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## The dependence of cw photoluminescence on excitation energy in a-P

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**Abstract.** The dependence of the photoluminescence of red amorphous phosphorus upon the energy of excitation photons is discussed in the framework of models of recombination at defects. The cw luminescence of this material at 4 K is found to show a shift in the emission energy proportional to the excitation energy below a critical energy near the bandgap. Near the same energy the width of the luminescence band switches from being linearly related to the excitation energy (low energies) to being independent of excitation energy (higher energies). We discuss the role of the processes involved in absorption in determining the excitation dependence of the luminescence, and conclude that the sharpness of the transition from linear variation with excitation energy to independence of energy indicates the influence of the mobility edge upon the initial distribution of optically injected carriers.

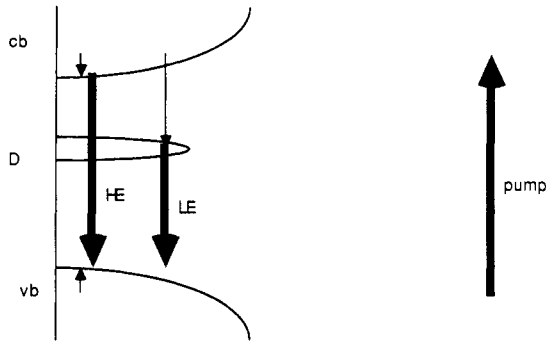
### 1. Optical transitions in amorphous semiconductors

Absence of periodicity and spatial localisation of electronic wavefunctions both eliminate the normal conservation of crystal momentum which acts as a selection rule on optical transitions in crystalline semiconductors. In a strongly disordered system it is expected that the total transition strength at a particular photon energy will be determined by a convolution between the occupied initial and empty final states, with some matrix element taken to describe the behaviour of all transitions with some particular initial energy.

It is usual in setting up such a description to take an average of the properties of states at a particular energy, an approximation that is very difficult to avoid. Even so, we still have little *a priori* information regarding the variation of the matrix elements with energy. A serious difficulty is therefore immediately apparent: in contrast to the case in crystalline semiconductors, for their amorphous counterparts optical excitation cannot normally be considered to lead to the creation of a readily deducible distribution of injected carriers. The effects of relaxation of the carriers subsequent to injection serve to complicate further the description of the optical excitation process. These difficulties are apparent both in the observed optical properties—which are usually very featureless except on a scale of tens of meV—and in the models adduced for their explanation. Thus the appearance of any sharply defined structure in the optical properties of an amorphous

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**Figure 1.** A single deep defect may be invoked to explain the low (LE) and high (HE) energy bands. This model is not consistent with all of the accumulated data.

semiconductor has potential consequences for the models of optical transitions in these systems.

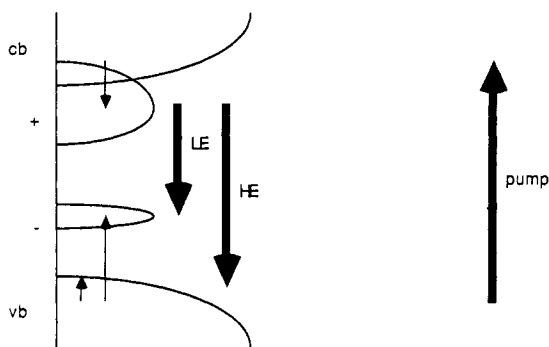
## 2. Radiative recombination in a-phosphorus

Detailed data on optical processes may be obtained for a-P because its bandgap lies in the near infra-red, which facilitates dye laser excitation, and its main photoluminescence is also readily detected using S1 and S20 photocathodes. This has enabled a detailed picture of the time dependence of the emission to be built up [1–4], which, in turn, severely constrains any model for recombination [5].

a-P is among the few amorphous semiconductors that show two clearly-resolved PL bands, which evolve differently as a function of time delay following pulsed excitation. The detailed characteristics of these bands are unique: the lower in energy (LE) dominates the recombination at short times and low temperatures; the higher in energy (HE) is dominant at long times and high temperatures ( $>1$  ms and  $>150$  K). The feature that causes most difficulty in formulating a model for the radiative recombination is that it is the *lower* band that shows a shift in position to lower energy with increasing time following excitation. It has been shown that thermalisation in the band tail is important in relaxation of optically injected carriers in a-Si:H, and the emission from such carriers lies higher in energy than that from the defect states—just as would be expected since the maximum available energy should correspond to cross-gap processes. In contrast a-P shows processes that demand a somewhat different description.

Possible models that might explain this behaviour are summarised in figures 1 and 2. For the model in figure 1, the energy shift with time should arise from thermalisation of holes and should appear for both of the bands—in contradiction with experiment (unless an exactly compensating opposite effect is also present for the HE process). It is very unlikely that thermalisation within the defect band could account for the observation because of the magnitude of the shift—about 200 meV in 200 ns. Similar conclusions apply if the rôle of the bands is reversed. Clearly it is hard to explain the shift of the lower band by invoking thermalisation alone.

To avoid these problems we have proposed that the shift be ascribed to a Coulomb term in the energy of the final state, associated with recombination between carriers



**Figure 2.** Illustration of a model involving recombination at intrinsic charged defects. This is closely analogous to the donor–acceptor recombination model applied to some crystalline systems, and for appropriate defect states appears to be consistent with the experimental data.

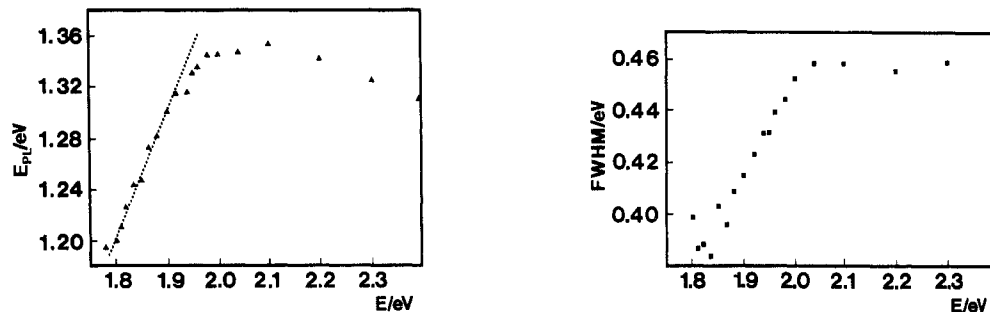
trapped on intrinsically charged defects (shown in figure 2). This model has been successful in explaining the main features of the time-dependent recombination in a consistent manner. It is based on the idea that the stable deep defects involve strong electron–phonon coupling leading to a negative effective correlation energy. The identification of appropriate charged defects does, however, pose some problems. The results of total-energy calculations [6] suggest that overcoordinated positively charged ( $P_4^+$ ) and undercoordinated negatively charged ( $P_2^-$ ) defects may be stable. Since these two configurations both arise from distortion at normal threefold sites it is difficult to see how negative effective correlation energy can be reconciled with Stokes-shifted radiative recombination. This does not eliminate the charged-defect model (the radiative process involved is well known in crystalline semiconductors) but leaves a serious problem in identifying the charged defect sites. For the remainder of the discussion we note that the Coulomb model is the only one that has the correct properties to describe our earlier time-resolved photoluminescence data, and henceforth we will refer to the hypothesis of there being two bands of charged defects implicated in recombination, although we will not at present propose a detailed assignment of the defects themselves.

One further feature of the photoluminescence must also be included in the model, however: as with several other amorphous semiconductors a-P shows a proportionality between the mean PL energy and the excitation energy up to some energy  $E_c$ . Above this excitation energy the PL energy is approximately independent of the excitation energy.

This means that there is some *correlation between the absorption and emission processes when the excitation photon has energy  $<E_c$* ; this correlation is lost for  $E > E_c$ . To explain this within the model sketched above proves difficult, because of the LE process both carriers are deeply trapped and so should have lost any information regarding their injection energy.

### 3. Details of the excitation process

Figure 3 shows the way in which the position of the PL peak (measured CW) and the PL bandwidth vary as the excitation energy is varied. The experiments were carried out on a pre-fatigued specimen of a-P held at 4 K in gaseous helium, and the excitation density



**Figure 3.** The left-hand graph shows the dependence of the energy at the peak of the CW PL band of a-P held at 4 K on the energy of exciting photons. The dotted line has unit slope. The right-hand graph shows the dependence of the full width at half-maximum of the PL band under the same conditions.

was kept very low to avoid saturation effects ( $< 100 \text{ mW cm}^{-2}$ ). Several striking features emerge:

- (i) for  $E < E_c$  the mean PL energy is directly proportional to  $E$ ;
- (ii) the slope for  $E < E_c$  is *unity* at low  $T$  ( $\approx 4 \text{ K}$ )—for other materials that have been studied the slope is usually lower than 1;
- (iii) at a critical energy close to  $E_c$  there is a change in the behaviour of the linewidth from proportionality to  $E$  ( $E < E_c$ ) to independence of  $E$  ( $E > E_c$ ).

Reference to the discussion (above) of the usual approach to description of the excitation process shows immediately that a convolution between bands, with smoothly varying matrix elements, *will not explain these results*. This assertion follows from the fact that a sharp demarcation energy of some sort is required in either the initial or the final states in order to give a sharp lower energy limit for the population in the conduction band. One obvious possible candidate is the mobility edge separating the extended from the localised states (we presume that at 4 K we need not consider separately the ‘transport energy’). For a broad and smoothly varying defect band (e.g. a Gaussian) or band tail (e.g. exponential) the population arising from excitation from an exponential band tail will give rise to a peak in the injected population for both the electrons and the holes (for appropriate values of the parameters describing the defect band/band tails). The latter case is widely believed to apply in a-Si:H, and it is characteristic of this situation that the PL energy depends on  $T$ , and on excitation intensity [7]. Such dependences are observed in a-Si:H but not in a-P.

We therefore identify the models which give rise to  $E_{PL} \propto E_x$  with unit coefficient. The most likely possibility is excitation to a broad defect band, in which case the emission peaks at a position directly related to the photon energy, and the presence of the mobility edge is taken to give rise to the knee. Modification of the optical transitions by a rapidly varying matrix element defines a maximum energy in the valence band from which transitions to localised defect states occur with high probability. This mechanism may be invoked for transitions directly to a broad defect band high in the gap—for example that expected for the  $P_4^+$  defect—but it must be emphasised that the nature of the localised wavefunctions and the spatial separation of the defects determine the details of the model, and must be averaged over to give the bulk behaviour.

This model also leads to an explanation of the striking feature in the variation of width of the PL peak with excitation energy: excitation at energies greater than the 'critical' energy will inject carriers into spatially extended states. These may then trap into either the band tail or defect band with a probability only weakly dependent on the energy of the state. This then gives rise to a population involved in recombination that does not change much as the excitation energy is varied. As the photon energy falls below the mobility gap the distribution of trapped carriers narrows as the energy decreases, in accordance with the data in figure 3. Note that this explanation gives a more satisfactory account than that invoked for the only other similar observation [8]. The model is not without its difficulties, however, since the theoretical expectation is that there should not be a particularly sharp variation in interband matrix elements as the mobility edge is crossed [9], and there has been no comparable calculation for the case involved here. It is worth noting, however, that a very similar experimental observation (but without the bandwidth variation) has recently been reported [10], on a system of matrix-isolated conjugated polymers. Here the effects of localisation are also responsible for the behaviour of the transition, but the matrix isolation leads to differences in detail.

#### 4. Conclusions

Red amorphous phosphorus shows a direct proportionality between the excitation energy  $E_x$  and the width of the PL spectrum, below some critical value of  $E_x$ . This can be reconciled with the model of the recombination involving carriers trapped at intrinsic charged defects if the excitation process is directly to a broad defect band and if the probability of this process decreases strongly with energy above the mobility edge.

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