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1990 J. Phys.: Condens. Matter 2 5455

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Steady-state photoluminescence of the P-rich phosphorus selenide glasses

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Received 13 October 1989, in final form 23 March 1990

Abstract. The continuous-wave photoluminescence (CW PL) spectra of a-P_xSe_{1-x} glasses of compositions $x = 0.66, 0.75, 0.8$, and 0.84 have been investigated for a wide range of excitation energies and intensities. It is found that the Gaussian mid-gap spectra typical of glassy chalcogenides broaden dramatically for excitation energies of 2.4 eV and above. This is shown to be due to the presence of a higher-energy PL band, which is excited most efficiently at high excitation energies. This band is weaker, but still detectable, at low excitation energies for the composition a-P₃Se, $x = 0.75$, and is then clearly resolved from the mid-gap band.

The high-energy band is identified with a luminescence process with a wide range of lifetimes, whose excitation spectrum is found to be sharply peaked at an energy dependent on the composition. Results of PL studies of crystalline P₄Se₃ are also described. It is found that the high-energy band is very much weaker in the crystal, if at all present.

1. Introduction

Photoluminescence studies of amorphous chalcogenides generally reveal a Gaussian PL emission band at about mid-gap energy, and with a full width at half maximum (FWHM) of approximately 0.2 to 0.3 eV [1–4]. This PL band can be interpreted in terms of a configuration-coordinate diagram model due to Street [4], who envisaged the radiative recombination centre as arising from a defect site. The ground and excited states are described by parabolic potentials, whose minima are displaced with respect to one another, due to some structural rearrangement on excitation of the centre; the radiative transition is from the vibrational minimum of the electronic excited state—hence the Stokes shift of the luminescence. The same ideas can also be used to describe a self-trapped exciton (STE) site, removing the need for an intrinsic population of defects. In c-As₂Se₃, it has been shown the PL arises from an STE, and the site at which it forms has been identified via ODMR experiments [5].

For excitation energies above the band gap, some materials, such as a-As₂Se₃, show no further sensitivity to the excitation energy [2]. In other systems, for example, a-As₂S₃, further PL processes with excitation and emission spectra different from that of the mid-gap luminescence have been observed; various explanations for these processes within the Stokes shift model have been presented, including hot PL [6] and exciton mobilities dependent on excitation energy [7].

The phosphorus selenides comprise a relatively unknown system, for which two glass-forming composition regions a-P_xSe_{1-x} exist, with x in the ranges $0 < x < 0.52$ and

$0.6 < x < 0.85$. The band gap shifts with composition, as described in [8], with the energy at which the absorption coefficient is 10^2 cm^{-1} decreasing from about 2.15 eV for a-P₂Se to 2.02 eV for a-P_{0.84}Se_{0.16} (although these values depend on the quenching rate of the glass).

The structure of the P-rich glasses has been studied by Verrall, Gladden and Elliott [9, 10] and Phillips *et al* [11], who find that the vibrational spectra of the P-rich glasses show several well-defined modes characteristic of the c-P₄Se₃ cage molecules that form the crystal structure. An important question is whether these cages remain unbroken in the glass, embedded in an amorphous matrix, or whether one or more bonds of each cage are opened to link the cage into the matrix [11].

The mid-gap photoluminescence band of some P–Se glasses was found to be characteristic of the chalcogenides, having the properties described above [8]. Frequency-resolved PL spectroscopy (FRS) of this band reveals a remarkably sharp lifetime distribution, with only two lifetimes, of the order of 10^{-3} s and 10^{-6} s, observed in both glasses and crystal, and which show very little statistical broadening in the glasses [12, 13].

A time-resolved study of PL in a-P₂Se has shown that at 10 to 50 ns after excitation by 12 ns pulses, the mid-gap band (excited by photons of 2.175 eV) lies 130 meV higher in energy than in CW experiments, and does not shift over the first 100 ns after excitation [14]. The time-resolved work also showed the existence of PL up to 0.7 eV above mid-gap energy, under higher-energy excitation. In order to establish whether this is a distinct second PL process, we have investigated the CW PL of some P-rich glasses under high-energy and high-intensity excitation, over the full PL spectral range.

2. Experimental details

Details of the preparation and characterisation of the samples were given previously [8, 14] and will not be repeated here. All amorphous samples were bulk glasses, quenched in air from a melt of the elements in stoichiometric proportions, and polycrystalline c-P₄Se₃ was also prepared in the same way.

The CW PL measurements described here were performed in two laboratories, using similar experimental apparatus. After careful correction for the responsivity of the detection systems, using calibrated tungsten lamps as standard spectral sources, spectra measured in the two laboratories under the same conditions for the same samples were found to be in good agreement. The detectors used were germanium pin diodes, and S1 and modified S20 photomultipliers, for the spectral ranges $0.7 < E < 1.4$, $1.1 < E < 1.6$, and $1.5 < E < 3$ eV respectively. The extremely wide PL spectra required the use of the three detectors with overlapping energy ranges, in order to determine the relative intensity of the different parts of the spectra. Response corrections were measured for each detector using the same spectral source and procedure, so only small scaling factors were needed to match part-spectra together.

Grating monochromators were used to disperse the PL, with a typical energy resolution of better than 3 meV. Edge filters were used for order-sorting where necessary, and to attenuate scattered excitation light.

Samples were held either in a He atmosphere in a continuous-flow cryostat at 4.2 K, or in superfluid He in a bath cryostat at 2 K. The temperature difference is of no significance for the form or intensity of the PL spectra, but the use of a bath cryostat enabled high photon fluxes to be used without raising the sample temperature unacceptably.

An Ar^+ -pumped dye laser, or the spectral lines of the Ar^+ laser itself, were used as excitation sources. In both cases, appropriate interference filters removed spontaneous emission, which, particularly with a broad emission-band dye such as Rhodamine 6G, could contribute significant contamination of the PL signal through scattering off the sample surface.

To measure the excitation spectra, a tungsten lamp was used to provide a wide excitation energy range. For the mid-gap PL band, the excitation light was passed through a grating monochromator, but for the high-energy PL band, the light was directed through interference filters, to obtain a higher light throughput than through a monochromator. This limited the number of wavelength bands available, however. The results were normalised to the number of incident photons per unit energy bandwidth.

We have not made a detailed study of fatiguing effects in the P–Se system, but have established that they can be made negligible. The intensity of low-energy PL is $a\text{-P}_3\text{Se}$ excited by 2.4 eV light (which penetrates to a depth of a few μm) was found to decay by no more than 30% after illumination for one hour. The typical experimental time was 20 minutes or less for an individual spectrum, and a similar exposure time was allowed before starting a set of measurements, or after a change of excitation wavelength. The whole spectral shape was found to be independent of the exposure time.

3. Results

3.1. PL at high excitation energies

PL at energies up to the excitation energy has been observed in other chalcogenides, for example $a\text{-As}_2\text{S}_3$ (see [6], [7] and references therein). Most of these studies were performed using pulsed illumination, which allows the use of much higher pulsed light intensities for the same average power upon the specimen. This in turn makes the measurement of fast processes with low quantum efficiencies feasible. By contrast, it was here possible to detect and resolve the high-energy PL in CW experiments, implying that its efficiency is untypically high. This is a new and most interesting aspect of the photoluminescence of the $a\text{-P}_x\text{Se}_{1-x}$ glasses.

Figures 1, 2 and 3 show spectra at three excitation energies, for $a\text{-P}_2\text{Se}$, $a\text{-P}_3\text{Se}$, and $a\text{-P}_{0.84}\text{Se}_{0.16}$, three compositions that span the P-rich glass-forming region. Figure 4 shows typical PL spectra for two of these compositions at lower excitation energies, and the dramatic increase in the width of the spectra of, for example, $a\text{-P}_2\text{Se}$ can be seen by comparing figures 1 and 4(b).

In order to quantify the behaviour of the higher-energy PL under different conditions, all the spectra were fitted by sums of two Gaussian bands, using a linear least-squares procedure. The mid-gap PL band has already been shown to be accurately Gaussian in shape [8], but for the upper band, no particular functional form was expected; a Gaussian was chosen for convenience. Nevertheless, it appears to be well described by this function, as can be seen in the diagram. The best fits obtained were plotted, and yielded the following parameters for the mid-gap band: $a\text{-P}_2\text{Se}$: $E_{\text{PL}} = 1.19$ eV, FWHM = 0.27 to 0.3 eV; $a\text{-P}_3\text{Se}$: $E_{\text{PL}} = 1.16$ eV, FWHM = 0.28 eV; $a\text{-P}_{0.84}\text{Se}_{0.16}$: $E_{\text{PL}} = 1.26$ eV, FWHM = 0.4 eV. The higher-energy band is found to vary between 1.57 eV and 1.7 eV without showing any systematic dependence on composition or E_{ex} .

The sensitivity of the PL peak energy E_{PL} to the excitation energy E_{ex} in chalcogenide glasses is well known. All the $a\text{-P}_x\text{Se}_{1-x}$ glasses show a linear dependence of E_{PL} on E_{ex} for sub-band-gap excitation (with a slope of less than unity). For E_{ex} greater than 2.4 eV,

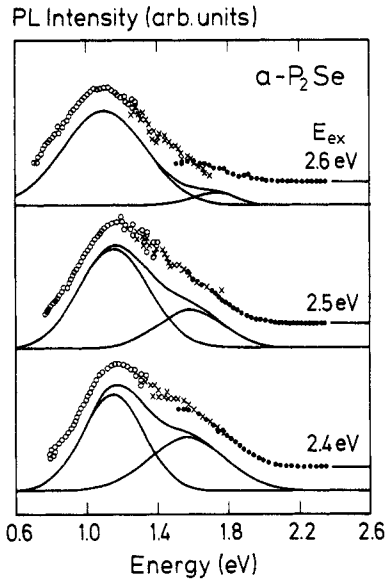


Figure 1. The CW PL spectra of a-P₂Se at the excitation energies indicated, normalised to unit height, and with baselines marked. Symbols ○, ×, and ● correspond to the Ge pin diode and S1 and S20 detectors respectively. Two-Gaussian fits to each spectrum are plotted (curves), with the two individual components, displayed vertically from the data for clarity.

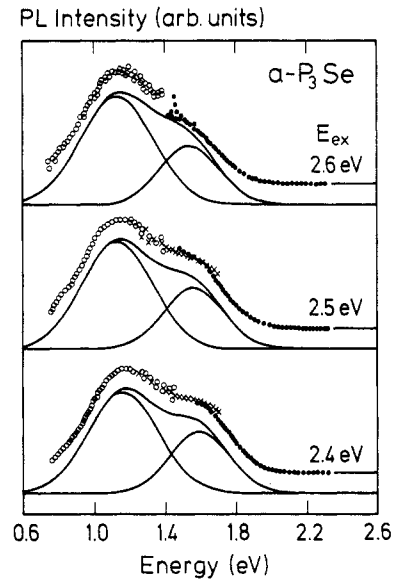


Figure 2. The CW PL spectra of a-P₃Se at the excitation energies marked, normalised to unit height, and with baselines marked. The meaning of all symbols are as for figure 1.

the above results show that the lower-energy band moves very little as E_{ex} increases. This observation is similar to that of Depinna *et al* [2] for a-As₂Se₃, for which E_{PL} depends linearly on E_{ex} (with unit slope) for $E_{ex} < 2.0$ eV, and is independent for $E_{ex} > 2$ eV.

3.2. PL at high excitation intensities

The shape of the PL spectra in the P-Se glasses was studied under conditions of very intense, low-photon-energy excitation, in order to find out whether high densities of excited states could be responsible for the high-energy PL. It was found that this is not the case. Low photon energies were used, in order to separate the effects of photon energy and density, and consequently very high fluxes were required to generate excited state densities comparable with those generated by above-band-gap light. The two energies used, 2.0 and 2.1 eV, correspond to values of the absorption coefficient of about 1 cm⁻¹ and 10 cm⁻¹ respectively, for a-P₂Se. The same energies correspond to values of the absorption coefficient of about a factor of three larger for a-P₃Se, which has a band gap approximately 50 meV narrower than a-P₂Se. We refer throughout to the room temperature values of the absorption coefficient; the shift with temperature has only been measured for a-P₂Se (our work), for which the gap widens by only 70 meV on cooling to 30 K. This may increase the penetration depth of light by a factor of 3–5 as compared to room temperature.

A linear dependence of PL intensity on excitation intensity was observed to change to a sub-linear dependence by the very highest intensities used here, which were of the order of 200 mW, focused to a spot of about 0.3 mm diameter. We estimate the excited

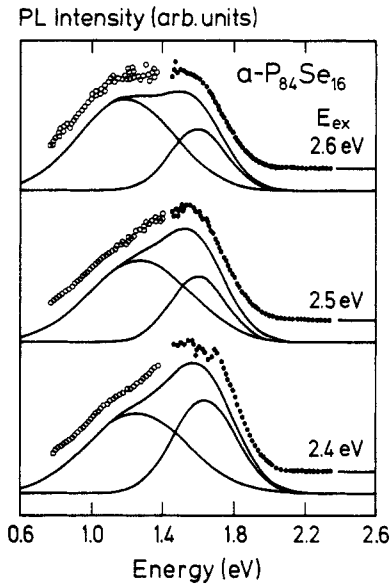


Figure 3. The CW PL spectra of $a\text{-P}_{0.84}\text{Se}_{0.16}$ at the excitation energies marked, normalised to unit height, and with baselines marked. The meanings of all symbols are as for figure 1.

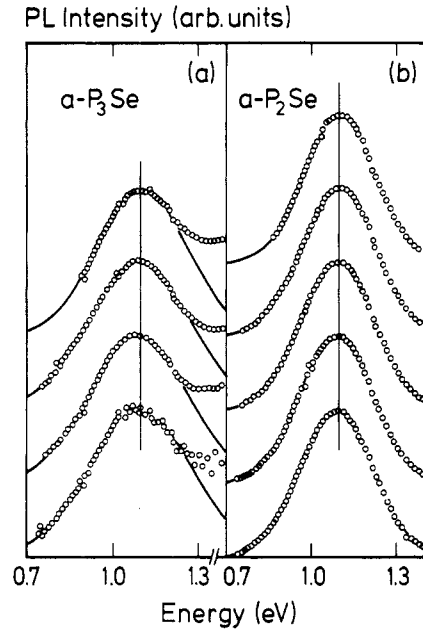


Figure 4. The CW PL spectra of $a\text{-P}_3\text{Se}$ (a) and $a\text{-P}_2\text{Se}$ (b) for an excitation energy of 2.1 eV, normalised to unit height and displaced by one vertical unit, together with single-Gaussian fits to the data. Estimated excited state densities were, from top to bottom: $a\text{-P}_3\text{Se}$; N , $N/2$, $N/20$, and $N/200$, where $N = 7 \times 10^{18} \text{ cm}^{-3}$, and $a\text{-P}_2\text{Se}$; N , $N/2$, $N/10$, $N/100$, and $N/1000$, where $N = 8 \times 10^{18} \text{ cm}^{-3}$. The vertical lines emphasise the consistency of the peak position.

state densities by assuming uniform absorption of the incident flux in a thickness $(1/\alpha)$ of the sample, for strongly absorbed light. For 2.1 eV excitation, with a sample thickness of about 4 mm, the transmission of the sample is still not significant. The density, N , is then given by the relationship $N = G\tau$, where G is the generation rate of the carriers per unit volume and τ is the average lifetime. Measurements of the PL lifetime distribution in these materials indicate a typical long lifetime of 10^{-3} s for the mid-gap PL [12]. The excitation densities so derived are indicated in the caption of figure 4. The maximum estimated density for $a\text{-P}_2\text{Se}$ was $8 \times 10^{18} \text{ cm}^{-3}$, which is an order of magnitude larger than the densities used at higher excitation energies. In the case of figure 1, for example, 0.2 mW excitation of energy 2.6 eV with a 1.5 mm diameter spot was used, which, with the same assumed lifetime, leads to an estimated maximum density of $8 \times 10^{17} \text{ cm}^{-3}$ ($\alpha(2.6 \text{ eV})$ was estimated to be $3 \times 10^4 \text{ cm}^{-1}$).

Spectra are shown for these two materials in figure 4, in which Gaussian fits to the data are again plotted. The results for 2.0 eV are not shown, but were similar. It is clear that the spectral shape is independent of carrier density, up to the maximum generated here. Although the measurements here extended only over the spectral range of the Ge diode, it is evident by comparison of figures 1 and 4(b) that no high-energy shoulder characteristic of the high-energy PL develops in the $a\text{-P}_2\text{Se}$ spectra. For $a\text{-P}_3\text{Se}$, the high-energy PL is excited by the 2.1 eV photons (see section 3.3) but comparison of figures 2

and 4(a) shows that the magnitude of the shoulder does not change. These spectra again show the accuracy of the Gaussian shape of the low-energy PL band. The fitting parameters obtained were: a-P₂Se: $E_{\text{PL}} = 1.078 \pm 0.002$ eV, FWHM = 0.2 eV; a-P₃Se: $E_{\text{PL}} = 1.095 \pm 0.005$ eV, FWHM = 0.2 eV. The shift of E_{PL} with E_{ex} is apparent by comparison of these parameters with those from figures 1 and 2. The reproducibility of these spectra is an indication that fatiguing effects during measurement were negligible.

The possibility of surface effects must also be considered, since with high photon energies, carriers are generated very close to the surface. Either intrinsic-surface-related states, or impurities could play a role. With regard to the latter, it is known that the surfaces of some of these glasses deteriorate in air, and we have observed recognisable new features in time-resolved PL spectra from contaminated surfaces, but all the samples used in the experiments reported here were freshly cleaved from large pieces of the synthesised material. These showed clean reflective conchoidal fractures and gave reproducible results from day to day. Some samples were up to two years old, but when fresh surfaces were prepared, the PL spectra were still reproducible. It should also be pointed out that the most likely degradation of the surface—for instance, through overheating due to very high photon fluxes—results in crystallisation into c-P₄Se₃, which, as will be seen below, shows substantially *less* high-energy PL, if any.

3.3. The excitation spectra of the PL bands

The different shape of the PL spectra excited with high- or low-energy photons implies that the two PL bands have quite different excitation spectra. These were therefore determined by measuring the PL intensity at the peaks of the two contributions, that is, at about 1.15 eV and 1.6 eV since, as can be seen from the Gaussian fits in figures 1–3, the contribution of either band at the peak position of the other is negligible for a-P₂Se and a-P₃Se and only small for a-P_{0.84}Se_{0.16}. In figure 5, we show excitation spectra for a-P₃Se, a-P₄Se, and a-P_{0.84}Se_{0.16}, normalised to the number of incident photons. The excitation spectra of the low-energy band show a shift with the band gap, as described earlier [8]. The high-energy excitation spectra also show a shift, peaking at about 2.32 eV and 2.16 eV respectively. The decrease of 160 meV should be compared to the decrease of about 50 meV in the respective values of the band-gap parameter E_{02} , measured as part of this work; the direction of the shift is the same in both cases. The fact that the excitation spectra move with the band gap strongly suggests that we are observing a genuine bulk property of these materials.

Because the excitation spectra show the high-energy PL is excited weakly even at 2.0 eV in a-P₃Se, the form of the high-energy PL spectrum was investigated under these conditions. Figure 6 shows PL spectra for c-P₄Se, a-P₂Se, and a-P₃Se, for excitation energies of 2.1 eV in all cases, and 2.0 eV for a-P₃Se. The high-energy ‘tails’ to the spectra have also been plotted on expanded scales, indicated on the diagram, and again Gaussian fits are displayed. For the crystalline material, (d), and for a-P₂Se, (c), the ‘tail’ is extremely weak; in the case of the former, only a factor of five above our ultimate sensitivity. The PL spectrum of a-P₂Se is approximately flat from 1.5 to 1.8 eV. The rise of the signal around 1.8 eV may correspond to a very weak, fast-decaying band which we have observed in time-resolved measurements at room temperature, and which would be consistent with hot PL (that is, PL emitted during the very rapid structural relaxation of the excited state of a defect/STE, in the usual Stokes shift model).

More interesting are the two spectra of a-P₃Se. Here, the high-energy PL is still weak, but it is strong enough to be clearly resolved from the lower band. The plot on an

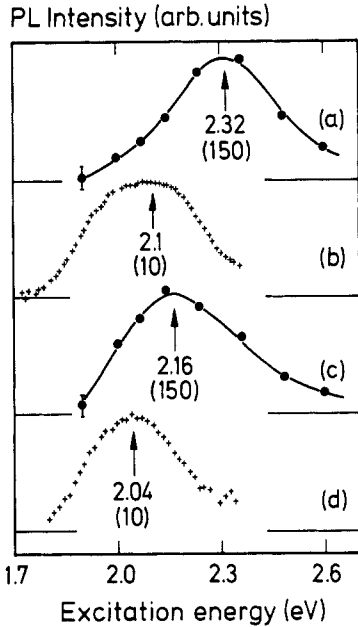


Figure 5. PL excitation spectra of (a), (b), $a\text{-P}_3\text{Se}$, (c) $a\text{-P}_{0.84}\text{Se}_{0.16}$, and (d) $a\text{-P}_4\text{Se}$, plotted as PL intensity per incident photon. Detection energies were either the peak of the mid-gap band (+) or 1.6 eV (●). The spectra are normalised to unit height, and the respective baselines are indicated by the large ticks. The smooth lines drawn through (a) and (c) are guides to the eye. The approximate peak positions are indicated by the arrows, and are given in eV; the figures in brackets are the approximate values of the absorption coefficient at the respective energies (cm^{-1}).

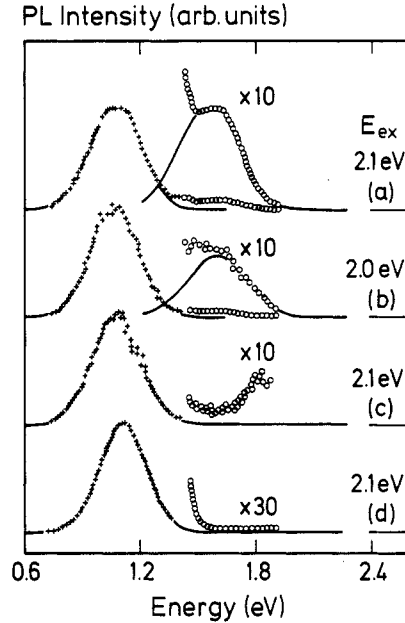


Figure 6. CW PL spectra at low excitation energies of (a), (b), $a\text{-P}_3\text{Se}$, (c) $a\text{-P}_2\text{Se}$, and (d) $c\text{-P}_4\text{Se}_3$, normalised to unit height and with baselines as indicated. Excitation energies are marked next to each curve. Gaussian fits to the low-energy part of each spectrum are plotted (full curves). The data for $E > 1.5$ eV are plotted on expanded vertical scales as shown on the diagram, and in (a) and (b), the upper component of a two-Gaussian fit to the spectrum is also plotted.

expanded scale (figure 6(a)) shows a distinct minimum between the two bands, which is lost as the excitation energy is increased beyond 2.1 eV, due to the broadening of the upper band (and, to a smaller extent, of the lower band). The FWHM of the upper Gaussian is only 0.22 eV for $E_{\text{ex}} = 2.1$ eV, increasing to 0.3 eV when $E_{\text{ex}} = 2.4$ eV.

4. Discussion

4.1. Summary of the experimental observations

The existence of two PL bands in the P-rich $a\text{-P}_x\text{Se}_{1-x}$ glasses has been demonstrated. The mid-gap-energy CW PL band has been studied previously [8], and PL has been seen in time-resolved measurements at higher energies [14]; this high-energy PL is also detectable using cw excitation. Both bands show a significant Stokes shift, and both are described by Gaussian lineshapes, making it possible to separate the two contributions to the PL spectrum.

The high-energy band is only weakly excited with below-band-gap light, when it is also as narrow as the mid-gap band. At an excitation energy of 2.4 eV, it is broader and

of comparable intensity to the mid-gap band. The excitation spectra of the two bands were measured; these peak at different energies in the same material, and the excitation spectra for both bands shift with the band gap for different compositions. Finally, the high-energy PL band is not observed in the crystal $c\text{-P}_4\text{Se}_3$. These facts indicate that two separate PL processes occur in the $a\text{-P}_x\text{Se}_{1-x}$ glasses.

4.2. The lower-energy PL band

The lower-energy PL band is excited under all conditions, and is typical of PL in glassy and crystalline chalcogenides. In the $a\text{-P}_x\text{Se}_{1-x}$ system, it shows a large Stokes shift, and no Coulomb shift to lower energies over the first 100 ns after pulsed excitation [14]. These observations are consistent with either the recombination of a self-trapped exciton (STE) or with recombination between a carrier in a deep band-tail state and one trapped at a defect. Recombination between carriers both trapped at charged defects is ruled out by the absence of the Coulomb shift. The discrete lifetime distribution [12] and the temperature independence of the PL energy for the lower band support the STE interpretation.

The closeness of the lifetimes in $a\text{-P}_2\text{Se}$, $a\text{-P}_3\text{Se}$, and $c\text{-P}_4\text{Se}_3$, as well as the very similar PL spectra (see [8] and figure 6) imply that the radiative centre responsible for this band is the same in the P-rich glasses and $c\text{-P}_4\text{Se}_3$.

Raman studies showed that a common structural feature, the P_4Se_3 cage molecule, exists in both P-rich glasses and crystalline $c\text{-P}_4\text{Se}_3$, and retains its vibrational properties in the glass [11]. It is proposed that the low-energy PL centre arises from interactions between these cages; this well-defined structural unit is believed to generate a PL site which is also well-defined, in both crystalline and amorphous states.

4.3. The higher-energy PL band

The high-energy PL originates from an excited state that is only present in the disordered materials. There are two differences in structure between the P-rich glasses and the crystal, namely, the matrix of excess P atoms required to inhibit crystallisation in the glass [8, 9], and the disorder itself. Four possibilities thus exist for the high-energy centre; a new site arising from an interaction between cages that is not found in the crystal, a site between cage and matrix, a site intrinsic to the matrix or, lastly, the band-tail states due to the disorder.

The attribution of the high-energy PL to a site in the P matrix can be ruled out. Such a site should produce PL similar to that of the high-energy (HE) PL band in a-P [3], but the time-resolved behaviour of the HE PL in a-P and $a\text{-P}_x\text{Se}_{1-x}$ is quite different. In a-P, no shift of the HE band is observed at short times, whereas in, for example, $a\text{-P}_2\text{Se}$, a large shift occurs [14, 15].

The suggestion of a new inter-cage site in the glass also seems rather unlikely in view of the large distribution of relative cage orientations in the crystal unit cell [16, 17].

The remaining options are a cage–matrix interaction, or the band tails. Recombination of carriers trapped in the band tails is consistent with the wide spectral range of the HE PL, its wide distribution of lifetimes which frequency-resolved PL spectroscopy measurements reveal (our measurements, to be published) and its large shift in energy on short time-scales. The spectral shape of the HE PL, although often well-described by a Gaussian at high E_{ex} , is not always of this form, as exemplified by $a\text{-P}_2\text{Se}$ under low-energy CW excitation (this work) and pulsed excitation [14]. In any case, the Gaussian

width for high E_{ex} is too large to be compatible with the interpretation of this lineshape via a Franck–Condon diagram, as mentioned in the introduction and described in [4]. The HE PL is therefore believed to arise from recombination of carriers trapped in band-tail states.

Much more information is needed on radiative recombination in this novel and interesting system; in particular, there is a need for picosecond time-resolved PL studies of the glasses in order to test whether the thermalisation model can explain the time-resolved shift of the HE band. The two proposed recombination channels imply that ODMR should reveal a distant-pair process and a geminate, perhaps excitonic process. Further work on $c\text{-P}_4\text{Se}_3$, especially on single crystals, is needed to determine the lower-energy PL mechanism and to establish whether it is the same as in the glasses.

5. Conclusions

The existence of two easily distinguishable and independent PL processes in the phosphorus-rich $a\text{-P}_x\text{Se}_{1-x}$ glasses has been shown, and the possible origins of these have been considered. It is concluded that both PL bands are intrinsic bulk properties of the $a\text{-P}_x\text{Se}_{1-x}$ glasses, and that the lower-energy band is identifiable as that observed in the crystal $c\text{-P}_4\text{Se}_3$.

The higher-energy PL band is found to be almost absent in the crystal. We believe it is a typical feature of PL in amorphous chalcogenides, since similar PL bands have now been observed in several other systems, although in the $a\text{-P}_x\text{Se}_{1-x}$ glasses, it is unusually efficient. The high efficiency has enabled us to investigate the excitation spectrum, and spectral shape as a function of excitation energy, in CW experiments at low temperatures. The excitation spectra are well-defined and peak at a higher energy than the excitation spectrum of the mid-gap PL; they support our conclusion that the high-energy PL is a bulk property, as they are seen to shift in energy with the band gap. The full details of the lifetime distribution of this PL band have yet to be measured, but from the wide range of lifetimes, and wide spectral range, we attribute it to recombination of carriers trapped in band-tail states.

Acknowledgments

We thank Jürgen Ristein for a careful reading of this manuscript and many helpful comments. This work was supported in part by the Science and Engineering Research Council of Great Britain, and by the Deutsche Forschungsgemeinschaft. DW would like to thank the Royal Society for the provision of a European Exchange Research Fellowship, and the Philipps-Universität Marburg for their hospitality.

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