the experimental phonon dispersion measurements.[24-26] These anomalies are expected to be quite small for alkali metals. The curves are dominated by electrostatic terms and the pseudopotential plays a minor role.

In view of the successful interpretation of the various properties of simple metals,[5-9] this model pseudopotential establishes, in its own right, its importance in the study of lattice dynamics.

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Kinetics of Two-Photon Absorption from Metastable Defect Levels in Solids

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The results of two-photon absorption from metastable defect levels are presented in terms of a wide range of the characteristic trapping parameters of a simple model of a solid. The instantaneous photocurrent maxima and the luminescence brightness maxima as obtained from exact solutions of the coupled nonlinear kinetic equations are shown to depend on the square of the laser flux, provided that the intensity is a few orders of magnitude smaller than the laser-damage threshold. The square-law dependence is lost close to the threshold. These results are independent of surface recombination and diffusion.

The two-photon absorption rate is proportional to the square of the light intensity (F) if the sample is illuminated with monochromatic light (and to the product of the intensities F_1, and F_2, if two different monochromatic beams are present). Direct measurements of the two-photon absorption rate have confirmed this.[1] Indirect methods based on the square-law dependence have since been taken as strong evidence of the existence of two-photon processes, in for example, luminescence,[1] photocon-

ductivity,[2] and photoemission experiments.[3,4] However, Yee[5] has shown recently that the concentration of generated carriers does not necessarily depend on F^2 in the case of two-photon conductivity in semiconductors. Because of diffusion and surface recombination of the carriers and absorption of the laser beam in the sample, this dependence is modified. Under certain conditions the two-photon conductivity may even be proportional to F.

All reported work on two-photon absorption has, to our knowledge, considered systems where the initial state is a densely populated ground state. During the process, the population of this state remains essentially unchanged. A question that immediately arises is, what effect, if any, would the consideration of a metastable initial state produce, if the initial state were such that it could be depopulated during the two-photon process? It is the purpose of this note to extend the work of Yee[5] by answering this question. We present further evidence that two-photon luminescence and conductivity are not always dependent on F^2.

The indirect method by which we propose to study two-photon processes will, of necessity, be time dependent. This will be due not to the nature of the source (i.e., laser pulse time) but rather to the fact that the process studied is of finite duration because of the depopulation of the initial state. In the case that the initial state is a metastable state such as a trap occupied by an electron (defect level of a solid above the thermal equilibrium Fermi level) then processes such as two-photon conductivity and luminescence will be time dependent. After the source is switched on, the concentration of generated charged carriers or electrons in the excited level rises, reaches a peak, and decays as the concentration of trapped carriers becomes depleted. The strong time dependence of luminescence or conductivity transients is expected to complicate the experimental identification of the two-photon process.

We consider the simple model, frequently used to discuss the kinetics of charged carriers in solids.[6-8] It consists of a single trap of depth E, a single type of recombination center, and a normally empty conduction band. If we denote the concentrations of trapped carriers, free charge carriers, and optically connected traps by n, n_c, and N, respectively; then, on irradiation with a given source of light, the charge carrier processes can be represented by the following set of kinetic equations[8]:

$$\frac{dn}{dt} = \beta n_c (N-n) - Pn \,, \tag{1}$$

$$\frac{dn}{dt} + \frac{dn_c}{dt} = -\gamma n_c (n_c + n) \,, \tag{2}$$

where β is the retrapping coefficient, γ is the recombination coefficient, and P is the generation coefficient. These equations provide an adequate description of optical stimulation, provided $E \gg kT$; and in the case of two-photon stimulation the generation coefficient depends on the square of the light intensity.[9] For the sake of simplicity we have neglected surface diffusion and recombination[5] (E = trap depth).

The luminescence brightness B and the instantaneous photocurrent i induced by two-photon effects are given by[8]

$$B \propto \gamma n_c (n_c + n) \,, \tag{3}$$

$$i \propto n_c \,. \tag{4}$$

However, for our calculations, it is necessary to know the range of possible values that the generation coefficient P can have in a solid.

The differential cross section for the absorption of two photons of the same frequency ω can be expressed as

$$\frac{d\sigma}{d\Omega} = r_0^2 \left(\frac{m}{\hbar}\right)^2 \frac{8\pi^3}{9} c^2 \omega^2 I \left| \sum_b \frac{2 \vec{r}_{f,b} \cdot \vec{r}_{b,i}}{\omega + \omega_b - \omega} \right|^2 (\vec{\epsilon}_1 \cdot \vec{\epsilon}_2)^2 \,, \tag{5}$$

where $r_0 = 2.82 \times 10^{-13}$ cm and is the classical electron radius, m is the electron mass, and I is the photon flux per unit frequency. The abbreviation $\vec{r}_{f,b}$ stands for the matrix element $\langle f | \vec{r} | b \rangle$ and the sum is over all intermediate states of the atom. The subscripts f, b, and i denote the final, intermediate, and initial states, respectively. $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ are the photon polarization vectors.

The relation between the total cross section σ and the generation coefficient P is given by $P = \sigma F$, where F is the photon flux (e.g., flux of a laser

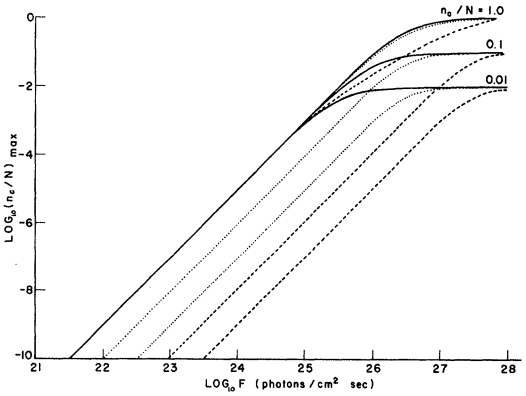

FIG. 1. Dependence of the instantaneous photocurrent maximum on intensity for different initial trap-filling ratios (n_0/N) and for different cases of retrapping: small retrapping, $R = 0$, solid line; large retrapping, $R = 100$, dashed line; intermediate retrapping, $R = 1$, dotted line.

beam). Now, in order to calculate σ, Eq. (5) has to be applied to a solid. This has already been done by Kleinman[10] who derived the following expression:

$$\sigma = \frac{r_0^2 8\pi^3 c^2 f_{f,b} f_{b,i}}{n'^2 \omega^2 \Delta\omega} F , \tag{6}$$

where n' is the refractive index of the medium, $\Delta\omega$ is the width of the absorption band around 2ω, and $f_{f,b}$ and $f_{b,i}$ are the oscillator strengths for transitions between the intermediate state and both the initial and final states. It is assumed that there is only one intermediate state and that the energy differences between this state and both final and initial states are much larger than $\hbar\omega$.

Equation (6) is now used to estimate P. Assuming that the oscillator strengths are unity, [10] that $\omega = 1.76\times10^{15}$ sec^{-1} (Nd laser) that $\Delta\omega = 0.1\omega$ and that $n' = 1.5$, then one obtains $P = 1.4\times10^{-47}F^2$ sec^{-1}, when F is given in photons/cm^2 sec. The upper limit of P is given by the laser-damage threshold[11] of the material. For a 50-nsec pulse this threshold is of the order of 100 J/cm^2 which corresponds to $F = 10^{28}$ photons/cm^2 sec. The upper limit is therefore assumed to be $P_{max} = 10^9$ sec^{-1}. It is convenient now to define the parameter $P^* = P/\gamma N$. For a typical trap density $N = 10^{16}$ cm^{-3} and assuming a recombination coefficient[12] $\gamma = 10^{-10}$ cm^3 sec^{-1} then P^* can be expected to reach 10^3.

Numerical solutions of B and i have been obtained from Eqs. (1)–(4) by standard numerical analysis techniques[13] for the following ranges of parameters:

$$0 \le R \le 10^2 , \quad 1 \le n_0/N \le 10^{-2} , \quad 10^{-10} \le P^* \le 10^3 ,$$

with $n_{c0} \equiv 0$ for all cases (n_0 and n_{c0} are the values of n and n_c at $t = 0$). $R \equiv \beta/\gamma$ is a measure of retrapping. For $t < 0$, $F = 0$ and for $t \ge 0$, F is a constant. Solutions of the kinetic equations have been obtained without making use of the assumptions[7,8] that $n_c \ll n$ and $dn_c/dt \ll dn/dt$.

All solutions exhibit a maximum when plotted vs time. In Fig. 1 we illustrate the change in the current maximum as a function of a change in light intensity for the above ranges of parameters. Not shown but similar is the corresponding plot of the brightness maxima vs intensity.

It would appear from Fig. 1 that an experiment to detect two-photon absorption from metastable defect states in a solid requires that either the retrapping be small and the traps initially full ($R \ll 1$, $n_0/N \sim 1$), or that the retrapping be large and the initial trap filling be small ($R \gg 1$, $n_0/N \ll 1$). Generally, however, the trapping parameters are not known. Therefore, care must be exercised that one obtains an F^2 dependence of the current maxima. As shown in the figure, this will generally be the case, provided the source intensity is less than 10^{25} photons/cm^2 sec.

An F^2 dependence of the current maxima can be taken as evidence of two-photon absorption. Further, the lack of an F^2 dependence neither rules out the possibility of two-photon processes (also shown by Yee) nor confirms it. Similar considerations apply to the F^2 dependence of brightness maxima.

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