Mechanisms for the absolute negative photoconductivity of insulators

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The microscopic mechanisms for negative photoconductivity of insulators ($j_{ph} = \sigma_{ph} E$, $\sigma_{ph} < 0$) have been detected for the first time. In models for hopping photoconductivity, the dominant contribution to the current is associated with the field-induced asymmetry of the photoexcitation and recombination of electrons. The sign of $\sigma_{ph}(\omega)$ is predicted to change as the light absorption moves through a resonance.

A new striking effect—absolute negative photoconductivity—was recently discovered in concentrated ruby crystals.[1–3] This effect involves a photostimulated generation of current in the direction opposite to the field

$$\mathbf{j}_{ph} = \sigma_{ph}\mathbf{E}; \qquad \sigma_{ph} < 0. \tag{1}$$

An absolute negative photoconductivity causes an insulator to be unstable—it increases its electric-field fluctuations (in ruby, these fluctuations increase to $E_0 \cong 10^6$ V/cm). Experimental data have so far been analyzed only at the level of the phenomenological model.[3] The microscopic mechanisms of absolute negative photoconductivity and the conditions under which it occurs are still unknown. This letter is concerned with the search for these mechanisms.

We will attribute the negative contribution of the photocurrent to the field-induced asymmetry of the photoexcitation and recombination of electrons. This contribution, as will be shown below, is most pronounced in the case of a hopping charge transfer. Let us examine the following general model. We assume that the electrons are localized in deep centers in the absence of light and that their mobility is negligible, since the photoexcited electrons have a larger localization length r_0, there is a slight overlap of the wave functions of the adjacent centers. The excited states may correspond to the impurity energy levels, which have a homogeneous or inhomogeneous broadening, of a narrow polaron band. We denote by $g_{\pm}(R, \omega, E)$ the average rate of photoproduction at the centers, respectively, to the right and to the left of the original center situated a distance R from them and by g_0 the rate of the transition in a center (Fig. 1). In the absence of a field, we have $g_+ = g_- \equiv g_1(R, \omega)$. Setting R equal to the average spacing between the centers, we estimate the contribution to the current due to the asymmetry of the transitions to be

$$j_{as} \cong e\frac{\kappa J}{\hbar\omega} R\xi; \qquad \xi = \frac{g_+ - g_-}{g_0 + g_+ + g_-}. \tag{2}$$

Here κ is the absorption coefficient of light, J is the intensity of light, and $\xi(E, \omega)$

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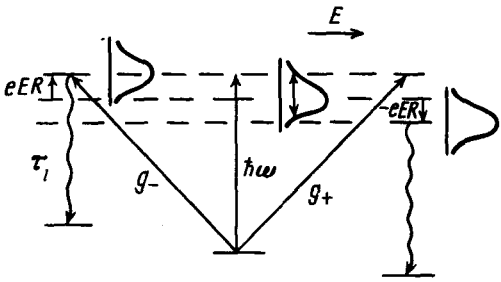

FIG. 1. A scheme showing the transitions resulting from a field-induced level shift ($g_- > g_+$).

represents the symmetry parameter. The recombination component of the current is omitted in Eq. (2). This can be done in the case of a symmetric recombination, e.g., a recombination in the center.[1)]

Let us examine the principal mechanisms for the onset of the excitation asymmetry. First, it is clear that the field E shifts the energy levels of various centers with respect to each other. In the case of adjacent centers separated a distance R from each other, the level shift is $\Delta\epsilon \cong eER$ (Fig. 1). A change in the relative positions of the levels is seen in the frequency dependence of the photoexcitation rates:

$$g_\pm (R, \omega, E) \rightleftharpoons g_1 (R, \omega \pm eER\hbar^{-1}). \tag{3}$$

Consequently, for small values of E we have

$$\xi \cong \frac{2eER}{\hbar (g_0 + 2g_1)} \frac{\partial g_1 (R, \omega)}{\partial \omega}. \tag{4}$$

We emphasize that the asymmetry in this mechanism is resonant in nature, the sign of j_{as} is determined by the deviation from resonance with respect to the line center $g_1(R, \omega)$ and the magnitude of j_{as} is determined by the width of this line, Γ.

The asymmetry is particularly large if the excitation in the center is suppressed, $g_0 \to 0$ (this condition need not necessarily hold in order to see the absolute negative photoconductivity). In this case, the value of ξ is estimated in terms of the absorption line width:

$$\xi \cong \frac{eER}{\hbar\Gamma}. \tag{5}$$

A small g_0 may be a consequence of the electronic-transition selection rule or energy selection rule. For example, transitions in a center and between centers correspond to different frequencies of light if these transitions give rise to configurations that differ in the charge state. Experimentally, such a situation was encountered in Ge :Zn :Sb crystals.[4] Note that a small g_0 does not imply that the recombination inside a center is weak. A recombination may proceed through the intermediate energy levels. The second asymmetry-originating channel is linked with the distortion of the wave functions of electrons. It is logical to assume that an excited state is polarized by the field more intensely than a ground state. A spatial displacement of the electron wave function accounts for the difference between the photoproduction rates of g_+ and g_- (Fig. 2).

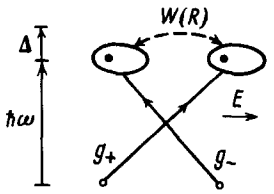

FIG. 2. A schematic diagram of a nonresonance asymmetry mechanism. The ellipses denote the regions in which the electrons are localized.

The value of ξ can be determined by assuming that the field E admixes to the wave function of an excited state a symmetry-compatible function which corresponds to the nonresonance energy level (Fig. 2). If Δ is the corresponding energy spacing, we will have $\xi \cong er_0E/\Delta$. The sign of ξ depends on the sign of Δ. The positive excited-state polarizability corresponds to the current j_{as} in the direction opposite the field (Fig. 2). The asymmetry mechanism considered by us is analogous to the mechanisms for the photovoltaic effect occurring in polar crystals.[5] This mechanism is not a resonance mechanism and generally gives smaller values of ξ than the resonance mechanism.

The negative value of $\sigma_{as} \equiv dj_{as}/dE$ alone is not enough for the absolute negative photoconductivity to exist. The reason for this is that there is the usual positive contribution to the photoconductivity σ_+, which stems from the motion of the photoexcited electrons in an electric field. The particular features of the model for hopping charge transfer we are considering are such that the values of σ_+ turn out to be small.[2)] To determine σ_+, we must introduce two additional parameters—the lifetime of an excited electron with respect to the recombination occurring in the center, τ_l, and the characteristic probability for a jump between the excited states, W. The quantity $W(R)$ may be related to either a homogeneous or inhomogeneous broadening of levels.[6,7] It usually decreases exponentially with increasing R and depends on the temperature in terms of the activation energy. Assuming that $\tau_l \gg \tau_{osc} \cong 10^{-14}$–$10^{-12}$ s are the vibrational-relaxation times, we can use the Einstein equation to estimate the electron mobility as eWR^2T^{-1}. Accordingly, we find

$$\sigma_+ \cong e^2 \frac{\kappa J}{\hbar\omega} W\tau_l R^2 T^{-1} . \tag{6}$$

The particular feature of (6) is the presence of the kinetic parameter $W\tau_l$. To the extent that the overlap integral of the wave functions is small, this parameter is essentially not bounded below.

Let us write out explicitly the condition under which the absolute negative photoconductivity occurs. Using (2), (5), and (6), we find

$$W\tau_l < T/\hbar\Gamma . \tag{7}$$

Inequality (7) or expressions similar to it do not impose stringent restrictions on the parameters of the hopping model. We expect that absolute negative photoconductivity occurs in many dielectrics in which the hopping photoconductivity is low.

The field E_0 produced as a result of the development of an electric instability can be estimated in a very simple manner as follows. Assuming that the mechanism for the

stabilization of an instability corresponds to the system's loss of resonance, we can write $E_0 \cong \hbar\Gamma/eN_0^{1/3}$, where N_0 is the impurity density. Setting $\Gamma = 10^{13}\ \mathrm{s}^{-1}$ and $N_0 = 10^{20}\ \mathrm{cm}^{-3}$, we find $E_0 \cong 10^5$ V/cm.

In addition to developing and refining the theory of absolute negative photoconductivity, it would be of interest to carry out experiments to detect the predicted resonance absolute negative photoconductivity. Among the promising candidates for investigation, we can single out semiconductors with shallow impurity levels and the highly doped laser crystals. From the standpoint of describing the effect, the laser crystals, in particular, ruby crystals, seem to be more complicated than semiconductors.

[1)]Equation (2) implicitly presupposes that nearly all low-lying levels are empty (strong cancellation). It is easy to show, however, that our results remain valid even in the case of an intermediate cancellation.

[2)]The opposite situation occurs in band mechanisms. Using the concepts developed in the study of photovoltaic-effect mechanisms,[5] we can show that the condition $\sigma_+ < \sigma_{as}$ imposes an unrealistic constraint on the lifetime of a photoelectron, $\tau_l \ll 10^{-15}$–10^{-17} s.

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