Mechanisms of absolute negative photoconductivity

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A microscopic theory of absolute negative hopping photoconductivity (ANP) is developed. The ANP mechanisms are attributed to the asymmetry of the phototransitions between the localized states in an external field. Resonant ANP, which is characterized by reversal of the sign of the current on going through the light-absorption resonance, is investigated. The cases of strong and weak compensations of the dielectric, and various types of optical transitions, are investigated.

INTRODUCTION

The requirement that a state in thermodynamic equilibrium be stable is known to lead to positive static conductivity.[1] Illumination lifts this restriction and the current, generally speaking, can be directed counter to the field:

$$\mathbf{j}=\sigma\mathbf{E}, \quad \sigma<0. \tag{1}$$

In this case it is natural to speak of absolute negative photoconductivity (ANP). It follows directly from (1) that the manifestations of ANP should differ radically from those of ordinary (positive) conductivity. In particular, the zero-current state of a medium (with $E=0$) becomes unstable to increase of field fluctuations.

The problem of identifying the ANP mechanisms lies not so much in pointing out the negative contributions to σ as in finding the conditions under which they prevail over the usual positive contributions, i.e., under which the total current is negative, $\mathbf{j}\cdot\mathbf{E}<0$.

The first studies of the ANP mechanisms were made in the late Fifties.[2,3] The mechanisms were based on the band description of the electrons under the assumption that their effective mass is negative. Owing to the time hierarchy typical of semiconductors,[4] $\tau_p \ll \tau_\varepsilon \ll \tau_e$ ($\tau_{p,\varepsilon}$ are the momentum and energy relaxation times and τ_e is the electron lifetime), the positive contribution made by the thermalized carriers to the photoconductivity was found to prevail over the negative contribution of the nonequilibrium electrons with $m^*<0$. In other words, the conditions for realizing ANP turned out to be very stringent. The predicted mechanisms were not realized in experiment.

In 1966 a different type of band mechanism was proposed[5,6] for ANP, requiring no negative mass. It was based on the known existence of a threshold for emission of an optical phonon and on the assumption that the electron lifetime is short, $\tau_e<\tau_\varepsilon$. However, even under this stringent requirement the conditions for ANP realization were not found to be very realistic. The mechanism predicted was not observed in experiment.

In 1980, in the course of spectroscopic experiments on concentrated-ruby crystals, a pronounced growth of a light-induced electric field was observed and investigated.[7] The field saturated at a level $E_0\approx 10^6$ V/cm.

The interpretation offered in Ref. 7 for the observations was found to be in error. A cycle of experiments[8–13] carried out in 1983–1985 confirmed the results of Ref. 7, yielded the known data, and revealed convincingly the existence of ANP in weak fields and the reversal of the sign of σ at sufficiently large E. A number of questions related to the motion of electric domains was also investigated for such an N-shaped current-voltage characteristic. Microscopic mechanisms were not investigated theoretically in Refs. 8–13. Although the ANP mechanism in ruby remained unclear, the experimental data seemed to indicate that the charge is transported by hopping rather than by a band mechanism. The need for finding hopping mechanisms for ANP was indicated also by "band estimates" based on premises advanced in Ref. 9 concerning the nature of ANP and on concepts developed in the study of the photovoltaic effect.[14]

Hopping mechanisms for ANP were posited[15] in 1985. In the present paper, which is an elaboration of Ref. 15, we propose a consistent microscopic theory of ANP and investigate the conditions for realizing this phenomenon. We state right away that it is not our aim to describe ANP in ruby. The point is that neither the characteristics of highly excited states of chromium, over which the charge is probably transported, nor any of their transport properties, have been extensively investigated. We hope that the proposed theory will help find new objects in which ANP is realized, and will serve as an additional impetus for extensive investigations of this new interesting phenomenon.

We note a few other recent theoretical papers on ANP. In Ref. 16, on the basis of an analysis of the published data on the photovoltaic effect, an interesting suggestion was made that ANP may be realized in certain dielectrics above the ferroelectric-transition point. ANP mechanisms were proposed in Refs. 17 and 18. From our standpoint, the last two references are inconsistent and cannot claim to describe the effect. No account was taken in Ref. 17 of the recombination contribution to the current, which cancels the accounted-for contribution from photoexcitation. In Ref. 18 the contribution to the photoconductivity was taken into account phenomenologically and inconsistently.

Our plan is the following. In §1 is formulated the basic model used subsequently to describe hopping photoconductivity, viz., a model of weakly interacting two-level centers, and its main features are discussed. We next introduce in §2 an asymmetry parameter ξ that is central to our theory. It

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characterizes the asymmetry of the probabilities of the photoinduced hops along and counter to the field. We consider the main asymmetry mechanisms that are connected with the energy-level shifts and with the distortions of the wave functions of the excited states in an external field. We demonstrate the important role of the resonant asymmetry mechanism, in which the sign of ξ depends on the detuning from the absorption-line center. Using the premise of photoexcitation asymmetry, we describe in §3 an elementary theory of asymmetric contributions to the current, $\mathbf{j}_{as} = \sigma_{as}E$, which can be directed counter to the field, i.e., correspond to $\sigma_{as} < 0$. We consider various types of optical transitions and different degrees of occupation of the initial states (weak and strong compensation). In §4 are investigated, under the same conditions, the positive contributions to the photoconductivity, $\sigma_+ > 0$, made by hopping over the excited level. The conditions for the realization of ANP, i.e., when $\sigma = \sigma_+ + \sigma_{as} < 0$, are the subject of §5, which contains estimates of the photoinduced fields as well as numerical estimates. In the Conclusion we review briefly the prospects of further theoretical investigations of the hopping mechanism of charge phototransport and estimate the possibilities of observing resonant ANP.

We neglect hereafter the intrinsic (dark) contribution to σ, i.e., assume the medium to be a dielectric. The ANP can then be regarded as an effect linear in E and in the light intensity J. We ignore also inessential effects such as anisotropy and polarization properties of the current.

§1. BASIC MODEL

Assume that in the absence of light the electrons are in localized states corresponding to an energy ε_1. These states can be related to structure defects (impurities, vacancies, etc.) or to small-radius polarons in the crystal.[19] The overlap of the electron wave functions at neighboring centers is assumed negligibly small, i.e., the medium is a dielectric. The light excites the electrons to higher energy levels. The electrons in the excited states are also localized, but their localization radius r_0 is much larger than in the ground state. The overlap of neighboring-center wave functions, when at least one of them corresponds to an excited state, is assumed finite albeit small. It is this overlap which causes the electrons to hop from center to center, i.e., leads to hopping conduction.[1)]

Elementary processes of three types are possible in this model. First, intracenter transitions induced by the light (and their inverses, recombination transitions). They do not contain the small overlap of the wave functions and do not lead by themselves to charge transport. Second, electron transitions from the ground state of one center to an excited state of another—intracenter photoexcitation. Third and last, electron hopping from one excited state to another (induced as a rule by phonons). The second and third types of transition are connected with charge transport; the probabilities of these processes contain small wave-function overlap integrals.

The character of the intercenter photoexcitation depends essentially on whether the lower level of the neighboring center is occupied or free. If it is free (Fig. 1a), we have a single-electron problem, and the inter- and intracenter transitions occur at the same frequencies of light. If both lower levels are occupied, two electrons turn out to be on the same center in the final state in the case of intercenter transitions (Fig. 1b). The simplest example of such a state is an H^- center, i.e., a hydrogen atom that has captured a second electron.[20] The difference between the final and initial energies of such a two-electron system exceeds the distance $\varepsilon_2 - \varepsilon_1$ between the upper and lower levels of one center by an amount equal to the Coulomb repulsion energy ε_c. Intercenter excitation takes place therefore at higher frequency than intracenter transitions. This frequency difference can be large compared with the energy-level widths. Two-particle states are frequency considered using a simplified description in which it is assumed that the inner strongly bound electron only screens the nuclear charge, so that the single-electron description can be used for the outer weakly bound one. We shall also be guided below by this approach.

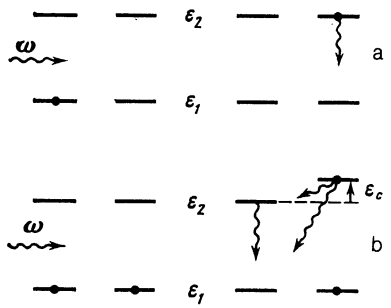

FIG. 1. a) Initial and final states of an electron in intercenter phototransition to an empty center, b) intercenter phototransition to an occupied center; the wave lines represent the recombination channels.

The transitions illustrated in Fig. 1 are typical of strong compensation of the dielectric, when almost all the centers are unoccupied. Transitions corresponding to Fig. 1b are typical of the opposite case of weak compensation.

§2. ASYMMETRY PARAMETER

Consider a pair of centers separated by a distance R, let $g_\pm$ denote the probability of the intercenter phototransitions along and counter to the field, and let g_0 be the rate of intracenter photoexcitation. The asymmetry parameter is then defined as[2)]

$$\xi = \frac{g_+ - g_-}{g_0 + g_+ + g_-}. \qquad (2)$$

The quantity ξ, just as g_0 and $g_\pm$, depends on the field E, on the radius vector R joining the center (its direction is fixed by the condition $\mathbf{E}\cdot\mathbf{R} > 0$), and the frequency ω of the light. In view of the central symmetry, $\xi = 0$ at $E = 0$.

We investigate the two basic mechanisms of the asymmetry. The first is due to the energy-level shifts of the different centers. For a center located at a point $\mathbf{r}$, the shift is $\delta\varepsilon = -e\mathbf{E}\cdot\mathbf{r}$. The relative shift of the levels leads, as can be seen from Fig. 2, to a difference between the resonant frequencies corresponding to intercenter transitions along and

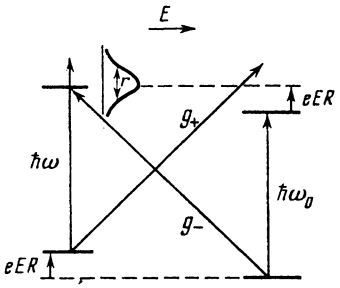

FIG. 2. Scheme of phototransitions for a pair of centers in field-induced level shifts. The bell-shaped curve near the excited energy level shows the absorption-line shape. Light frequencies above resonance, $\omega > \omega_0$, correspond to motion of the charge counter to the field, $g_- > g_+$.

counter to the field. Denoting by $g_1(\mathbf{R}, \omega)$ the rate of the intercenter photoexcitation in the absence of a field, we have, obviously,

$$g_\pm = g_1(R, \omega \pm e\mathbf{RE}/\hbar). \tag{3}$$

Consequently, at small E the asymmetry parameter is

$$\xi = \frac{2e\mathbf{ER}}{\hbar(g_0+2g_1)} \frac{dg_1}{d\omega}. \tag{4}$$

The most important property of ξ as a function of ω is its connection with the absorption resonances. The maxima and minima of ξ are reached at the points where the change of $g_1(\omega)$ is most abrupt. The sign of ξ is reversed at the absorption maximum. Thus, depending on the light frequency, the electrons can be predominantly displaced both along the field and counter to it. The frequency dependence of ξ will be discussed in greater detail later in this section.

The probability of an intercenter transition, as already noted, contains a small parameter due to the weak overlap of the wave functions [as a rule, $g_1 \propto \exp(-R/r_0)$]. The probability of the intracenter transition g_0 does not contain such a small parameter. Therefore $g_0 \gg g_1$ in most cases. We, however, are interested in the feasibility of the inverse limiting situation $g_1 \gtrsim g_0$, when the asymmetry is extremely large. This case, quite understandably, is particularly favorable for ANP. If we are dealing with a transition to an empty center (see Fig. 1a), g_0 can contain a small quantity connected with the selection rules for intracenter transitions (these rules do not apply, of course to intercenter transitions). If the symmetry of the ground and excited states is such that dipole intracenter transitions are forbidden (s–s transitions, etc.), situations are possible in which $g_0 \lesssim g_1$, the smallness of g_1 notwithstanding. That such situations are realistic is indicated indirectly by the fact that the lifetimes of metastable states in certain laser crystals exceeds by many orders the characteristic times of the dipole transitions.[21] For transitions to an occupied center (see Fig. 1b), the smallness of g_0 can be simply due to the energy hindrance, i.e., to the fact that the resonant frequencies are substantially different for the intra- and intercenter transitions. We shall return to the relation between g_0 and g_1 in §5, where we assess the ANP-realization conditions.

In those cases when $g_1 \gtrsim g_0$ and the asymmetry is extremely large, expression (4) takes the particularly simple form

$$\xi \approx \frac{eER}{\hbar} \frac{d}{d\omega} \ln g_1. \tag{5}$$

Let us discuss the spectral properties of ξ. The transition rates $g_{0,1}$ are equal to the squares of the corresponding matrix elements multiplied by a phonon factor corresponding to the displacements of the normal modes.[22,23] It is this factor which determines the frequency dependence of the absorption. The absorption spectrum consists frequently of a narrow zero-phonon peak and a phonon wing extending to the short-wave region.[23] The wing width $\delta\omega$ is governed by polaron-like effects. The width Γ of the zero-phonon line is determined by other than polaron interactions.[19,23] Usually Γ is larger by several orders than the reciprocal lifetime τ_ε^{-1}, typical of dipole transitions,[23] of the electron in the excited state. In optics Γ is frequently called the rate of transverse or phase relaxation.

For a Lorentzian zero-phonon line and at $g_0 \lesssim g_1$ Eq. (5) yields

$$\xi(\omega) = -\frac{2e\mathbf{ER}}{\hbar} \frac{(\omega-\omega_0)}{[(\omega-\omega_0)^2+\Gamma^2]}. \tag{6}$$

Motion of the charge counter to the field corresponds to detunings $\Delta = \omega - \omega_0 > 0$. The maximum of $|\xi(\omega)|$ is reached at $\Delta = \Gamma$:

$$|\xi|_{max} \approx e\mathbf{ER}/\hbar\Gamma. \tag{7}$$

For the phonon wing we have $\Gamma \to \delta\omega$.

We consider now the second asymmetry mechanism. It is due to the field-induced distortions of the excited-state wave functions (the ground-state perturbation due to its strong localization can be neglected). This mechanism is illustrated in Fig. 3. The displacement of the electron cloud makes the probabilities g_+ and g_- different, and it can be easily seen that a polarizability positive in the excited state corresponds to a negative ξ, i.e., to hopping counter to the field. This asymmetry mechanism is similar in its context to the mechanisms of the photovoltaic effect in polar crystals.[14] The role of the field reduces to making the medium noncentrosymmetric. One can calculate ξ by postulating a supplementary level corresponding to a state of different symmetry

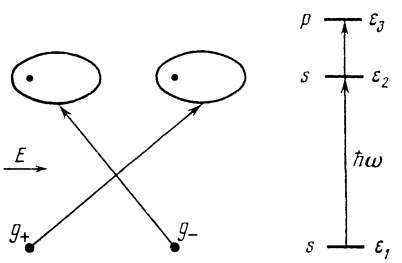

FIG. 3. Nonresonant asymmetry mechanism. The ellipses denote the electron-localization regions. It can be seen that the distance between the right-hand unexcited electron and the left-hand excited one is shorter than the distance from the left unexcited to the right excited electron. Therefore $g_- > g_+$. In the right hand side of the figure is shown the energy-level scheme.

and located close to the optically excited energy levels. This can be, for example an s or p state (Fig. 3). The field mixes a p state with the excited s state,

$$\delta\psi_2 = \frac{\langle p|e\mathbf{E}\mathbf{r}|s\rangle}{\varepsilon_2-\varepsilon_3}\psi_3, \tag{8}$$

producing the polarization of the medium. Straightforward but cumbersome calculations lead to values of ξ that differ from (4)–(7) mainly by the parameter $\Gamma/(\varepsilon_2-\varepsilon_3)$. Thus, at $g_0 \lesssim g_1$ we have in place of (7)

$$\xi \approx e\mathbf{E}\mathbf{R}/\hbar(\varepsilon_2-\varepsilon_3). \tag{9}$$

In contrast to the resonance mechanism, the asymmetry parameter does not depend on the frequency of the light. Its sign is determined by the difference $\varepsilon_2-\varepsilon_3$, which can be negative as well as positive.

It is natural to assume that the energy widths $\hbar\Gamma$ and $\hbar\delta\varepsilon$ are much smaller than the characteristic distances between the levels. The strongest of the considered asymmetry mechanisms is then the first—the resonance mechanism. It is also the roughest; Eqs. (3) and (4) make minimum use of assumptions concerning the structure of the centers. The second asymmetry mechanism, connected with distortions of the wave functions, is apparently important for the investigations of the hopping mechanisms of the photogalvanic effect in polar crystals.

§3. THE PHOTOCONDUCTIVITY σ_{as}

Let us find the contribution made to the photoconductivity σ_{as} by the field-induced asymmetry of the excitation and recombination processes. This calls for a change from the properties of an individual center or of a pair of centers to a macroscopic property of the medium, viz., the current density j_{as}. If the centers are randomly disposed, the distance R between neighbors will fluctuate about a mean value $\bar{R}$. Therefore the probabilities $g_\pm$ of intercenter transitions, and with them also ξ, will have an exponentially strong spread. In addition, fluctuations of the transition frequency ω_0 are possible, meaning inhomogeneous broadening of the absorption line. The determination of the current in this situation is a task of percolation theory.[24] In the context of this theory, we set the hop length equal to $c\bar{R}$ in the expressions for ξ, where c is a constant of the order of unity (and will hereafter be omitted). If the centers form a periodic lattice (the case of a small-radius polaron), then $c=1$ and $\bar{R}$ is equal to the lattice constant a. In addition, when calculating j_{as} we shall neglect the spread of the energy levels. This is possible if the inhomogeneous broadening of the absorption line is $\Gamma_N < \Gamma$. This approach is partially justified by the fact that in solids the homogeneous broadening Γ can be quite large, especially at high temperatures.[23]

When j_{as} is determined, a distinction must be made between the cases of strong and weak compensation of the dielectric. We introduce the compensation parameter $K = N_0/N$, where N_0 is the density of the empty center and N is the total density. Strong and weak compensations correspond then to $1-K \ll 1$ and $K \ll 1$, respectively. We consider first the strong-compensation limit, when a small fraction of the lower levels is occupied. Let the light frequency be close to the frequency $\hbar^{-1}(\varepsilon_2-\varepsilon_1)$ of the intracenter transitions. Then the intercenter transitions will cause the electrons to land on the upper levels of the empty centers (Fig. 1a). The recombination has in this case an intracenter character and makes no contribution to the current. We note here that the low rate g_0 of the intracenter excitation, due to the selection rules, does not mean that the intracenter recombination is weak. This recombination can proceed via intermediate energy levels with allowed transitions. Taking into account the obvious relation

$$N_1(g_0+g_++g_-) = \varkappa J/\hbar\omega,$$

in which $N_1 = N - N_0$ is the density of the occupied centers, we can write

$$j_{as} = e(\varkappa J/\hbar\omega)\bar{R}\xi(E, \bar{R}, \omega). \tag{10}$$

Assuming that $g_0 \lesssim g_1$ and using (6), we obtain in the region of the zero-phonon peak

$$\sigma_{as} = -e^2\frac{\varkappa J}{\hbar\omega}\frac{\bar{R}^2}{\hbar}\frac{\Delta}{(\Delta^2+\Gamma^2)}. \tag{11}$$

In the region of the absorption wing, $|\sigma_{as}|_{\max}$ is decreased by a factor $\Gamma/\delta\omega$ compared with the value given by (11). If $g_0 \gg g_1$, Eq. (11) is decreased by an additional factor g_1/g_0.

It should be noted that Eq. (11) can be obtained formally within the framework of the "crystal" model. In this model, the two-level centers form a regular crystal lattice, and localization of the excited electrons is the result of the fact that the energy overlap integral between nearest neighbors, which determines the tunneling time, is $I \ll \hbar\tau_e^{-1}$. The calculation of σ_{as} is carried out in the site representation of the standard density-matrix method of optics.[25,26]

Even though in the case of strong compensation the main absorption takes place at frequencies close to resonance for one center ($\omega = \hbar^{-1}(\varepsilon_2-\varepsilon_1)$), ANP can be realized also by using a weaker absorption peak corresponding to intercenter transitions to occupied sites. This peak is shifted towards higher light frequencies and is due to rarely encountered pairs of occupied centers. The density of such pairs is obviously of the order of $N_1(1-K) \ll N_1$. Accordingly, $\varkappa$ will also contain the small quantity $1-K$. The recombination is in this case of the intercenter type, since the lower state is occupied by an electron. As before, however, the recombination is symmetric and makes no contribution to j_{as}. We arrive therefore again at Eq. (10). It must be borne in mind here that, while losing in gain $\varkappa$, we can win in ξ, since the rate of the intracenter transition $g_0 \to 0$. It is interesting to note that in our case the current j_{as} is a distinctive consecutive motion of electron pairs (Fig. 4).

We proceed now to the case of weak compensation $K \ll 1$, when almost all the centers are occupied by electrons. A characteristic feature of this case is partial cancellation of the contributions made to j_{as} by excitation and recombination. In fact, assume that in the absence of light all the centers are occupied, i.e., $K=0$. Since intracenter recombination into the ground state is impossible for an electron photoexcited to a neighboring center, the electron must re-

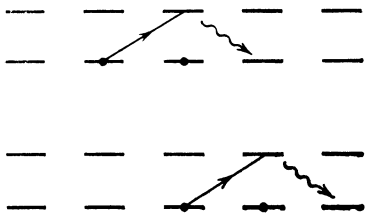

FIG. 4. Particle motion in a strongly compensated dielectric at light frequencies resonant to intercenter transitions to occupied centers. Two successive excitation–recombination cycles are shown. It can be seen that pairs of occupied centers moving as a unit in the same direction are rarely encountered in the case of asymmetric photoexcitation and symmetric recombination.

turn to its initial position (Fig. 1b). There is therefore no resultant displacement of the electron in the excitation-recombination cycle, and $j_{as}=0$. We now include a small degree of compensation, i.e., the presence of empty places. It can be seen from Fig. 5 that a contribution to j_{as} is made only by "active" centers, i.e., centers occupied by electrons and located in the immediate vicinity of the empty ones in such a way that after the intercenter recombination the electron cannot recombine symmetrically. The density of such centers is equal to that of the empty ones: $N_0 \ll N_1 \approx N$. Therefore in the limit of weak compensation j_{as} contains K explicitly:

$$j_{as}=e(\varkappa J/\hbar\omega)\bar{R}_z^2(E)K. \tag{12}$$

Just as in (10), this result can be rigorously obtained for the "crystal" model. Calculation of the recombination contribution to j_{as} reduces then to finding a correlator of the type $\langle \hat{n}_i^2(1-\hat{n}_j^1)\rangle$ ($\hat{n}_i$ is the particle-number operator for the site i) in an approximation linear in E and J. It must be stated that Eq. (12) is valid if hopping over the upper levels is completely neglected, i.e., in the zeroth approximation in the parameter $W\tau_e$, where W is the characteristic probability of hopping to a neighboring center, and τ_e is the electron lifetime with respect to intercenter recombination.[3)] When account is taken of hopping over the upper levels, the excitation and recombination current components no longer cancel out, so that the active centers are not the only ones that can contribute to j_{as}. It can be shown that when $K \ll W\tau_e \ll 1$ it is necessary to make in (12) the substitution $K \to W\tau_e$, while at $W\tau_e \gg 1$ the current j_{as} saturates at the level specified by Eq. (10).

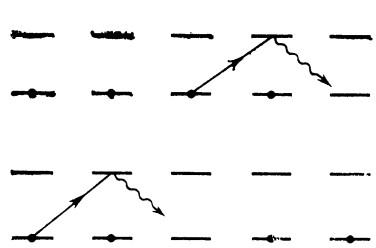

FIG. 5. Two successive excitation–recombination cycles in a weakly compensated dielectric. The solid arrows show intercenter transitions from active centers. Electron motion to the right is equivalent to oppositely directed hole motion.

§4. THE PHOTOCONDUCTIVITY σ_+

A negative σ_{as} is still insufficient for ANP to exist. As already mentioned, there is an independent positive photoconductivity contribution σ_+, due to electron hopping over excited states. It can be expressed in the form

$$\sigma_+ = e\mu n, \tag{13}$$

where n is the density of the excited electrons and μ their mobility.

When finding σ_+, just as in the calculation of σ_{as}, a distinction must be made between the cases of strong and weak compensation. This, however, is practically the only analogy between σ_+ and σ_{as}. It is clear even from general considerations that the processes determining σ_+ and the parameters in terms in which they are expressed differ from those considered in the preceding sections. In particular, the density n is proportional to the carrier lifetime τ_e. The mobility μ, obviously, contains the characteristic probability W of hopping over the upper levels. In turn, W depends on the manner in which this hopping is implemented—via the polaron shift of the levels or via the energy spread of the states (inhomogeneous broadening). The presence in σ_+ of an additional dimensionless parameter $W\tau_e$ that can be made small enough in our model plays an important role in the ANP theory.

We proceed to calculate σ_+. We consider first the strong-compensation limit $1-K \ll 1$. Since almost all the lower levels turn out to be empty, the lifetime τ_e is determined by the fast intracenter processes. It is natural to assume then that $W\tau_e \ll 1$, i.e., within the lifetime of its excited state the electron can negotiate not more than one hop to a neighboring center. The condition $W\tau_e \ll 1$ together with the inequality $\Gamma_N < \Gamma$, which means a photoexcitation rate independent of the center position (see also §3), enables us to find the electron mobility for specific hopping mechanisms.

Assume that inhomogeneous broadening prevails over the polaron shift, $\hbar\Gamma_N > \varepsilon_p$, so that the probability W pertains to one-phonon hopping between levels that are close in energy. We can then use the known results of Miller and Abrahams.[24,27] It need only be recognized that the problem of finding σ_+ differs from that of determining the intrinsic hopping conductivity. The point is that at $W\tau_e \ll 1$ the photoelectrons are very far from equilibrium and are not thermalized. Therefore induced processes with participation of phonons, which have equal probabilities of decreasing and increasing the carrier energies, make no contribution to σ_+. The quantity W must therefore be taken to mean the probability of a transition with spontaneous emission of a phonon. For a deformation interaction with acoustic phonons we have[24,27]

$$W \approx \frac{1}{\hbar}\frac{\bar{R}^2}{a^2}\left(\frac{\Gamma_N}{\Omega_D}\right)^3 \frac{E_1^2 I^2}{\hbar^2\Omega_D^2 M c_s^2}. \tag{14}$$

Here Ω_D is the Debye frequency, M the unit-cell mass, E_1 the deformation-potential constant, c_s the speed of sound, and $I = I_0 \exp(-\bar{R}/r_0)$, the standard energy overlap integral. It must further be kept in mind that since the carriers are not in equilibrium we cannot determine μ by using the

known Einstein relation. Instead, quite understandably, the estimate $\mu \approx eD/\hbar\Gamma_N$ is valid, where $D \approx W\bar{R}^2$ is the diffusion coefficient. Taking into account, finally the inequality $n = \varkappa J\tau_e/\hbar\omega$, which is obvious in the case of strong compensation, we get

$$\sigma_+ \approx e^2 \frac{\varkappa J}{\hbar\omega} \frac{\bar{R}^2\tau_e}{\hbar} \left(\frac{\bar{R}}{a}\right)^2 \frac{E_1^2 I^2}{(\hbar\Omega_D)^3 M c_s^2}. \quad (15)$$

We turn now to the case when σ_+ is determined by the polaron effect, $\varepsilon_p \gg \hbar\Gamma_N, \hbar\Omega_D$. This can be the case of either a system of defects or a narrow-band crystal. The simplest results for W and μ are obtained at high temperatures $T > 1/2\hbar\Omega_D$ and at sufficiently small overlap integrals $I^2 < T\varepsilon_p$. In this limit, the small-radius polaron theory leads to a hopping probability.

$$W \approx \frac{I^2}{\hbar(T\varepsilon_p)^{1/2}} \exp\left(-\frac{\varepsilon_p}{T}\right), \quad (16)$$

that decreases exponentially with increasing ε_p and T.[19,27] The electron self-localization time is usually very short, $\tau_{sloc} \lesssim 10^{-13}$ s $< \tau_\varepsilon$, and the Einstein relation can be used to find $\mu = edT^{-1}$. Consequently,

$$\sigma_+ \approx e^2 \frac{\varkappa J}{\hbar\omega} \frac{\bar{R}^2\tau_e}{\hbar} \frac{I^2}{T^{3/2}\varepsilon_p^{1/2}} \exp\left(-\frac{\varepsilon_p}{T}\right). \quad (17)$$

According to (17), σ_+ decreases steeply with decrease of T, undoubtedly a favorable result for realization of ANP. It must be stated that the rapid decrease of W and σ_+ continues also at higher temperatures, $T \lesssim \hbar\Omega_D$. Its description, however, becomes more complicated.[19]

Note that the estimates (15) and (17) are valid not only in the most typical situation, when ω is at resonance with the intracenter transitions (Fig. 1a), but also in the case of light frequencies corresponding to intercenter photoexcitation (Fig. 1b).

We proceed now to the case of weak compensation, $K \ll 1$. Its distinguishing property is an increase of the photoelectron density n compared with $\varkappa J\tau_e/\hbar\omega$. The point is that an electron that lands via an intercenter transition on an upper level of an occupied center can hop over later to a neighboring (also occupied) center, from which recombination is no longer possible. If this has occurred, the electron must continue to wander until it finds an empty center. In the course of the wandering, the carriers become thermalized ($T < \hbar\Gamma_N$). It can be shown that at any ratio of W and τ_e the populations of all upper levels turn out to be equal under stationary conditions, and the density is $n \approx \varkappa J\tau_e/K\hbar\omega$. Using Einstein's relation, we get

$$\sigma_+ \approx \frac{1}{K} \frac{e^2\bar{R}^2}{T} \frac{\varkappa J}{\hbar\omega} W\tau_e. \quad (18)$$

The probability W is given either by Eq. (14) multiplied by the activation exponential $\exp(-\varepsilon_a T^{-1})$, with $\varepsilon_a \approx \hbar\Gamma_N$ (see Ref. 24) or by Eq. (16). Recall that in (16) and (17) τ_e is the time of intercenter recombination.[4)] Therefore, in contrast to the strong-compensation limit, the parameter $W\tau_e$ does not contain a small overlap integral.

§5. CONDITIONS FOR ANP REALIZATION; PHOTOINDUCED FIELDS

In the case of strong compensation of the dielectric, $1 - K \ll 1$, by using Eqs. (7), (10), and (13), the conditions for realization of ANP, $\sigma_+ < |\sigma_{as}|$, can be written in the form

$$\mu < e\bar{R}^2/\hbar\Gamma\tau_e. \quad (19)$$

To assess the strength of this inequality, we present a numerical estimate. Putting $\bar{R} = 100$ Å ($N = 10^{18}$ cm^{-3}), $\Gamma = 50$ cm^{-1}, and $\tau_e = 10^{-9}$ s, we get $\mu < 0.2$ [V$^{-1}\cdot$s$^{-1}\cdot$cm^2]. For hopping mechanisms this restriction is generally speaking quite weak. One must not forget, however, that (19) was written subject to restrictions on the model parameters. In addition, the mobility μ is itself model-dependent. The necessary conditions for ANP must therefore be analyzed in greater detail.

One of our most important assumptions is that the intracenter photoexcitation is weak, $g_0 \lesssim g_1$. Were it possible to suppress the intracenter excitation completely, the inequality (19) would certainly hold at low center densities N. It is impossible, however, to have exactly $g_0 = 0$. Whereas the intracenter transitions are forbidden by the selection rules in the long-wave approximation and for the average configuration of the nuclei, they can become allowed in higher-order approximations. The lifting of the hindrance can be due to the action of fluctuating fields produced by the charged centers. Roughly speaking, the parameters of the expansion of g_0 in terms of the multipoles and of the deviations from equilibrium are respectively $(e^2/\hbar c)^2$ and $\hbar\Omega_D/Mc_s^2$. The parameter that characterizes the influence of the field fluctuations is (see Ref. 24) $(e^2/\bar{\varepsilon}\bar{R}\Delta)^2(r_0/\bar{R})^2(1-K)^{2/3}$, where Δ is the characteristic distance between the energy levels and $\bar{\varepsilon}$ is the dielectric constant. The actual competition is only between the first two of these quantities, and the third can be regarded as small. Denoting by η the largest of the indicated parameters, we can write for the maximum intercenter distance $\bar{R}$ on which we still have $g_0 \lesssim g_1$

$$\eta \approx \exp(-2\bar{R}/r_0). \quad (20)$$

We assume $\eta = 10^{-3}$–10^{-4} for numerical estimates (stronger hindrances on optical transitions are, of course, also possible).

If the mobility μ is due to inhomogeneous broadening, we easily obtain from (19), using (15),

$$\eta\Gamma\tau_e \left(\frac{\Gamma_N}{\Omega_D}\right)^2 \frac{I_0^2 E_1^2}{(\hbar\Omega_D)^3 M c_s^2} < 1. \quad (21)$$

For Coulomb wave functions we have $I_0 \approx e^2/r_0\bar{\varepsilon}$. The inequality $W\tau_e < 1$ used by us to obtain (15) follows automatically from (21). By way of a numerical estimate, putting $\Gamma_N = \Gamma/2$ and assuming $a = 3$ Å, $c_s = 5\cdot 10^{-5}$ cm/s, $M = 10^{-22}$ g, and $E_1 = I_0 = 1$ eV, we get

$$\Gamma^3\tau_e < 2\cdot(10^{27}-10^{28})\ \text{s}^{-2}. \quad (22)$$

For $\tau_e = 10^{-9}$ s Eq. (22) yields $\Gamma \lesssim 10$ cm^{-1}. This condition can be readily met for zero-phonon lines. The parameters assumed correspond to $\Omega_D \approx 5\cdot 10^{13}$ s^{-1}.

Assume now that the mobility μ is determined by the polaron effect. If the coupling with the phonons is strong, the zero-phonon peak on the absorption curve is exponentially small and is usually unobservable. It is reasonable therefore to replace the width in (17) by the wing width $\delta\omega \approx \hbar^{-1}(\varepsilon_p T)^{1/2}$ ($T \gtrsim \hbar\Omega_D$).[19,23] Using (17), we obtain as an ANP realization condition

$$\tau_e < \frac{\hbar T}{\eta I_0^2} \exp\left(\frac{\varepsilon_p}{T}\right). \tag{23}$$

At $T = (150\text{–}300)$ K, $\eta = 10^{-4}$, and the values I_0 and τ_e assumed above, Eq. (23) leads to lower bounds $\varepsilon_p > (0.18\text{–}0.35)$ eV on the activation energy. It must also be borne in mind that the relaxation of the condition $\sigma_+ < |\sigma_{as}|$ with decrease of T, a relaxation strongly pronounced at high temperatures ($T > 1/2\hbar\Omega_D$), continues also at lower temperatures, albeit at somewhat slower rates. This follows from the expressions given in Ref. 19 for the width $\delta\omega$ and for the mobility μ.

We note, finally, that less stringent conditions than (21) and (23) can be expected when the used absorption lines correspond to intercenter transitions to occupied centers (Fig. 1b). In this case, intracenter excitation is energy-forbidden.

Let us touch upon the case of weak compensation, $K \ll 1$, of a dielectric. Features of this case are an appreciable increase of the lifetime $\delta\omega$ and unfavorable dependences of σ_{as} and σ_+ on K. Roughly speaking, the inequalities obtained above become stronger: their left-hand sides are multiplied by the parameter $K^{-1}\exp(\overline{R}/r_0) \gg 1$. ANP realization becomes therefore difficult.

Assume that the condition $\sigma = \sigma_{as} + \sigma_+ < 0$, that the total photoconductivity be negative is met. In that case a zero-current state with $E = 0$ becomes unstable and the field fluctuations begin to increase exponentially. Let us examine the strength of the saturated field E_0. The instability can be eliminated either by decreasing $|\sigma_{as}|$ at large E, or by linearly increasing σ_+. The decrease of $|\sigma_{as}|$ corresponds to detuning of the two-level systems away from resonance. In this case

$$E_0 \approx \hbar\Gamma N^{1/3}/e, \tag{24}$$

where N is the total density of the defects. An increase of σ_+ sets in starting with fields $E_0 \approx \hbar\Gamma_N N^{1/3}/e$ or $E_0 \approx TN^{1/3}/e$, depending on whether the charge-transport mechanism is connected with level scatter or with the polaron effect. When effects nonlinear in E are taken into account, we arrive automatically at an N-shaped $j(E)$ dependence, the same as in the phenomenological model of Ref. 9.

We obtain now numerical estimates of j_{as} and E_0. Assuming, in accordance with Ref. 22, that the absorption coefficient for allowed intracenter transitions is

$$\varkappa \approx 4\pi^2 (e^2/\hbar c)(\omega/\Gamma) r_0^2 N_1$$

(N_1 is the density of the occupied centers), we get from (7) and (10)

$$j_{as} \approx 4\pi^2 \frac{e^2}{\hbar c} \frac{e^2 r_0 N^{1/3}}{\hbar^2 \Gamma^2} (1-K) JE\eta. \tag{25}$$

Putting $\eta \equiv \exp(-2\overline{R}/r_0) \approx 10^{-4}$, $\Gamma = 3\cdot 10^{13}$ s^{-1}, $1 - K = 10^{-1}$, and using Eq. (24) to estimate E_0, we get

$$j_{as}\,[\text{A/cm}^2] \approx 10^{-10} r_0[\text{Å}]\, J\,[\text{W/cm}^2]\, E\,[\text{V/cm}], \qquad E_0[\text{V/cm}] = 10^6 r_0^{-1}[\text{Å}]. \tag{26}$$

The absorption coefficient corresponding to these parameters is $\varkappa[\text{cm}^{-1}] = 10^2 r_0^{-1}[\text{Å}]$.

CONCLUSION

A characteristic feature of the approach used by us is the tight entanglement of elements typical of such different fields as impurity-center spectroscopy and the transport properties of disordered media. The promise offered by this research trend is directly indicated by the fact that the first objects in which ANP was observed and was clearly manifested were ruby crystals—the classical object of spectroscopic research. In our opinion, the results demonstrate that hopping mechanisms of ANP are realistic and superior to the known band mechanisms. They indicate the direction and prospects of further research. As for the theory, it is necessary first to lift the restriction $\Gamma_N < \Gamma$ on the inhomogeneous broadening. We need more detailed calculations of σ_{as} and σ_+ for real materials and specific situations that satisfy the set of general requirements, vis., the presence of a pair of distinctly pronounced levels corresponding to a forbidden optical transition, a short lifetime on the upper level, and the presence of a strong or at least moderate compensation.[5)] It would be of considerable interest to investigate on the basis of the proposed model the hopping mechanisms of the photovoltaic effect. One can expect here an appreciable strengthening of the photoinduced fields and the presence of anomalous polarization properties.

The choice of the object for the observation and investigation of the predicted resonant ANP is quite important. It is clear from general considerations that this object must be either a semiconducting crystal with shallow impurity level (in which case the optical and transport properties have been relatively well investigated), or a laser crystal. Definite experimental prerequisites exist in this case. Thus, intercenter transitions from the ground to an excited localized state, without intracenter transitions, were actually observed in Zn-doped Ge crystals.[28,29] Absorption-line field splitting corresponding to frequencies $\pm\hbar^{-1}eEN^{-1/3}$ were observed. It can be seen from the foregoing estimates, however, that one can hardly expect the necessary conditions for ANP to be met with large margin and for many materials (it is difficult to expect σ_{as} to exceed σ_+ by several orders of magnitude). There are also a number of subjective difficulties that hinder the satisfaction of the general requirements (which are generally speaking not stringent) formulated above. Thus, in spectroscopy one is usually interested in the strongest absorption lines, and the structures of the weak lines are not considered. The lifetimes must usually be deduced from indirect data. Control of the degree of compensation in laser crystals has hardly been studied, nor have processes of charge transport over excited states.

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[1)]The medium is assumed to be centrosymmetric, so that there is no photovoltaic effect and the charge is transported only by the electric field.
[2)]It pertains to small-radius polarons in a crystal, where their motion can be considered as a sequence of independent transitions between pairs of sites forming a periodic lattice with $R = a$.[19]
[3)]At $K \ll 1$ the recombination can have a two-step character (Fig. 1b). The excited two-electron state first goes over into two one-electron states (one excited, the other not), after which a rapid intracenter transition takes place.
[4)]It might seem that the presence of intermediate two-electron levels can decrease τ_e and σ_+ radically, and contribute by the same token to realization of ANP. This, however, is not so. In the case of strong localization, the intermediate levels assume the role of sinks and we arrive at a nonstationary situation. If the localization is weak, the hopping over intermediate levels contributes as before to the increase of σ_+.
[5)]It is possible that the degree of compensation can be controlled by optical pumping to the lower working level.

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