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Transient photoinduced optical absorption spectroscopy in trigonal single-crystal selenium

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The spectrum of the transient photoinduced optical absorption (PA) in trigonal single-crystal selenium is reported. Three components of the PA spectrum are distinguished. The first two arise from the excited state of the center that gives rise to the mid-gap photoluminescence. One of these may be the result of photon-assisted hopping of self-trapped excitons. The other may arise from photoionization of electron polarons from the potential well caused by the distortion around them. The last component decays very slowly and has a distribution of time constants. It is identified as the optical ionization of electrons from traps which are probably defect related.

INTRODUCTION

Recent measurements[1] of time-resolved photoluminescence (PL) in single-crystal trigonal Se demonstrated that all features of the PL could be described by a model in which the electron-phonon coupling is linear, even though it is extraordinarily strong. The mechanism leading to such a strong linear coupling is especially interesting since the same mechanism is probably the origin of the negative effective correlation energy in chalcogenide glasses.[2] The temperature dependence of the magnitude and time decay of the photoinduced optical absorption (PA) arising from the excited PL center provided crucial information for construction of the linear coupling model. In this paper we report detailed measurements of the spectrum of the PA, as well as its polarization and time dependence. We find that the PA consists of three components. Two of these are associated with the excited state of the PL center, as shown by their time decay and excitation-intensity dependence, whereas the third is probably the ionization spectrum of electron traps. The two PL-related components can be separated because their polarizations are very different. One of these may arise from photon-assisted hopping of self-trapped excitations.

RESULTS

The experimental technique has already been described.[1] It is important to note that, for polarization measurements, the infrared polarizer is placed before the monochromator. The time decay of the PA shows[1] that it consists of one part which decays with the same single time constant as the PL (120 μs at 122 K) and another which decays extremely slowly, with a distribution of time constants longer than a few ms. The spectrum and polarization dependence of the fast PA is shown in Fig. 1. The spectrum of the PL is included for comparison.

As can be seen from Fig. 1, the spectrum of the faster PA appears, itself, to contain two components. One, with a peak near 0.8 eV, is more strongly polarized along the c axis with $I_{\parallel}/I_{\perp}=1.76\pm0.07$; the other has $I_{\parallel}/I_{\perp}=1.10\pm0.06$. Assuming that each component has a photon-energy-independent polarization, their spectra can be separated. The low-energy component is obtained by multiplying the spectrum measured with electric vector (E) perpendicular to the c axis by the polarization of the high-energy component and subtracting this product from the spectrum for $E \parallel c$. The high-energy spectrum is then obtained by subtracting the low-energy spectrum from the unpolarized spectrum. The resulting spectra are shown in Fig. 2, along with the PL spectrum (which is very weakly polarized[1]).

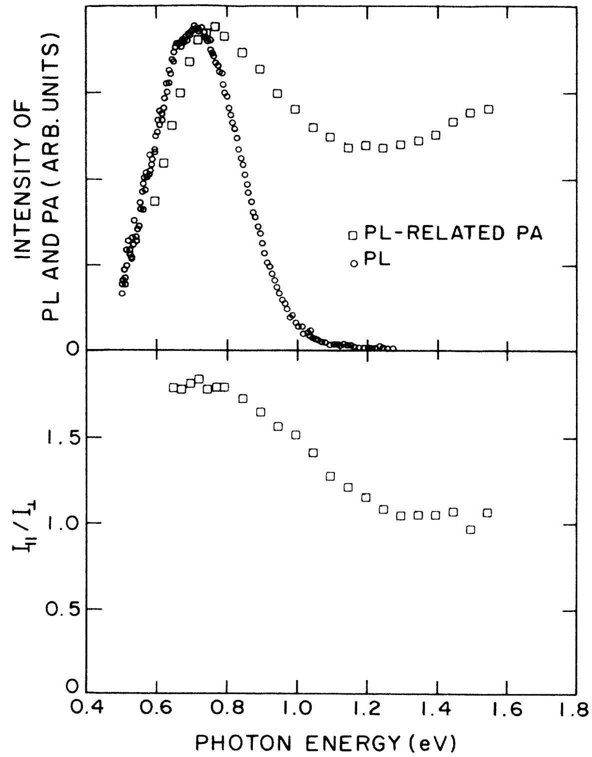

FIG. 1. *Upper panel*: the spectrum of the PL-related PA compared with the spectrum of the PL. *Lower panel*: the ratio of the intensity of the PL-related PA in the direction parallel to the c axis, $I_{\parallel}$, to that in the direction perpendicular to the c axis, $I_{\perp}$.

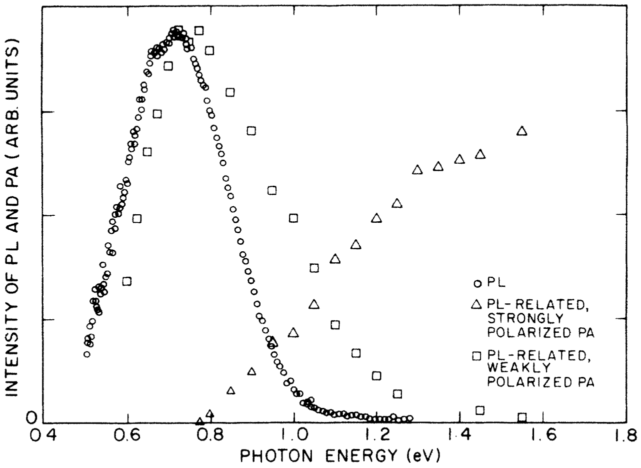

FIG. 2. Decomposition of the spectrum of the PL-related PA into strongly and weakly polarized components, compared with the spectrum of the PL.

Figure 3(a) shows the unpolarized slow PA spectra, integrated over different time intervals and with different excitation photon energies. Figure 3(b) shows the time dependence of the high-energy portion of this PA for $E \| c$ and $E \perp c$. It appears that this slower PA contains at least three components. Figure 3(a) shows that part of the PA has a threshold near 0.6 eV and part near 0.9 eV. Figure 3(b) shows that there is a peak near 1.4 eV which has a different polarization and time dependence from the peak at 1.6 eV. We have not tried to separate the spectra of these constituents of the slow PA. Their relative magnitudes appear to depend on uncontrolled parameters, which suggests that they are defect related.

DISCUSSION

It is striking that the low-energy side of the PL spectrum is very similar to that of the faster PA. As can be seen in Fig. 1, this result does not depend on our separation of the two components of the PA from the excited PL center. The separation suggests, however, that the low-energy component consists of a peak with the same roughly Gaussian shape and width as the PL. To examine what the origin of this PA peak might be, we refer to the configurational-coordinate diagram for the PL center, shown by solid curves in Fig. 4.

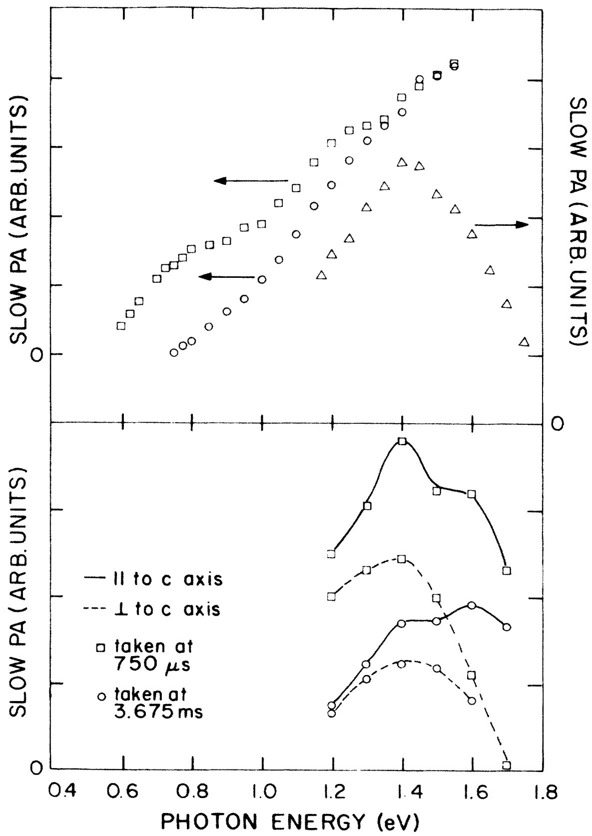

FIG. 3. *Upper panel*: the spectra of the slow PA with □— excitation photon energy =1.875 eV, integrated over time from 500 μs to 1 ms; ○— excitation photon energy =1.875 eV, integrated over time from 1 to 3 ms; △— excitation photon energy =1.90 eV, integrated over time from 1 to 3 ms (note zero shift). The electron traps with 0.6-eV threshold are emptied completely at 1 ms. The spectrum for high-energy excitations has a peak at 1.4 eV. *Lower panel*: spectra of the slow PA for excitation photon energy of 1.90 eV for polarization parallel and perpendicular to the *c* axis at different times after the excitation pulse. The lines only serve as guides to the eye. There are two major components in this energy range. One of them is peaked at 1.4 eV, is moderately polarized, and decays more quickly. The other is peaked at 1.6 eV, is strongly polarized, and decays more slowly.

Under optical excitation, the system is excited to the free-exciton state E_2 from the ground state E_1. Previous measurements[1] showed that thermal activation is required to overcome the barrier at B before the exciton is trapped at the PL center. While in the excited state (E_3), this center can absorb photons from the probe beam before decaying radiatively or nonradiatively via point C to the ground state. As discussed previously,[1] this diagram explains all the features of the time and temperature dependence of the PL and PA, but it does not, at first glance, explain the PA spectrum. On the basis of this diagram we expect a PA band with a Gaussian threshold, peaked near 1.1 eV, resulting from optical transitions from the trapped-exciton state (E_3) to the free-exciton state (E_2). Such a spectrum *is* observed[3] in crystalline As_2Se_3. However, this is obviously not the case for *c*-Se (Fig. 1).

In order to account for the peak at 0.77 eV in the separated spectrum of Fig. 2, we are forced to augment the diagram of Fig. 4 with the dashed curve. Its curvature and displacement relative to E_3 are determined from the shape and position of the PA peak. It should be pointed out that the generalized coordinate which is changed by q_0 in trapping the free exciton (from E_2 to E_3) is probably not the same as the coordinate which is changed by q_0' under the PA transition, although empirically, $|q_0| - |q_0'|$. The fact that the minimum at D' is at about the same energy as that at D of the initially excited PL center suggests that this new configuration simply corresponds to a different PL center. The PA peak would then correspond to photoassisted hopping of trapped excitons. These probably are self-trapped excitons, for the probability of photoassisted hopping of excitons between

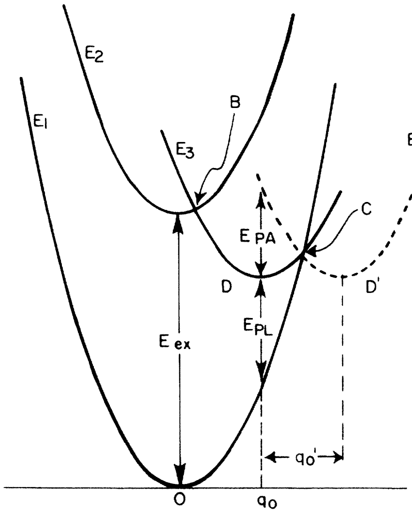

FIG. 4. Configurational coordinate diagram. E_1 is the ground state. E_2 is the free-exciton state. E_3 is the trapped-exciton (PL center) state. E_3' may also be a PL center. The corresponding PA then results from photon-assisted hopping of the trapped exciton. Note that q_0' is a displacement of a completely different generalized coordinate than that for q_0.

spatially separated defects or impurities is very small. Emin[4] has discussed the possibility of photoassisted hopping of polarons. This argument should hold equally well for excitons, albeit with different matrix elements. It is clear that if the two sites for self-trapping are independent the minima at D and D' should be separated by $\sqrt{2q_0}$. We find that q_0' and q_0 are much closer in magnitude than this, suggesting that they are not associated with independent trapping sites. Furthermore, the temperature dependence of the PL bandwidth shows[1] that the phonon frequency related to the curvature of the parabolas in Fig. 4 is that of the lowest-frequency optical mode in c-Se. This mode corresponds to rigid rotation of each Se chain around its helical axis. It may be, therefore, that the new center D' is at a site related to the original one (D) by a rotation of the helix or a translation along the helical axis, and that the long-range strain field associated with the self-trapping couples these sites together.

Turning now to the slow PA, we note that it is similar in many ways to the optical quenching of the frozen-in photoconductivity studied long ago by Stuke[5] and by Fuhs and Stuke.[6] The spectrum of this quenching consists of two components with thresholds at 0.65 and 0.9 eV and has an overall maximum at 1.4 eV. We find that the slow PA saturates (it increases no faster than $I^{0.24}$) for an excitation density greater than -10^{16} cm^3, similar to the saturation density reported by Fuhs and Stuke. Finally, these workers found a slow, nonexponential decay of the frozen-in photocurrent. Although they probed much longer times than we do, it is reasonable to assume that the decay they observed was part of the same rate distribution that we see in the PA. The saturation and other evidence led Stuke and Fuhs and Stuke to propose that the frozen-in photocurrent was the result of electron trapping. The optical quenching results from ionization of electrons from their traps. We suggest that the slow PA is caused by the same process. The spectra resolved by the time and polarization dependence further [Fig. 3(b)] suggest that there may be more than two types of traps.

Finally, we discuss the fast high-energy component of the PA. Although this decays with the same time dependence as the PL, it has a threshold similar to that of the slow PA ($\sim$0.8 eV). On the other hand, it is different from the slow PA in that it is less polarized ($\sim$5% compared to $\sim$25% for the slow PA) and shows no peak at 1.4 eV. This high-energy component may result from photoexcitation of a self-trapped charge carrier, the electron, for example, out of the potential well caused by the self-trapping. This process is possible for the electron when it is free or part of an exciton. The trapped carriers seen in the slow PA might then be self-trapped electrons bound to impurities or defects. This would account for the similarities in the spectra. We have no explanation, however, for the stronger polarization of the slow PA or for the peak in its spectrum.

CONCLUSIONS

The PA spectrum of c-Se is quite complicated, consisting of two components which decay with the same time constant as the PL and several others that decay more slowly. The polarization dependence allowed us to separate the two fast components. The spectrum of one of these leads us to propose that it results from photoassisted hopping of self-trapped excitons. The other fast component may result from a release of electron polarons from the potential well caused by the distortion around them. The slowly decaying PA spectrum bears a strong resemblance to that of the optical quenching of the frozen-in photoconductivity. We, therefore, propose that this PA has the same origin: optical ionization of electrons from traps. Of course, distortions may play an important role in this trapping as well.

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