 defect has bond lengths of 2.2 \AA , very close to the normal P–P bonds. The bond angle was 104° . They give rise to a level around mid-gap whose wavefunction was heavily localised on the P_2 atom. A local vibratory mode of this defect occurs at 324 cm^{-1} .

The P_4 defect has bonds which ranged from 2.20 \AA to 2.46 \AA . The bond angles ranged from 96° to 101° . It might be expected that the P_4 defect would possess a local mode above the highest optic mode. However, we found that the force constants were softened by the dilatation of the bonds and consequently this mode fell close to the top of the one-phonon spectrum. The electronic level of the P_4 atom fell close to the bottom of the conduction band: above it in the case of the IVAP and below it in the case of the VAP. Its state was more delocalised than that of the P_2 state, suggesting that it would give rise to a broad band in the solid.

The structure of the IVAP and VAP bound with an exciton was very different from their ground states described above. For all the cases studied, the P_4 defect dissociated in the excited state. Large Stokes shifts are then to be expected. On the other hand, promoting an electron from a valence band state into the P_4 state and relaxing the structure produced lower Stokes shifts.

These observations are consistent with the model of Sobiesierski and Phillips for the HE and LE processes.

Finally, one of the more surprising results of this study is that the 14-atom cluster (which contained only six P atoms) still qualitatively reproduced many of the results found with the larger clusters. This is encouraging for the use of small clusters in obtaining information about phenomena observed in the solid state.

Acknowledgments

We are grateful to Richard Phillips for many useful discussions, to Robert Pasley for help with preliminary work, and also to Malcolm Heggie, Grenville Lister and Daniël Joubert for many helpful suggestions.

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