Transient photoluminescence and excited-state optical absorption in trigonal selenium

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The results of an investigation of the transient mid-gap photoluminescence (PL) and photoinduced optical absorption in trigonal Se are presented. Direct evidence is found for a barrier of 35 ± 5 meV to trapping of free excitons at the PL center. All the features of the PL, including the high-temperature nonradiative decay, can be explained with a simple model in which electron-phonon coupling in the excited state of the PL center, although very strong ($S=50$), is nonetheless linear.

I. INTRODUCTION

The absence of spin paramagnetism in chalcogenide glasses, despite the pinned Fermi energy, led to the idea[1] that the electronic properties of these materials are dominated by a negative effective correlation energy (negative U). In glassy As_2Se_3, for example, the effective attraction between electrons is 0.7 eV.[2] Since the Coulomb repulsion is probably of the same magnitude, the electron-phonon coupling, which leads to the attraction, is very large (~ 1 eV). The most direct evidence for the strong coupling comes from photoluminescence (PL) experiments. Street[3] showed that the large Stokes shift and bandwidth of the PL are consistent with strong coupling. A great deal of effort has been devoted toward understanding the nature of the PL centers and the distortion which takes place when the electronic state is changed, because these same distortions probably lead to the negative U.

The similarity between the PL of glassy and crystalline chalcogenides of the same composition strongly suggests that the PL centers in the two phases are the same. Since certain features of the PL, such as the decay rates, have narrower distributions in the crystal than in the glass, there is a much better chance of understanding the PL mechanism in the former. Whereas detailed studies of the midgap PL in As_2Se_3 and As_2S_3 have been carried out[4] for both phases, this is not the case for Se. The midgap PL was observed only recently[5] for crystalline (c-) Se even though that in amorphous (a-) Se was reported a long time ago.[6,7] In this paper we present the results of an investigation of the transient PL and the photoinduced optical absorption PA of the excited PL center in trigonal c-Se. The results provide evidence supporting the idea of Lundt and Weiser[8] that the PL process begins with the creation of free excitons but that these must overcome an energy barrier of (35 ± 5) meV before trapping at the centers that give rise to the mid-gap PL. It is this barrier which gives the unusual temperature dependence of the quantum efficiency of the PL in c-Se. We find that all the features of the PL can be explained in the *linear* electron-phonon coupling limit, a result that is surprising since the coupling is so strong.

II. RESULTS

The PL and PA were excited by 10 ns pulses from a tunable dye laser pumped by a pulsed yttrium aluminum garnet (YAG) laser. Three types of photodiodes (InAs, Ge, Si) were employed to obtain optimal response in different photon-energy regions. For measurements of PL (PA) spectra the emitted (transmitted) light was dispersed by a grating monochromator. The source of the probe beam in the PA experiment was a tungsten lamp. Other experimental details have been reported elsewhere.[9] Measurements were made on both melt-grown and vapor-grown, trigonal, single-crystal selenium which were provided by Thuillier and Weiser, respectively. All the important features of the PL and PA in these two kinds of samples are the same. The excitation photon energies used were 1.925 eV and 1.875 eV. The experiments were done in the region of sublinear intensity dependence of the PL, which sets in at excitation densities above 10^{17} photons/cm^3. However, even when varied by more than two orders of magnitude, the excitation intensity has no effect on the shape of the PL time decay. The total light decay (spectrally integrated) of the PL for $T>50$ K is plotted in Fig. 1. The PL decays at each temperature

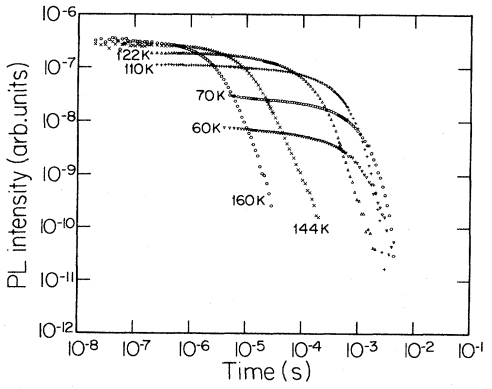

FIG. 1. The time decay of PL (spectrally integrated) at various temperatures.

with a single rate, which is constant below 90 K, but increases at higher temperatures. The initial intensity (the intensity at times short compared with the decay time) is constant below 50 K and increases with temperature at higher temperatures as seen in Fig. 1. The spectrum of the midgap PL, shown in Fig. 2, consists of a roughly Gaussian band with peak energy of 0.72 ± 0.04 eV with a width which increases from 0.09 eV at 4.2 K to 0.12 eV at 100 K. This is clearly the same as the midgap PL seen by Lundt and Weiser.[5]

Another component of the PL appears at $T<50$ K. This component has a significantly different spectrum: it is peaked at <0.5 eV (the lowest energy detected in the experiment), but is broad enough to overlap the midgap PL. However, this new component decays much faster than the midgap PL; therefore, the two components can be separated in our time-resolved experiment even though their spectra overlap. This faster PL process will not be discussed further in this paper.

Transient PA experiments above 50 K revealed two components, one of which decays much more slowly than the midgap PL (the decay time is at least 0.1 s at all T). We shall discuss this component later. The faster component of the PA results from absorption by the excited state of the midgap PL center. This can be seen very clearly from its time dependence. Like PL, the PA decays with a single rate for each temperature. Figure 3, where the decay rates and initial intensities are plotted for the PL and PA, shows that the two phenomena decay at exactly the same rate at all T and their intensities are proportional. This represents the first observation of the PA associated with the excited state of the PL center in c-Se. Such observations have previously been reported[9] for a- and c-As_2Se_3. The spectra of the faster and slower components of the PA are plotted in Fig. 2.

Our transient results are consistent with the measurements of Lundt and Weiser,[5] who used continuous excitation, except that they reported no polarization of the midgap PL, whereas we find a small (15%) polarization parallel to the c axis of the crystal which is independent

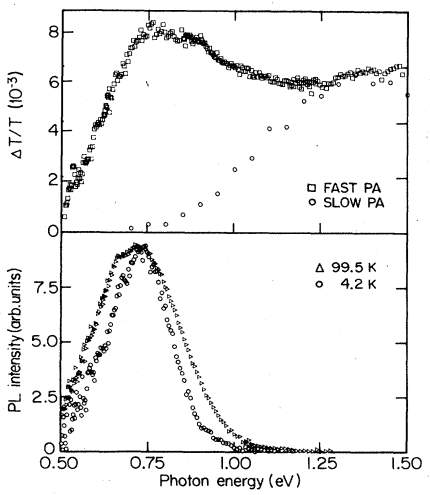

FIG. 2. Spectra of PL (lower) and PA (upper). The intensities of the PL at 4.2 K and the slow PA are multiplied by factors of 6.

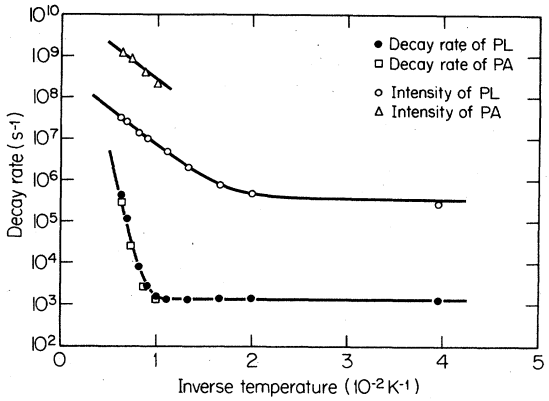

FIG. 3. Temperature dependences of the decay rates and the initial intensities of the PL and PA. The continuous curves are of the form $[A+B\exp(-E/kT)]$. The values for decay rates are absolute, but for intensities are relative. The decay rates of PL and PA are the same at each T and the initial intensities are proportional.

of T from 4.2 K to 160 K. Our transient experiments provide more detailed evidence for the model, suggested by Lundt and Weiser,[8] to explain the temperature dependence of the quantum efficiency η. They found that η increases with T at low T, reaching a maximum at $T\sim100$ K and falling at higher T. As seen in Fig. 3, the initial intensity of the PL at short times is constant below 50 K and is activated with an activation energy of (35 ± 5) meV, above 50 K. On the other hand, the decay rate is constant up to 90 K and then increases more rapidly than the initial intensity [the activation energy of the decay rate is (175 ± 20) meV]. As discussed below, the increase of the rate at high T is the result of a nonradiative process. Therefore, the quantum efficiency peaks at 100 K because the initial intensity of the PL increases above 50 K but the PL is quenched above 100 K by the nonradiative process.

III. DISCUSSION

Because the decay of the PL is accurately exponential (Fig. 1), the density of the excited PL centers is given by

$$n(t,T)=n(0,T)\exp[-\nu(T)t]\ , \tag{1}$$

where $n(0,T)$ is the density excited at times short compared with the lifetime (ν^{-1}) at temperature T. The decay rate $\nu(T)$ is the sum of radiative and nonradiative rates ν_r and ν_{nr}, and since the PL results only from radiative decay, its intensity is given by

$$I_{PL}(t,T)=\nu_r(T)n(t,T)\ . \tag{2}$$

On the other hand, the PA is proportional to the total density of excited PL centers, $n(t,T)$. We, therefore, conclude from the proportionality of the magnitudes of the PL and PA at short times and high T (Fig. 3) that the radiative rate ν_r is independent of T and the temperature dependence of I_{PL} at short times is that of the initial density of excited centers, $n(0,T)$. This contrasts with the behavior of the PL in c-As_2Se_3, in which ν_r increases with temperature but $n(0,T)$ is roughly constant over the same

range.[9] This means that the temperature dependence of ν at high T is the result of an increase of ν_{nr} with T. Extrapolation of $n(0,T)$ to infinite temperature shows that this quantity is smaller by a factor of ~ 50 at 100 K than in the high-temperature limit. The measured value of η at this temperature is $\sim 5\%$. It is clear, therefore, that below 100 K the low value of η is completely explained by the value of $n(0,T)$. There is no room for nonradiative recombination because this would further reduce η. The observed decay rate below 100 K is therefore the radiative rate: $\nu_r = (1.35 \pm 0.05) \times 10^3$ s^{-1}. The slow, but still exponential, decay suggests that the radiative transition is limited by a selection rule, e.g., the excited state may be a triplet as proposed for the PL center[9] in As_2Se_3.

The temperature dependence of $n(0,T)$ shows that there is a barrier which must be overcome before the PL center is excited. Lundt and Weiser[5] provided strong evidence that the first step in the mid-gap PL process is the creation of free excitons. At ~ 100 K the excitation spectrum of the PL coincides with the free-exciton absorption, and at low T free-exciton (band-edge) PL is observed. It, therefore, appears that the 35 meV barrier measured from $n(0,T)$ is that for trapping of a free exciton at the PL center. Lundt and Weiser proposed such a barrier,[8] and from the temperature dependence of the quantum efficiency estimated its height to be 17–20 meV. Since the temperature dependence of η is a product of two thermally activated factors, the barrier to trapping and the nonradiative recombination, it is more difficult to obtain the activation energies in the steady state than in the transient experiment.

A configurational coordinate diagram which describes all the features of the midgap PL was proposed by Lundt and Weiser[8] and is given in Fig. 4. We write the energies for the ground (E_1), free exciton (E_2), and trapped exciton (E_3) states as

$$\begin{aligned} E_1 &= \tfrac{1}{2} M\omega_g^2 q^2 , \\ E_2 &= \tfrac{1}{2} M\omega_g^2 q^2 + E_{ex} , \\ E_3 &= \tfrac{1}{2} M\omega_e^2 (q - q_0)^2 + E_{PL} + \tfrac{1}{2} M\omega_g^2 q_0^2 . \end{aligned} \tag{3}$$

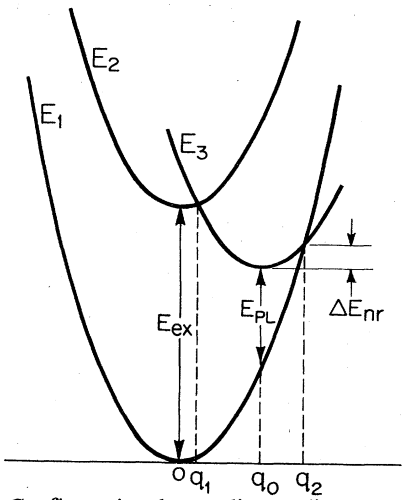

FIG. 4. Configurational coordinate diagram. E_1 is the ground state. E_2 is the free-exciton state. E_3 is the trapped-exciton (PL center) state.

The energy to create a free indirect exciton from the ground state is known[10] to be $E_{ex} = 1.85$ eV; the peak of the midgap PL band is $E_{PL} = (0.72 \pm 0.04)$ eV. The force constant for the ground state, $M\omega_g^2$, which is identical to that of the free-exciton state, can, in principle, be different from that of the excited state, $M\omega_e^2$. The latter is equivalent to a quadratic as well as linear electron-phonon coupling. Using Eq. (3) one find, as usual, that the PL band is approximately Gaussian, $\exp[-(\hbar\omega - E_{PL})/2\sigma^2]$ with[11]

$$\begin{aligned} \sigma(T) &= \sigma_0 \left[\coth \left(\frac{\hbar\omega_e}{2kT} \right) \right]^{1/2} , \\ \sigma_0 &= \left[\tfrac{1}{2} M\omega_g^2 q_0^2 \frac{\hbar^2\omega_g^2}{\hbar\omega_e} \right]^{1/2} , \end{aligned} \tag{4}$$

where ω_g and ω_e are the phonon frequencies corresponding to the ground state and the trapped-exciton state, respectively.

The 4.2 K measurement (Fig. 2) gives $\sigma_0 = (0.092 \pm 0.005)$ eV, and the width at 99.5 K then determines $\hbar\omega_e = (11.5 \pm 2.5)$ meV. Because we have measured the barrier for exciton trapping $[E_3(q_1) - E_{ex}$ in Fig. 4], we can determine $\hbar\omega_g$. We find that $\hbar\omega_g = \hbar\omega_e$ to within 3 meV, which means that, in spite of the large size, the electron-phonon coupling is linear. This phonon energy is close to that (12.7 meV) of the lowest $k = 0$ optical mode[12] in trigonal Se. The diagram of Fig. 4 further suggests that, at sufficiently high T, there will be nonradiative decay because of the crossing of E_3 and E_1 at q_2 as suggested by Lundt and Weiser.[8] The parameters determined above require that the activation energy for this process be (170 ± 70) meV. This is in good agreement with the activation energy of the nonradiative rate [(175 ± 20) meV] seen above 100 K in Fig. 3. This shows that the coupling remains linear to q_2.

In view of the excellent description of our results obtained from the simple diagram of Fig. 4, the induced absorption spectrum of the excited PL center (Fig. 2) is very surprising. We expected to observe a transition between the trapped-exciton state (E_3 in Fig. 4) and the free-exciton state (E_2). Such a transition was observed in As_2Se_3.[9] Its PA spectrum consists of a peak at energy $E_{ex} - E_{PL}$ dropping off gradually on the high-energy side, but having the same Gaussian shape and width as the PL on the low-energy side. For c-Se this peak was expected to be at 1.13 eV. Such a transition is clearly absent in the spectrum of Fig. 2. Instead, the spectrum is composed of two components. One of these appears similar to that of the very slowly decaying component as seen in Fig. 2. If this is subtracted, the remaining PA spectrum is remarkably similar to that of PL itself, both in peak position and bandwidth. At present, this is simply not understood.

IV. CONCLUSION

We have found direct evidence for the barrier to trapping of free excitons at the PL center in trigonal Se. This allowed us to determine all parameters of the configurational-coordinate diagram of Fig. 4. The most remarkable result of this work is that the simple diagram

works so well. In particular, although the electron-phonon coupling parameter (the ratio of Stokes shift to $2\hbar\omega_g$) is $S=50$, i.e., the coupling is extremely large, it remains linear. One expects for a highly localized PL center that such strong coupling would be accompanied by nonlinearity. This may indicate that the lattice distortion in the excited state of the PL center is less localized than previously imagined.

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