pure samples with a controlled amount of magnetic impurities of a type chemically very similar to the host atoms, preferentially also giving resonant spin-flip scattering to the conduction electrons. The condition $\kappa \gg 1$ assumed in this calculation is not a serious obstacle, because our previous work has indicated that the κ dependence of ρ_f is weak both in the high-field [see Eq. (20)] and in the low-field[2] limits. Furthermore, by using very thin films, even type-I materials can exhibit flux-flow behavior with an effective $\kappa \gg 1$.[4] Because of the wide variation of ρ_f predicted here, experimental work under the gapless conditions studied here is desirable.

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Two-Photon Photogeneration in Amorphous Selenium

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Two-photon photogeneration has been observed in amorphous selenium. The field dependence of this uniform bulk photogeneration process saturates at low fields and fits a Poole-Frenkel model down to 300 V/cm. The previously reported strong field dependence of the generation efficiency at low fields for strongly absorbed light is attributed to surface recombination.

Time-of-flight and charge-integration measurements have been invaluable tools for studying intrinsic photogeneration and charge transport in insulators. This is primarily because they enable one to determine the bulk current and effective transit time for either carrier (depending on the polarity of the bias voltage). Knowledge of both the current and the transit time then allows the rate of supply of carriers to the bulk to be unambiguously determined. For various experimental reasons these measurements have generally been restricted to the use of strongly absorbed light. Under these circumstances, however, since all of the carriers are produced very near the surface, surface recombination, trapping, and exciton dissociation, as well as bulk recombination in the generation region, can strongly influence the results. This is particularly serious for those materials where the onset of strong optical absorption occurs lower in energy than the onset of efficient photogeneration of free charge. In amorphous selenium, for example, it has not been possible to separate unambiguously the electric field dependence of intrinsic photogeneration from surface recombination and trapping effects[1-3] (all of which affect the rate of carrier supply), since only very strongly absorbed light generates carriers efficiently. Similar problems occur in molecular materials ranging from orthorhombic sulfur to anthracene.

We suggest that two-photon processes provide a powerful tool for the study of intrinsic photogeneration in these materials, since they allow carrier pairs to be created in the bulk with energies equal to pairs created by very strongly absorbed light near the surface. We report here the observation of two-photon absorption in amorphous selenium and the results of unambiguous photogeneration efficiency measurements using the two-photon process to generate bulk carriers *uniformly*. The observed efficiency of this bulk generation process is consistent with a Poole-Frenkel mechanism from 3×10^2 to 10^5 V/cm. This indicates that the linear field depen-

dence of the rate of carrier supply previously reported[2] below 10^4 V/cm, which was attributed to a linear field dependence of photogeneration efficiency,[2,3] is actually caused by surface recombination or trapping, rather than by an intrinsic generation process.

The samples used in this study are 20- to 50-μm-thick films of selenium, vacuum evaporated onto aluminum or nesa-glass substrates held at 55°C. The films are amorphous and have a very high dark resistivity. The sandwich cell geometry is completed by evaporating semitransparent top electrodes of gold or aluminum. Since the electrodes form blocking contacts to the selenium, the sample forms a simple capacitor of capacitance C and thickness L, with an internal electric field $E = V/L$. The film is then illuminated through the electrode by a 25-nsec light pulse from either a filtered spark source or a passively Q-switched Nd-glass laser. In the small signal case (photogenerated charge $\ll CV$), the photogenerated charges drift across the sample at constant velocity $\mu_{e,h}E$, where $\mu_{e,h}$ is the drift mobility for electrons or holes. The resulting current pulse is observed on an oscilloscope.

For a strongly absorbed light pulse, a rectangular current pulse is observed of duration $T_t = L^2/\mu_{e,h}V$ ($T_t \ll \tau_{e,h}$, the carrier lifetimes, and $T_t \gg$ the width of the light pulse). Holes or electrons are observed, depending on the polarity of the illuminated electrode. Under these conditions, our samples give results for $\mu_{e,h}$, current pulse shape, and intensity dependence of photogenerated current which agree with those previously reported.[1,2,4]

For the weakly absorbed laser pulse ($h\nu = 1.17$ eV) with the gold electrode biased positively, a rectangular current pulse is observed due to photoemission from gold into selenium.[5] With the nesa or aluminum electrodes biased positively, a triangular current pulse is observed which peaks at $t = 0$ (the time of the laser pulse) and decreases linearly to zero at time $T_t = L^2/\mu_h V$. A typical current pulse is shown in the inset in Fig. 1, where the transit time equals the width of the base of the triangle. The hole drift mobility μ_h is the same as for strongly absorbed light. This is the type of current pulse that would be expected for uniform generation throughout the sample of free holes. Of course, pairs of holes and electrons are generated, but since the hole mobility is 30 times the electron mobility, the electron current pulse is not resolved in this measurement (although it is seen when the integral

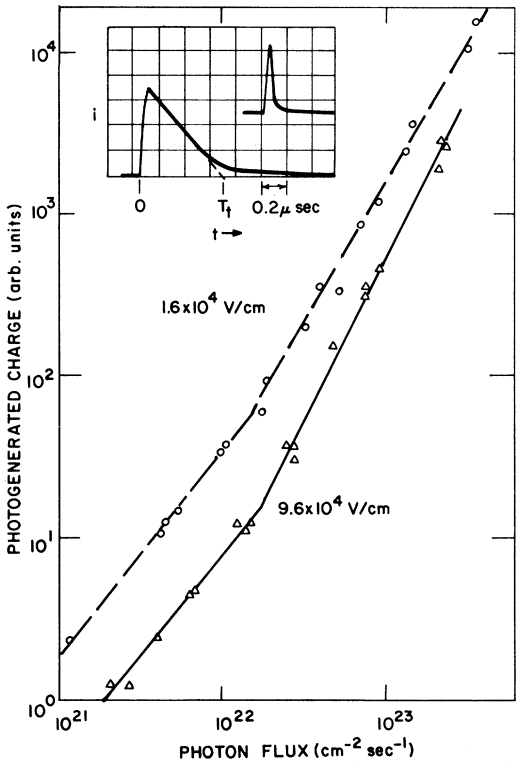

FIG. 1. Photogenerated charge as a function of flux of 1.17-eV photons for a 58-μm-thick amorphous selenium layer. The applied field is given for each curve and the arbitrary charge units are different for the two curves. Inset, photocurrent pulse for this sample with 300 V applied. Also shown (displaced in time), output of the photodiode monitoring the light pulse.

of the current is observed). The integral of the triangular pulse, which is proportional to the photogenerated charge, is shown as a function of incident photon flux F for two values of the applied electric field in Fig. 1. In the region where the pulse shape could be measured accurately ($\gtrsim 2\times10^{22}$ photons cm^{-2} sec^{-1}), plotting the peak photocurrent instead gave equivalent results. For large values of photon flux ($F \gtrsim 10^{22}$ cm^{-2} sec^{-1}) the charge varies as F^n, where n has been observed to vary between 1.8 and 2.1. This shows that the uniform bulk photogeneration observed is due to a two-photon absorption process in this intensity region. Preliminary time-resolved measurements of the nonlinear absorption indicate that this is a two-step process proceeding through real intermediate states, rather than an instantaneous process proceeding through virtual intermediate states.[6] At lower intensities, $n = 1.25$, indicating a transition to a one-photon process involving excitations of holes from im-

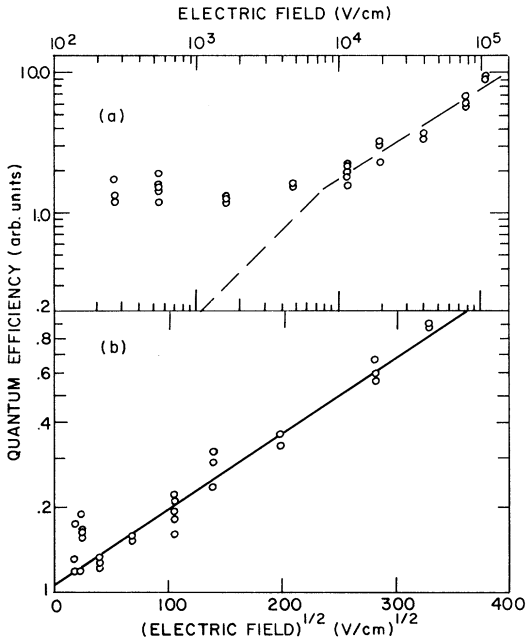

FIG. 2. Quantum efficiency of two-photon absorption as a function of electric field and the square root of electric field for a 51-μm-thick amorphous selenium layer. Dashed line, typical quantum efficiencies for strongly absorbed light (see Ref. 2).

perfections or impurities.

For bulk absorbed light, the most direct measure of the photogenerated charge is the initial value of the current in the triangular current pulse since no carriers have yet left the sample. In the large-signal case, where the photogenerated charge $\gtrsim CV$, the current pulse is no longer triangular as a result of the collapse of the internal field as the holes transit the sample. (The electrons can be considered stationary on this time scale.) However, the initial current is still proportional to the photogenerated charge since the internal field has not yet been affected. Since the room-temperature drift mobility in selenium is field independent, we take the photogeneration efficiency η to be proportional to the initial current divided by the applied field.

This photogeneration efficiency for two-photon absorption is shown as a function of initial electric field by the data points in Fig. 2 (a). Relative efficiency is plotted since the two-photon absorption coefficient is unknown. The plotted points have been corrected for variations in laser power by dividing the measured photocurrent by the square of the peak power of the exciting laser pulse. The scatter in the data at high fields is due primarily to pulse-to-pulse variations in laser-mode structure. The total experimental error in this region ($>10^3$ V/cm) is estimated to be equal to the typical scatter observed. At lower fields, noise and the previously mentioned distortion in pulse shape (since one CV of charge is photogenerated at $\sim 10^3$ V/cm) cause additional error, as can be seen from the increased scatter. The possible influence of trapped space charge on the low-field results was investigated by extensive dark resting of some samples and by measuring internal fields using higher field transits excited by strongly absorbed light. This effect was found to be negligible. Also shown in Fig. 2(a), by the dashed line, is the reported single-photon photogeneration efficiency for 2.34-eV light (twice the laser photon energy), normalized to the two-photon data at high field. Essentially identical single-photon results are observed in our samples. *In contrast to the linear field dependence of photogeneration reported below 10^4 V/cm for single-photon excitation, the two-photon results show the low-field saturation predicted for a generation process involving field-aided thermal dissociation of the photogenerated hole-electron pairs.*

The photogeneration efficiency is replotted in Fig. 2(b) as a function of the square root of the electric field. The resulting straight line shows the data to be described over the entire field range by a function of the form

$$\eta = \eta_0 \exp[(\beta E^{1/2} - \epsilon_0)/kT],$$

where η_0, β, and ϵ_0 are constants, and E is the electric field. This expression is predicted by a Poole-Frenkel model for $\eta \ll 1$ and has been previously proposed to explain photogeneration in selenium for strongly absorbed light above $\sim 10^4$ V/cm.[1,2] The slope of the straight line gives a value for β of $(2.45 \pm 0.2) \times 10^{-24}$ J $(\mathrm{V/m})^{-1/2}$, which is equal within experimental error to the value observed for 2.34-eV light.[1] Since β is wavelength dependent in the 2.34-eV wavelength region, this result suggests that the state into which the carriers are photoexcited is identical for 2.34-eV light and for two photons of 1.17-eV light.

The deviation of the field dependence of single-photon photogeneration in selenium from the predictions of a field-aided thermal dissociation model (Onsager theory[7] or Poole-Frenkel effect[1,2]) at low field has been the subject of much speculation. It has been suggested that this deviation may be due to failure of the isotropic-media theory to describe the random-walk pro-

cess in a locally anisotropic material such as selenium.[3] This is inconsistent with our results since it predicts that the field dependence of photogeneration efficiency is independent of absorption depth. Other possibilities discussed have been monomolecular (since the efficiency is independent of light intensity) bulk recombination in the generation region[2,3,8] and surface recombination.[2,8]

Our results show that bulk recombination is not an appropriate explanation since this process requires that the transition field E_c separating the regions of linear field dependence and Poole-Frenkel dependence vary linearly with absorption depth as long as the recombination remains monomolecular.[9] For bulk absorption the transition field would shift to $\sim 10^6$ V/cm. Instead, the linear region disappears. If the absorption region has a different recombination lifetime than the bulk, this argument is not as strong, but some shift should be seen as a function of wavelength and none is reported. Those processes also predict equal hole and electron efficiencies,[9] in disagreement with experiment. The absence of bulk trapping effects associated with the recombination centers has also been used as evidence against the importance of bulk recombination.[2]

If surface recombination were the dominant process at low fields, it has been shown that the transition field E_c would vary inversely with optical absorption depth.[2,3] This would require $E_c \lesssim 100$ V/cm for bulk absorbed light in our samples, in agreement with our results. The absence of this variation for strongly absorbed light has been used to reject surface recombination as a factor in the low-field behavior.[2,3,8] The conclusion is open to question, however, since it has been shown that the low-field behavior and the location of the transition field E_c are strongly sample and history dependent.[10,11] The history dependence is probably caused by trapping of charge near the surface. The resultant lowering of the field in the generation region allows a greater number of carriers to diffuse to the surface and recombine, thereby decreasing the carrier supply. We therefore feel our bulk photogeneration measurements indicate that surface effects cause the strong field dependence of photogenerated carrier supply at low fields for strongly absorbed light in selenium.

In conclusion, we have demonstrated two-photon absorption in amorphous selenium and have used this process to study bulk photogeneration in this material. It has been shown that the electric field dependence of the bulk photogeneration efficiency fits a Poole-Frenkel model, saturating at low field, in contrast to the strong field dependence reported at low fields for strongly absorbed light. This disagreement has been ascribed to the effect of surface recombination on the carrier supply in the strongly absorbed case.

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