Deep impurity-center ionization by far-infrared radiation

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An analysis is made of the ionization of deep impurity centers by high-intensity far-infrared and submillimeter-wavelength radiation, with photon energies tens of times lower than the impurity ionization energy. Within a broad range of intensities and wavelengths, terahertz electric fields of the exciting radiation act as a dc field. Under these conditions, deep-center ionization can be described as multiphonon-assisted tunneling, in which carrier emission is accompanied by defect tunneling in configuration space and electron tunneling in the electric field. The field dependence of the ionization probability permits one to determine the defect tunneling times and the character of the defect adiabatic potentials. The ionization probability deviates from the field dependence $e(E) \propto \exp(E/E_0)$ (where $E$ is the wave field, and $E_0$ is a characteristic field) corresponding to multiphonon-assisted tunneling ionization in relatively low fields, where the defects are ionized through the Poole–Frenkel effect, and in very strong fields, where the ionization is produced by direct tunneling without thermal activation. The effects resulting from the high radiation frequency are considered and it is shown that, at low temperatures, they become dominant. © 1997 American Institute of Physics.

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INTRODUCTION

The interest in the spectroscopy of semiconductors and semiconductor structures in the far-infrared (FIR) and submillimeter (SBM) ranges (wavelengths extending from 30 to 1000 μm, corresponding to photon energies from 35 to 1 meV) is stimulated primarily by the fact that they include the characteristic energies of many elementary excitations in semiconductors. Among these are the plasma oscillation energy, the ionization energies of typical shallow donors and acceptors, the cyclotron and spin interaction energies, the characteristic size-quantization energies of the electron subsystem, optical phonon energies etc. For many decades the FIR and SBM ranges have been among the hardest to access experimentally. The advent of novel radiation sources in the recent twenty to thirty years has made possible a large number of experiments making use of grating monochromators, Fabry–Perot interferometers, backward-wave tubes, and relatively lower-power, electrically or optically pumped cw lasers emitting discrete lines. SBM and FIR spectroscopy has become an efficient tool in studies of material properties and of the various phenomena in different areas of research. The appearance of high-power pulsed FIR and SBM lasers (first of the TEA CO$_2$-pumped, molecular-gas type$^{1,2}$ and, subsequently, of free-electron lasers$^{3,4}$ and $p$-Ge semiconductor devices$^{5-10}$) capable of delivering nanosecond pulses of high intensity, up to a few MW, has opened up totally new vistas in investigation of semiconductors in the FIR range and provided a basis for development of far-infrared spectroscopy of semiconductors at high excitation levels, which was first made use of at the Ioffe Physicotechnical Institute.$^{11}$

In this frequency range, the high radiation intensity gives rise to a variety of nonlinear phenomena in semiconductors and semiconductor structures (see, e.g., review$^{12}$), such as, for example, multiphoton absorption,$^{13-19}$ absorption saturation (bleaching),$^{20-30}$ nonlinear cyclotron resonance,$^{31,32}$ impact ionization,$^{33,34}$ nonlinear photoacoustic spectroscopy,$^{35}$ high-harmonic generation,$^{36,37}$ and the high-frequency Stark effect,$^{38}$ whose characteristics differ substantially from their counterparts observed both in the visible and infrared ranges and in the range extending from microwaves to dc electric fields. The reason for this lies in that the FIR–SBM range is actually a domain where the interaction in the electron–photon system undergoes a transition from the quantum to classical limit, thus creating a unique possibility to study the same physical phenomenon in conditions where by properly varying the frequency or intensity of radiation one can make dominant either the discrete properties of light or its wave characteristics. Submillimeter and far-infrared spectroscopy at high-excitation levels has also an essential advantage in that it makes a technique more sensitive due to the high intensity of radiation, i.e. to the larger number of photons. Since the photon energy is here much less than the gap width and, hence, there can be no direct one-photon generation of free carriers, observation of the relatively weak effects of carrier redistribution in momentum and energy becomes possible. The high radiation intensity permits one also to study in detail such photoelectric phenomena as, for instance, the
linear and nonlinear electron-gas heating,21,29,33,34,39–44 photoelectric phenomena associated with Bloch oscillations,55,46 photon drag of electrons,11,15,47–52 photogalvanic effect,53–57 photoresistive effects produced in semiconductor structures in plasma reflection,58–62 and multiphoton resonant tunneling in quantum-well structures,18 as well as to use them in development of radiation detectors.

This work deals with the new nonlinear effect of deep-impurity ionization by FIR radiation at photon energies a few tens of times lower than the impurity binding energy reported in Ref. 69. We are going to consider impurity centers with no direct coupling of light to localized vibrational modes. The ionization process is studied by the photoconductivity method,70 which is traditionally used in optical research and is capable of detecting extremely small (<0.01%) changes in carrier concentration, thus providing a high measurement sensitivity.

If there are no free carriers in the semiconductor, deep impurities can be ionized through tunneling in the strong electric field of the radiation. In most cases, the FIR radiation acts here as a strong dc electric field, and the ionization probability does not depend on the radiation frequency. An increase of the frequency and decrease of temperature result in the ionization probability becoming dependent on frequency, which signals the transition to the case when the magnitude of the photon energy becomes significant.

Deep impurity centers play a dominant part in the electronic properties of semiconductor materials and have therefore become a subject of extensive investigation.71–77 It is the deep centers that determine usually the nonequilibrium carrier lifetimes by acting as centers of nonradiative recombination and thermal ionization. Investigation of the effect of electric field on thermal ionization and carrier trapping has been traditionally used to probe deep impurities. In particular, investigation of the ionization or capture in a strong electric field is actually the only way to find the parameters of the multiphonon transitions determining the nonradiative recombination rate. Deep-level transient spectroscopy (DLTS) is also among the most extensively employed tools. Most of the deep-center parameters (ionization energy, nonradiative and radiative trapping cross sections) were obtained using various modifications of DLTS. It should be noted, however, that nonuniformities of the electric field in a structure make interpretation of the results obtained difficult. Direct application of strong static electric fields is usually complicated by the onset of field nonuniformities in the sample and quite frequently initiates avalanche breakdown. Using the electric field of high-intensity, short laser pulses in the far-infrared range at THz frequencies avoids such problems and permits contactless and uniform application of strong electric fields. Despite the high radiation intensities involved, there is none or only insignificant heating of the electron gas or of the crystal lattice under these conditions. This is the result of the extremely weak absorption of the FIR radiation due to the low concentration of free carriers (the carriers are frozen out on the centers), as well as to the use of short, nanosecond-range pulses, which do not perturb substantially the phonon system.

Thus discovery of multiphonon tunneling ionization under contactless application of a strong uniform electric field and using short radiation pulses with duration shorter than the nonequilibrium carrier lifetimes has permitted development of a new method for probing deep impurity centers in semiconductors, offering a possibility of determining the multiphonon parameters of deep-level impurities, the structure of their adiabatic potentials, and the trapping kinetics of nonequilibrium carriers.

The present review deals with the ionization of deep-impurity centers by high-intensity, pulsed FIR–SBM radiation. Section 1 considers the theory of deep-impurity ionization by a dc and high-frequency electric field, Sec. 2 discusses the experimental techniques used and subjects of investigation, Sec. 3 analyzes the conditions under which one observes tunneling ionization and considers other possible mechanisms, Sec. 4 presents and discusses in detail the relevant experimental results, Sec. 5 looks into the application of the method of multiphonon impurity ionization by FIR–SBM radiation to studies of relaxation dynamics in the particular case of the trapping kinetics of nonequilibrium carriers in GaP:Te, and Sec. 6 sums up the review with main conclusions. The Appendix includes effects of linear and nonlinear electron-gas heating by far-infrared radiation, and it shows that these phenomena do not play a significant role in the experiments discussed here.

1. DEEP-IMPURITY IONIZATION BY AN ELECTRIC FIELD

1.1. Adiabatic approximation

The binding energy of deep centers exceeds by far the average phonon energy, and therefore only multiphonon-assisted processes can give rise to thermal emission. Since electronic transitions occur much faster than transitions in the phonon system, one can use the adiabatic approximation in the description of electron-phonon interaction.78

Consider the simplest case of the deep impurity having only one bound state. Obviously enough, this model is directly applicable to the capture by neutral centers, and, as this will be shown in Sec. 1.5, the main conclusions reached here remain valid also for deep attractive centers. The position of the localized level is determined by the potential generated by the impurity and is substantially dependent on the distance from the impurity to the nearest atoms. Thus vibrations of the impurity and of the lattice modulate the position of the localized electronic level, as this is shown in Fig. 1. Strong thermal vibrations can eventually drive the level to continuum, thus producing ionization of the impurity.79 Quantitative consideration is usually made using a single-mode model, which describes the impurity vibrations through variation of only one configuration coordinate \( x \). This approximation is valid, because the multiphonon ionization of deep impurities and the trapping by the latter are dominated by the breathing mode of localized vibrations. The adiabatic approximation treats electronic transitions as occurring at a fixed configuration coordinate \( x \), with the vibrations of the impurity itself being determined by the potential, which is generated by the surrounding atoms, with due inclusion of the mean polarization field induced by the localized electron. Such potential averaged over electronic
motion is called adiabatic, and it includes the electron energy at a fixed coordinate $x$.

Figure 2 shows two main possible configuration-coordinate diagrams: (a) for the case of weak electron-phonon coupling and (b) for strong electron-phonon interaction, where self-trapping occurs, as is the case, for example, with DX and EL2 centers in III-V semiconductors. The potential curve $U_1(x)$ corresponds to the case of the electron bound to the impurity, and $U_2(x)$, to that of an ionized impurity and a free electron with zero kinetic energy. The energy separating the two potentials is determined by the electron binding energy $\varepsilon_b(x)$ at a fixed configuration coordinate $x$:

$$U_1(x) = U_2(x) - \varepsilon_b(x).$$

The equilibrium positions of the ground state (with the electron bound to the impurity) and the ionized state are shifted with respect to one another as the result of electron-phonon coupling. Accordingly, the optical-ionization energy, by the Franck–Condon principle, can be written as $\varepsilon_{opt} = \varepsilon_b(x=x_0)$, where $x_0$ is the equilibrium value of the ground-state configuration coordinate. As seen from Fig. 2, the energy of optical ionization is larger than that of thermal ionization $\varepsilon_T$. The relaxation energy $\Delta\varepsilon = \varepsilon_{opt} - \varepsilon_T$ characterizes the electron-phonon coupling strength, since the stronger is the coupling, the larger is $\Delta\varepsilon$. The electron-phonon coupling can be conveniently characterized by a dimensionless parameter

$$\beta = \frac{\Delta\varepsilon}{\varepsilon_T}.$$ 

The configuration of Fig. 2a corresponds to weak electron-phonon coupling ($\beta < 1$), and the difference between $\varepsilon_{opt}$ and $\varepsilon_T$ is, as a rule, small. Actually, no difference has thus been observed between $\varepsilon_{opt}$ and $\varepsilon_T$ in germanium and sili-
con. There are, however, cases, where the relaxation energy is fairly high, for instance, with the oxygen impurity in GaP, which is in state 2, where $\beta=0.56_{75,80}$.

The configuration-coordinate diagram of Fig. 2b illustrates the case of $\beta>1$, where the optical and thermal ionization energies differ considerably. This diagram is used to describe, for instance, the DX and EL2 centers, where this difference was experimentally revealed.\textsuperscript{71,74–77} Such self-trapped states have a large potential barrier suppressing the return of free electrons to the localized state, thus giving rise to the phenomenon of persistent photoconductivity. In these conditions, there is no radiative capture into the impurity state. The various features of the adiabatic configurational potentials play an essential role in nonradiative trapping of free carriers.\textsuperscript{75} We shall restrict ourselves to the simple model of two identical displaced parabolic curves, which was first proposed by Huang and Rhys\textsuperscript{78} and is presently widely employed in the theory of multiphonon transitions. By this model

$$U_1(x) = \frac{M \omega^2 x^2}{2}$$

$$U_1(x) = \frac{M \omega^2 (x-x_0)^2}{2} - E_T,$$

where $M$ is the mass of the impurity, and $\omega$ is the vibrational frequency.

### 1.2. Multiphonon-assisted thermal emission

Consider first thermally-activated carrier emission from a deep center with no electric field present. For simplicity and definiteness, we shall consider electrons, although a considerable part of measurements were carried out on acceptors in Ge and Si. The model to be treated here is equally applicable to the electrons and holes.

Classical approximation gives the following expression for the emission probability

$$e^{-\psi} \approx \exp\left(-\frac{\varepsilon_T + \varepsilon_T}{k_B T}\right),$$

where $\varepsilon_T = U_1(x_c)$, and $x_c$ is the coordinate at the intersection of the potentials $U_1(x)$ and $U_2(x)$, at which the electron binding energy is zero, $\varepsilon_\phi(x_c)=0$ (see Fig. 2). Thus $\varepsilon_T + \varepsilon_T$ is actually the lowest excitation energy required to detach the electron within the classical approach to the motion of impurities. The model of Huang and Rhys, where the adiabatic potentials $U_1(x)$ and $U_2(x)$ are two identical parabolic curves, $\varepsilon_T = (\varepsilon_T - \Delta\varepsilon)^2/4\Delta\varepsilon$. In the weak-binding case ($\Delta\varepsilon \ll \varepsilon_T$), where $\varepsilon_T \gg \varepsilon_T$, no process with an activation energy $\varepsilon_T + \varepsilon_T$ was ever observed to follow relation (5). Usually the activation energy is much less than $\varepsilon_T + \varepsilon_T$, since the electron is emitted from the vibrational level lying at $\varepsilon_T + \varepsilon_T$ (the energy $\varepsilon_T$ is reckoned from the minimum of potential $U_2$, and $\varepsilon_T < \varepsilon_T$) because the defect tunnels from the configuration corresponding to the ground state to that of the ionized impurity (Fig. 2). As the vibrational energy $\varepsilon_T + \varepsilon_T$ increases, the tunneling barrier separating the $U_1$ and $U_2$ potentials becomes lower, and, hence, the tunneling probability increases. On the other hand, the population of the $\varepsilon_T + \varepsilon_T$ level decreases with increasing $\varepsilon_T$ proportional to $\exp(-\varepsilon_T/k_B T)$. Thus for each temperature there is an optimum energy $\varepsilon_T = \varepsilon_T^0$, at which the tunneling probability is the largest.\textsuperscript{75,81–83}

We shall consider the defect tunneling process in semiclassical approximation. In this approach, the particle has a well-defined trajectory even under the potential barrier, where the kinetic energy is negative. The probability of thermally activated emission of a defect, $P(\varepsilon)$, with a vibrational energy $\varepsilon_T + \varepsilon_T$ at a temperature $T$ is given by the expression

$$P(\varepsilon) \approx \exp(-\psi)$$

with

$$\psi(\varepsilon) = \frac{\varepsilon_T + \varepsilon_T}{k_B T} + 2|S(\varepsilon)|,$$

where $S(\varepsilon)$ is the action multiplied by $i/\hbar$. The first term in Eq. (7) describes the population of the $\varepsilon_T + \varepsilon_T$ level, and the second, the defect tunneling from the ground to an ionized state. Since $P(\varepsilon)$ depends exponentially on energy $\varepsilon$, tunneling occurs within a narrow energy interval close to the energy of optimum tunneling $\varepsilon_T^0$ (see Fig. 2). This optimum tunneling energy is determined by the vibrational energy at which $\Psi(\varepsilon)$ has a minimum:

$$\frac{d\psi}{d\varepsilon}\bigg|_{\varepsilon=\varepsilon_T^0} = 2\frac{|S(\varepsilon)|}{d\varepsilon}\bigg|_{\varepsilon=\varepsilon_T^0} + \frac{1}{k_B T} = 0.$$  

The derivative $d|S|/d\varepsilon$ in Eq. (8) multiplied by $\hbar$ determines the tunneling time through the barrier $\tau$.\textsuperscript{84,85} Thus in the case of multiphonon tunneling ionization the time of tunneling by the optimum trajectory is determined by temperature and is $\hbar/k_B T$.

Following Refs. 75, 81–83, $S(\varepsilon)$ can be divided into two parts:

$$S(\varepsilon) = -S_1(\varepsilon) + S_2(\varepsilon),$$

$$S_i(\varepsilon) = \sqrt{2M} \int_{a_i}^{x_c} dx \sqrt{U_i(x) - \varepsilon}, \quad i = 1, 2,$$

corresponding to two parts of the tunneling trajectory, namely, 1, under potential $U_1$, from the turning point $a_1$ to point $x_c$, where the adiabatic potential curves cross, and 2, under potential $U_2$, from $a_2$ to $x_c$. The actual direction of tunneling along the $x$ coordinate is specified by the sign of $S_i$ in Eq. (9). The tunneling trajectories for both adiabatic potential configurations are depicted in Fig. 2 by arrows. Tunneling in the two configurational potentials shown in Figs. 2a and 2b is essentially different in that $S_1(\varepsilon)$ and $S_2(\varepsilon)$ have the same sign in the case of weak electron-phonon coupling with $\beta<1$ (Fig. 2a) and opposite signs in the case of self-trapping, $\beta>1$ (Fig. 2b).\textsuperscript{36} Recalling that $|S_2|>|S_1|$ we come to $|S_1|=|S_2|-|S_1|$ for the configuration of Fig. 2a, and to $|S_1|=|S_1|+|S_2|$ for the self-trapping case. Introduce the tunneling times $\tau_1$ and $\tau_2$ under the corresponding adiabatic potentials for the optimum energy of thermally activated tunneling:
\[ \tau_i = h \frac{d|S_i|}{d\varepsilon_{\pm \varepsilon_0}} \bigg|_{\varepsilon_{\pm \varepsilon_0}} = \sqrt{\frac{M}{2}} \left| \int_{x_1}^{x_e} \frac{dx}{\sqrt{U_i(x) - \varepsilon_{\pm \varepsilon_0}}} \right| \quad i = 1, 2. \]  

Equations (8) and (11) yield

\[ \tau = \tau_2 \pm \tau_1 = \frac{h}{2k_B T} \]  

where the minus sign corresponds to the configuration of Fig. 2a, and the plus, to that of Fig. 2b. Since \( \varepsilon_0 \) is usually much less than \( \varepsilon_T \), the time \( \tau_1 \) is practically temperature-independent and can be calculated for \( \varepsilon_0 = 0 \).

In the case of weak electron-phonon coupling \((\varepsilon_2 \gg \varepsilon_T)\), Eq. (8) yields within the Huang–Rhys model a simple relation for the optimum defect-tunneling energy \( \varepsilon_0 \)

\[ \varepsilon_0 = \varepsilon_T/\left[ \exp(h \omega/k_B T) - 1 \right]. \]  

which shows that in the low-temperature domain \((k_B T < h \omega)\) we indeed have \( \varepsilon_0 \ll \varepsilon_T \). Setting \( \varepsilon_0 = 0 \) in Eq. (11) in the calculation of \( \tau_1 \) we come to

\[ \tau_1 = \sqrt{\frac{M}{2}} \int_{x_1}^{x_e} \frac{dx}{\sqrt{U_i(x)}} \]  

Equation (14) yields in the case of weak electron-phonon coupling, \( \beta < 1 \), the following expression for the tunneling time \( \tau_1 \):

\[ \tau_1 = \frac{1}{2\omega} \ln \left( \frac{\varepsilon_T}{\varepsilon_{opt} - \varepsilon_T} \right) \]  

and for the self-trapping case \((\beta > 1)\):

\[ \tau_1 = \frac{1}{2\omega} \ln \left( \frac{\varepsilon_{opt} - \varepsilon_T}{\varepsilon_T} \right) \]  

Thus Eq. (12) defines the temperature dependence of the tunneling time \( \tau_2 \).

1.3. Multiphonon-assisted tunneling ionization in an electric field

Carrier emission in static electric fields was first considered in Ref. 87 and calculated numerically in Ref. 88; analytical expressions for the probability of deep impurity-center ionization were obtained in Refs. 89, 90, and the subsequent analysis will draw essentially from the latter works.

In a uniform electric field, the potential with a constant slope in the field-vector direction is added to the potential well binding the electron to the impurity. The electron is now capable of tunneling through the triangular potential barrier thus formed at a negative kinetic energy \(-\varepsilon\) (Fig. 3), with the corresponding adiabatic potential shifted down in energy, \( U_{2e} = U_2 - \varepsilon \) (dashed line in Fig. 2). In these conditions, the defect tunneling trajectory in configuration space shortens, and the barrier height becomes lower. We start by considering the case of high temperatures and relatively weak fields, where the field introduces a correction only to thermal ionization, and \( \varepsilon \) is much smaller than \( \varepsilon_0 \). The optimum defect tunneling energy \( \varepsilon_0 \) remains here unchanged, and, to first order in \( \varepsilon \), the correction to the argument of the exponential \( \Psi \) determining the ionization probability [see Eqs. (6) and (7)] can be found by varying in \( \varepsilon \) the function \( S(\varepsilon_0, \varepsilon) \) defined by Eqs. (9) and (10), with \( U_2 \) being replaced by \( U_{2e} \). We obtain

\[ \Psi(\varepsilon_0, \varepsilon) = \Psi|_{\varepsilon = 0} + 2 \frac{d|S_{2e}|}{d\varepsilon}\bigg|_{\varepsilon = 0, x_0 = \text{const}}, \]  

where

\[ S_{2e} = \sqrt{\frac{2M}{h}} \int_{x_2}^{x_e} dx \sqrt{U_2(x) - \varepsilon - \varepsilon_0}. \]  

The probability for a thermally-emitted carrier with kinetic energy \(-\varepsilon\) now becomes

\[ e(\varepsilon) = e(0) \exp(2e \tau_2 / h) \]  

where \( \tau_2 \) is the tunneling time defined by Eq. (11), and \( e(0) \) is the ionization probability with no electric field present. The increase of the probability of electron emission with energy \(-\varepsilon\) by the factor \( \exp(2e \tau_2 / h) \) is primarily due to the lowering of barrier height when the defect is tunneling from point \( x_e \) to the turning point under the adiabatic potential curve \( U_{2e} \) at the vibrational level \( \varepsilon_0 \). While this factor grows with \( \varepsilon \), the probability of electron tunneling through the triangular barrier whose height is determined by \( \varepsilon \) (see Fig. 3) drops rapidly proportional to \( \exp[-(4e^{2\gamma}/\sqrt{2m^*}(3h\varepsilon E))] \), where \( E \) is the electric field, and \( m^* \) is the electron effective mass. Thus the probability of multiphonon tunneling ionization with the electron escaping with a negative energy \(-\varepsilon\) can be written as
The exponential behavior of $e(E, \varepsilon)$ results in the existence of an optimum electron energy $-\varepsilon_m$ determined by the maximum of the exponential in Eq. (20):

$$
\varepsilon_m = \frac{\tau^2 e^2 E^2}{2m^*}.
$$

This optimum electron energy $\varepsilon_m$ corresponds to the energy at which the time of electron tunneling in an electric field $E$ is equal to the time $\tau_2$ determining the defect tunneling under the potential curve $U_2$ at the vibrational level $\omega_0$ optimum for thermally stimulated tunneling. Indeed, the tunneling time in an electric field $E$ under a triangular barrier of height $\varepsilon$ is given by the relation

$$
\tau_e = \sqrt{\frac{m^*}{2}} \int_0^{\varepsilon_f} \frac{dz}{(\varepsilon - \varepsilon z)} = \frac{\sqrt{2m^*\varepsilon e^2}}{e E}. \tag{22}
$$

As follows from Eqs. (21) and (22), $\tau_e = \tau_2$ for $\varepsilon = \varepsilon_m$. Thus the result obtained has a simple physical interpretation, namely, the optimum electron energy is determined by the equality of the tunneling time of the electron in an electric field to that of the defect in configuration space under the potential $U_2$ corresponding to the defect without the electron.

Inserting $\varepsilon_m$ thus found into Eq. (20) yields for the multiphonon tunneling ionization probability as a function of electric field the following expression:

$$
e(E) = e(0) \exp \left( \frac{2}{E_0^2} \right) = e(0) \exp \left( \frac{\tau_e^2 e^2 E^2}{3m^*h^2} \right). \tag{23}
$$

The emission in an electric field increases by a factor $\exp(E^2/E_0^2)$, where $E_0^2 = (3m^*h^2)/(\tau_2^2 e^2)$ is the characteristic field determined by the tunneling time $\tau_2$ and, hence, depending on temperature. As seen from Eqs. (23) and (12), the ionization probability grows exponentially with squared electric field, and increases rapidly with decreasing temperature. The increase of the ratio $e(E)/e(0)$ with decreasing temperature is accounted for by the fact that at low temperatures the optimum energy $\varepsilon_0 = 0$ for thermally stimulated tunneling tends to zero, and the tunneling time $\tau_2$ grows to infinity. Hence a small decrease of the adiabatic potential $U_2$ of an ionized impurity leads to a large increase of the emission probability. The temperature and field behavior of the carrier emission probability in a dc electric field was observed to follow Eq. (23). \cite{90,91,92}

### 1.4. Direct ionization by electron tunneling

The emission probability as a function of electric field in Eq. (23) was obtained with due account of the fact that the corrections to multiphonon emission resulting from electron tunneling are small, in other words, that the energy of electron tunneling $\varepsilon_m$ is much smaller than that of defect tunneling $\varepsilon_0$ and of thermally stimulated ionization $\varepsilon_T$. This condition defines the upper bound on the electric field where the consideration presented in Sec. 1.3 is valid:

\begin{equation}
e(E, \varepsilon) \approx \exp(2e\tau_2/h) \exp \left( - \frac{4e^3 \sqrt{2m^*}}{3h e^2} \right). \tag{20}
\end{equation}

As the temperature increases, one will have to take into account the possibility of thermal activation of the impurity. In the case where $U_{2e}$ crosses the $U_1$ parabolic curve close to its minimum, multiphonon transitions result in a correction to $\varphi$ which, while being temperature-dependent, is insignificant in the strong-field domain. \cite{93} Equations (26) and (27) show that the emission probability in direct tunneling depends on electric field weaker than under conditions of the multiphonon-assisted process (Eq. (23)).
In conclusion to this Section we present a general expression obtained in the frame of the Huang and Rhys model:

\[ e(\overline{Z}) \propto \exp(-\varphi), \]  

\[ \varphi = \frac{e_T}{\hbar \omega} \left[ 1 - y \right] \left[ \pm 2 \omega \tau_2(y) - (1 + \xi^2)^{1/2} + \xi \cosh \frac{1}{2} \Theta \right] \]

\[ + \frac{2}{3} E_0 \alpha^{-1/2}/f, \]  

where

\[ 2 \omega \tau_2(y) = \frac{1}{2} \Theta \pm \ln \left( \frac{1 + (1 + \xi^2)^{1/2}}{\xi^2} \right), \quad \Theta = \frac{\hbar \omega}{k_B T}, \]  

\[ \xi = \left[ \frac{1}{c} \left( 1 - y \right) \sinh \frac{1}{2} \Theta \right]^{-1}, \quad c = \frac{e_T}{\Delta e} = -1 + \frac{4}{b}. \]  

The plus and minus signs in the expression for \( \varphi \) refer to the cases of \( y < 1 \) and \( y > 1 \), respectively, and the value of \( y \) is found by solving the equation

\[ \left( E/E_0 \right)^{1/2} = 2 \omega \tau_2(y). \]  

The above expressions determine the character of the exponential dependence within a broad range of electric fields and temperatures and reduces to the limiting cases described by Eqs. (23) and (26).

### 1.5. Charge effect

Most deep centers bear a charge, which should be taken into account when considering ionization processes. There is the well-known Poole–Frenkel effect consisting in a decrease of the thermal ionization energy of attractive Coulomb centers in the presence of an external electric field, which lowers the barrier generated by the Coulomb potential (see Fig. 5). The theory of this effect was developed by Frenkel, who showed that the ionization probability grows exponentially with the square root of the external electric field. The Poole–Frenkel effect is a dominant mechanism in the increase of the ionization probability of attractive centers by electric field for not too high fields, where the ejection is dominated by over-barrier emission, and carrier tunneling does not play a significant role. This phenomenon was observed in I–V characteristics under a dc bias in a large number of insulators and semiconductors. Straightforward calculation shows that application of an electric field \( E \) lowers the ionization barrier in the direction opposite to the field (Fig. 5b) by an amount \( \varepsilon_{PF} \): \[ \varepsilon_{PF} = \frac{Z e^3 E}{\kappa}, \]  

where \( Z \) is the charge on the center, and \( \kappa \) is the dielectric constant.

As a result, an electric field increases the probability of thermal emission

\[ e(E) \propto \exp(\varepsilon_{PF}/k_B T). \]  

The general theory of the Poole–Frenkel effect and the deviations from the simple relations (33) and (34) are considered in detail in Ref. 83. It can be shown that inclusion of multiphonon effects results in \( k_B T \) in Eq. (34) being replaced by \( k_B T^* \), where

\[ \frac{1}{k_B T^*} = \frac{\tau_2}{\hbar} + \frac{1}{k_B T} \pm \frac{2 \tau_1}{\hbar}. \]  

The plus sign corresponds here to the case of weak electron-phonon coupling, and the minus, to self-trapping, thus reducing or increasing, respectively, the slope of the \( \ln[e(E)] \times \sqrt{E} \) relation.

Obviously enough, the Poole–Frenkel effect can take place in relatively weak fields, where the lowering of the barrier does not exceed the Coulomb energy scale in semiconductors, i.e. in electric fields \( E \) lower than the field determined from the equation \( e_{PF}(E) = Z^2 R_y^* \), where \( R_y^* = e^4 m^* / 2 \kappa^2 \hbar^2 \) is the effective electron energy in the Coulomb potential of a charged impurity (the Rydberg energy). In stronger electric fields or at lower temperatures, tunneling effects become dominant, with the role of the charge being reduced to increasing the transparency of the barrier through the lowering of its height. In this limit one
can readily obtain an expression for the correction to the probability of tunneling ionization involving a multiphonon transition. In the limit that \( e_m > Ry^* \), this correction calculated in Ref. 95 produces an additional factor in Eq. (23) for the emission probability \( e(E) \). Taking into account the Coulomb charge, the probability of multiphonon-assisted tunneling ionization can be written as

\[
e(E) = e(0) \exp \left[ 2 \sqrt{2 m^* Ry^*/eE} - \ln \left( \frac{4 \tau_3^3 e^2 E^2}{m^* \hbar} \right) \right] \exp \left( \frac{\tau_3^3 e^2 E^2}{3 m^* \hbar} \right). \tag{36}
\]

We readily see that the correction due to the impurity charge in Eq. (36) tends to unity with increasing electric field and becomes insignificant in strong fields.

Thus taking into account the Poole–Frenkel effect and multiphonon tunneling ionization we come to the conclusion that the log ionization probability grows with the field first as \( \sqrt{E} \) and, in the high-field domain, as \( E^2 \).

### 1.6. Ionization by submillimeter radiation

The choice between the quantummechanical and classical treatment of an electromagnetic field depends on the relation between the period of the radiation field \( \Omega^{-1} \) and the characteristic times of the processes occurring in the system under study. Keldysh96 showed that multiphonon ionization of semiconductors under high-frequency illumination and tunneling ionization in a dc electric field are just two limiting cases of the same nonlinear process. It was also demonstrated that, for a given incident intensity, the ionization probability increases with frequency, and that this growth is characterized by a parameter \( \Omega \tau_5 \), where \( \tau_5 \) is the electron under-barrier tunneling time in the electric wave field, with the barrier height determined by the ground-state binding energy. These results (see also Ref. 97) are fully applicable to analyzing direct electron tunneling ionization from deep centers. For these conditions, the height of the barrier for electron tunneling is determined by the electron binding energy with the impurity at equilibrium, i.e. by \( e_{opt} \). The time required for an electron to tunnel through a barrier of height \( e_{opt} \) in an electric field \( E \) can be written

\[
\tau = \frac{\sqrt{2 m^* e_{opt}}}{eE} \tag{37}
\]

If for the value of \( E \) corresponding to the maximum wave field amplitude this time is shorter than the wave period \( \Omega^{-1} \), i.e.

\[
\Omega < \frac{eE}{\sqrt{2 m^* e_{opt}}} \tag{38}
\]

then the action of the high-frequency field is equivalent to application of a dc electric field. The tunneling ionization probability does not depend in this case on frequency, and the tunneling probability is given by Eqs. (26) and (27). As follows from Ref. 96, where a general expression for the electron transition probability was obtained for the total frequency range, one can readily derive the frequency correction to the exponential factor in Eq. (26) if condition (38) is met:

![Electron tunneling trajectory under a triangular barrier for an initial energy \(-e_m(1)\) in a dc electric field and \((2)\) in an ac field. During the tunneling, the ac electric field \(E \cos(\Omega t)\) changes the slope of the barrier, and the electron absorbs photons.](image)

\[
\varphi = 4 \sqrt{\frac{2 m^* e_{opt}^{3/2}}{\hbar eE}} \left( 1 - \frac{m^* \Omega^2 e_{opt}}{5 e_e^2 E^2} \right). \tag{39}
\]

The effect of a high-frequency electric field on the ejection probability is due to two mechanisms, namely, (i) barrier modulation, and (ii) a possibility of tunneling at a lower barrier height through absorption of photons. While the first mechanism brings about an exponential decrease of the tunneling probability, the second results in its exponential growth. As the frequency is increased, the energy absorbed in tunneling increases too and tends to the binding energy, thus resulting in ionization through multiphonon absorption. The ejection probability also grows in this case with increasing frequency, since the photon energy increases, and, accordingly, the number of photon required to initiate an optical transition decreases (see Fig. 6).

While in the case of multiphonon-assisted tunneling ionization the electric field does not act on the motion of the defect itself, the tunneling of an electron should certainly change in an ac electric field. In the limit of multiphonon tunneling ionization in a dc electric field (see Sec. 1.3) we found that the optimum energy for electron tunneling \( e_m \) is determined by the condition of the tunneling time of the electron \( \tau_e \), (22), being equal to that of the defect \( \tau_2 \), with the latter being determined by the temperature and defect vibrational frequency (12):

\[
\tau_e = \tau_2(e_m) = \tau_2. \tag{40}
\]

The same condition determines the optimum electron energy before tunneling in an ac electric field \( e_{init} = -e_m \) (see...
Fig. 6) (note that in an ac field the initial and final tunneling energies are different, because energy can be absorbed during the tunneling).

The process of multiphonon tunneling ionization can be divided into three stages: (1) thermal excitation transfers the defect with a bound electron to the vibrational level corresponding to the vibrational energy \( \epsilon_0 \); (2) the vibrational system undergoes rearrangement to the potential corresponding to a free electron with a negative kinetic energy \(-\epsilon_m\), i.e. the system transfers to the adiabatic potential \( U_{2m} \); (3) the electron tunnels to the free state with the initial energy \(-\epsilon_m\). The two latter processes are tunneling assisted. Condition (40) for determining the energy \( \epsilon_m \) can be derived similarly to the way this was done in Sec. 1.3, if one represents the probability of electron tunneling with an initial energy \(-\epsilon\) in a general case by

\[
p_e(\epsilon) \propto \exp(-2S_e(\epsilon)),
\]

where \( S_e(\epsilon) \) is the electron action multiplied by \( i/\hbar \), and introduces the electron tunneling time \( \tau_e(\epsilon) \) in the form

\[
\tau_e(\epsilon) = \hbar \frac{dS_e(\epsilon)}{d\epsilon}.
\]

Let us calculate now \( \epsilon_m \) as a function of frequency and wave-field amplitude under the condition that the electron tunneling time \( \tau_e \) is determined by the time \( \tau_2 \), and find the electron tunneling probability for these conditions. In the case of tunneling under a time-varying potential we can express \( S_e \) through the Lagrangian \( L_e \) (Ref. 98)

\[
\hbar S_e(\epsilon_m) = \int_0^{\tau_e} L_e(\tau) d\tau + \epsilon_m \tau_e.
\]

The dependence of the Lagrangian \( L_e \) on \( \tau \) is determined by the dependence of the electron on coordinate \( z \) (Fig. 6) and velocity \( \dot{z} = dz/d\tau \) at time \( \tau \):

\[
L_e(\tau) = -\frac{m^*}{2} \dot{z}^2 - U_e(z),
\]

where \( U_e \) is the potential energy in an electric field. All the quantities are calculated by the rules of classical mechanics, but with due account of the fact that the time \( t \) is replaced by imaginary time \( \tau = it \), since the motion takes place in the classically forbidden region under the barrier. Accordingly, in the case where the electric field vector is directed opposite to the \( z \) axis we have

\[
U_e = -eEz \cos(\Omega t) = -eEz \cosh(\Omega \tau).
\]

The tunneling trajectory \( z(\tau) \) and "velocity" \( \dot{z}(\tau) \) should be found from the classical equation of motion:

\[
-\frac{m^*}{2} \frac{d^2z}{d\tau^2} = -\frac{\partial U_{2e}}{\partial z}
\]

subject to the boundary conditions

\[
z(\tau)|_{\tau = \tau_2} = 0
\]

for the tunneling beginning at the imaginary time \(-\tau_e\) and

\[
\dot{z}(\tau)|_{\tau = 0} = 0
\]

after the completion of the tunneling (\( \tau = 0 \)) at the turning point (see Fig. 6).

The minus sign of the second derivative in Eq. (46) appears as a result of the replacement of \( t \) by \( i\tau \). Equation (46) reduces to the form

\[
\frac{d^2z}{d\tau^2} = -\frac{eE}{m^*} \cosh(\Omega \tau).
\]

Taking into account Eqs. (47) and (48), Eq. (49) yields

\[
\dot{z} = \frac{eE}{m^* \Omega} \sinh(\Omega \tau)
\]

and

\[
z = \frac{eE}{m^* \Omega}(\cosh(\Omega \tau_e) - \cosh(\Omega \tau)).
\]

At the initial instant of time, \( \tau = -\tau_e \), the "velocity" is determined by the total electron energy \(-\epsilon_m\), because the potential energy \( U_e(z=0) = 0 \) [see Eq. (45) and Fig. 6]. Thus we come to the condition

\[
z(\tau)|_{\tau = -\tau_e} = \frac{2\epsilon_m}{m^*}
\]

whence follows the relation connecting \( \epsilon_m \) with the tunneling time \( \tau_e \):

\[
\epsilon_m = \frac{(eE)^2}{2m^* \Omega^2} \sinh^2(\Omega \tau_e).
\]

We see that for a given tunneling time \( \tau_e \) the energy \( \epsilon_m \) increases with frequency. In the limiting case of low frequencies, \( \Omega \tau_e < 1 \), the relation between \( \epsilon_m \) and \( \tau_e \) determined by Eq. (53) coincides with Eq. (22). Note that using Eq. (43) one can readily verify that relation (42) for \( \tau_e \) does indeed hold.

Equations (41), (43), (44), and (50) and (51) can be used to obtain the following relation for the electron tunneling probability \( p_e(E, \Omega) \) for a fixed tunneling time \( \tau_e \):

\[
p_e(E) \propto \exp\left(-\frac{(eE)^2}{2m^* \Omega^2} \left[2\Omega \tau_e \sinh^2(\Omega \tau_e) + \Omega \tau_e - \frac{1}{2} \sinh(2\Omega \tau_e)\right]\right).
\]

Taking into account Eq. (53), relation (54) agrees with exponential accuracy the result obtained in Ref. 96 and coincides with the ionization probability in an ac electric field calculated in quasi-classical approximation with the use of the vector gauge, where the scalar potential is zero.

Setting \( \tau_e = \tau_2 \) and taking into account the increase of the defect tunneling probability under multiphonon thermally-activated ionization, which is determined by the factor \( \exp(2\epsilon_{\text{ion}} / \hbar) \) [see Eqs. (19) and (20) in Sec. 1.3], we obtain for the resultant probability of multiphonon-assisted defect tunneling ionization under illumination an expression similar to Eq. (23), where one should now substitute \( \tau_2^* \) for \( \tau_2 \):

\[
e(E, \Omega) = e(0) \exp\left(\frac{\tau_2^* (eE)^2}{3m^* \hbar}\right).
\]
In the limit $\Omega \tau < 1$ we obtain from Eq. (56):

$$\tau_2^{\mu \gamma} = \tau_2 \left[ 1 + \frac{1}{5} (\Omega \tau_2)^2 \right].$$

(57)

We see that an increase in frequency results in a growth of the tunneling ionization probability, which is due to the increasing initial energy of the tunneling electron $e_m$ [see Eq. (53)], i.e. to the increase in absolute magnitude of the optimum electron transition energy.

The dependence of the multiphonon emission probability on electric field amplitude [both for dc, Eq. (23), and high-frequency, Eq. (55), fields] was derived under the condition that electron tunneling gives only a small correction to multiphonon-assisted emission, in other words, that the energy of electron tunneling $e_m$ is much less than that of defect tunneling $E_0$ and thermal ionization energy $e_T$. This condition determines the upper limit to the electric fields for which the above consideration is valid.

2. EXPERIMENTAL METHODS AND SUBJECTS OF INVESTIGATION

Ionization of deep impurities by high-intensity submillimeter radiation was discovered and studied in a large number of semiconductors containing such impurities. One measured the photoresponse of a sample to pulsed radiation of a submillimeter laser, which is generated by a change in free carrier concentration through impurity ionization. The radiation sources used were TEA CO$_2$-pumped, high-power tunable submillimeter pulsed molecular-gas lasers with NH$_3$, CH$_3$F, and D$_2$O. The principle of operation of such lasers was developed and used to achieve cw lasing by Chang and Bridges in 1969 and, in 1974, de Temple extended it to obtain pulsed laser operation. The choice of the CO$_2$ laser for optical pumping was based on the ability of tuning it within the 9.2–10.6 $\mu$m-range, which includes strong vibrational-rotational absorption lines of many molecules. More than 1000 compounds are presently employed as gain media for CO$_2$-pumped lasers. The use for pumping of high-intensity radiation from TEA CO$_2$ lasers operating at 100 kW and more opens new possibilities in this respect, since the strong electric field of the light wave results in a broadening of molecular levels and permits one to excite states fairly distant from the pumping frequency. One can thus achieve lasing at a number of wavelengths which would not be accessible with low-power cw-pump radiation. The search for conditions favorable for lasing in the FIR-SBM range reduces primarily to finding appropriate gain media and lines for the CO$_2$ pumping laser which would be in resonance with the corresponding molecular transitions. Thousands of lines covering the whole range of FIR-SBM radiation (20 $\mu$m to 2 mm) have thus far been found for most of the media.

Looking for new lasing lines is, however, not as essential for semiconductor research as finding strong and stable, single radiation lines. This is particularly important for pulsed lasers, whose high-power pump radiation results in broadening of the gain-medium molecular levels and, hence, in observation of a large number of additional lines.

The most sophisticated element in the laser system under consideration is the pumping laser. In earlier days, development of an optically pumped laser required, in the first place, building in the laboratory a high-power pulsed CO$_2$ laser with a high level of suppression of electromagnetic interference, which was an obstacle to extending the range of applicability of high-excitation FIR-SBM spectroscopy. Now the availability of high-stability, high-power commercial TEA CO$_2$ lasers (URANIT 104, 204) permits one to assemble such a system with no difficulties at all. The characteristics of strong single lines covering the range from 30 to 500 $\mu$m, the corresponding gain media and lines of the TEA CO$_2$ laser which are used for pumping are listed in Table I. The photon energies corresponding to these wavelengths lie in the 35–2 meV range and in all cases are substantially lower than the binding energies of the deep impurities studied. The radiation pulse length varied for different lines from 10 to 100 ns. The radiated power was 50 kW. The radiation was focused to a spot of about 1 mm$^2$, with the maximum intensity reaching as high as 5 MW/cm$^2$. More details on the system can be found in Refs. 11, 48.

The intensity, shape and spatial distribution of the laser radiations were monitored with fast noncooled photodetectors operating in the submillimeter range and based on the photon drag effect, intraband $\mu$-photoconductivity, stimulated tunneling effect in metal/semiconductor structures under plasma reflection, as well as with the Spirikon pyroelectric array. The pulsed signal proportional to the change in sample resistance under laser illumination was measured in a standard photosresponse measurement circuit with a load resistance $R_L = 50 \Omega$ (see inset to Fig. 7). The bias voltage across the sample, 5 V/cm, was substantially lower than the impurity avalanche-breakdown threshold. The measurements were carried out within the 30–150 K range, where at thermal equilibrium practically all carriers are frozen out on the impurity. The samples were placed in an optical cryostat. Penetration of light in the medium IR range into the cryostat was prevented by the use of crystalline quartz filters and, in the visible, by a 1-mm thick black-polyethylene filter.

The tunneling ionization processes were studied on deep...
impurity centers of two different types, namely, (i) those with weak electron-phonon coupling, $\beta < 1$ (Au, Hg, Cu, Zn in germanium, Au in silicon, and Te in gallium phosphide) and (ii) with strong electron-phonon coupling where self-trapping takes place, $\beta > 1$ (tellurium in $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ and $\text{Al}_x\text{Ga}_{1-x}\text{As}$).

The thermal ionization energy of acceptor impurities $\varepsilon_T$ in germanium was $150$ meV (Au), $90$ meV (Hg), $40$ meV (Cu), and $30$ meV (Zn), for Au in silicon—$300$ meV, and for the donor tellurium in gallium phosphide, $90$ meV (Ref. 75). Note that tellurium in gallium phosphide is essentially a deeply-buried shallow Coulomb center.

Doping with tellurium of $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ samples with $x = 0.28$ and 0.5, and of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with $x = 0.35$ resulted in electronic conduction, and one observed all the main features characteristic of DX centers, in particular, the persistent photoconductivity.  

3. OBSERVATION OF THE TUNNELING IONIZATION OF DEEP-IMPURITY CENTERS BY HIGH-INTENSITY FIR-SBM RADIATION

Semiconductors containing deep and shallow impurity centers have been used successfully already for a long time as low-temperature detectors in the IR and FIR ranges. The long-wavelength limit to their use is bounded by the binding energy of the impurity, with no response obtained from deep centers such as, for instance, Ge:Au and Ge:Hg in the FIR and, all the more so, in the submillimeter regions of the spectrum. This pattern is observed, however, only at relatively low light intensities. Excitation of a semiconductor containing generated deep impurities by strong pulsed FIR-SBM laser radiation produced a photoconductive signal by ionizing the deep impurity centers, despite the fact that the pump photon energy was tens of times lower than their thermal ionization energy, $\varepsilon_T$. A signal which increased superlinearly with the incident intensity was observed from all studied samples of Ge, Si, GaP, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ within a broad range of temperatures and wavelengths employed. The sign of the photoconductive signal corresponds to a decrease of the sample resistance, and its characteristic decay time is different for different types of impurities and different temperatures. The length of the photoresponse pulse for deep substitutional impurities is somewhat longer than that of the laser pulse (Fig. 7) and varies depending on temperature from $100$ ns to $10$ $\mu$s, which corresponds to the photoexcited carrier lifetimes (see, e.g., Refs. 75, 112, 113). In the case of self-trapped DX$^-$ centers in $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ one observes an increase in sample conductivity which persists for several hundreds of seconds after the excitation pulse, which is characteristic of the decay of persistent photoconductivity in the samples with DX$^-$ centers. Figure 8 compares photoresponse signals obtained from an $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ sample on two time scales (Fig. 8b) with the pump pulse (Fig. 8a). The observation of positive persistent photoconductivity under FIR-SBM excitation suggests that this signal is due to electron detachment from the DX centers.

FIG. 7. Oscillographic traces of the excitation pulse and of the photoconductive signals generated in a sample with deep impurities illuminated by FIR–SBM radiation. Inset shows the measurement circuit.

FIG. 8. Oscillographic traces of (a) excitation pulse with $\lambda = 90.5$ $\mu$m and of the photoconductive signals generated by illuminating with FIR-SBM radiation an $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ sample (b) in the dark and (c) in the state of persistent photoconductivity produced by exposing the sample preliminarily to light in the near IR range.
Variation of the sample conductivity induced by SBM radiation can be due either to processes involving radiation absorption by free carriers (electron gas heating, $\mu$ photoconductivity) or to the appearance of additional free carriers in ionization.

We shall dwell first on the possible effect of heating the lattice or the electron gas, since this is the most natural mechanism of photoconductivity under intense illumination. Carrier heating was studied in detail in the submillimeter range samples with shallow impurities and at not too low temperatures, i.e., where the impurities are ionized and the conditions are most favorable for heating. As follows from these studies, presented in the Appendix, in the case of excitation of samples with deep impurities, electron gas heating can be excluded as the cause of the observed impurity ionization based on the kinetics of the detected signals. To begin with, electron gas heating in the temperature and concentration ranges considered here should produce negative photoconduction, whereas the photoconductivity observed experimentally is positive. Besides, the photoresponse signal due to electron heating should either reproduce in shape the pump pulse or be more complex, but it should not be longer than the latter (see Appendix and Refs. 39, 114), whereas the observed signals correspond to excited-carrier trapping times and are substantially longer than the pump pulses. The impurity ionization manifests itself most clearly in the case of submillimeter-range persistent photoconductivity in samples containing DX centers.

Thus observation of positive photoconductive signals with times substantially in excess of the pump pulse length excludes electron gas heating and the corresponding photoconductivity as a possible mechanism of the observed photoresponse (see Appendix). The suppression of heating in samples doped primarily by deep centers and maintained at sufficiently low temperatures is due to carrier freezeout at impurities and, hence, to the absence of noticeable radiation absorption. Thus the photoresponse is indeed caused by photoionization of deep impurities by light with the photon energy $h\Omega$ much less than the thermal ionization energy of impurities $e_T$.

Figure 9 displays the dependence of the photoresponse of mercury-doped germanium samples ($e_T=90$ meV) on light intensity measured at $T=64$ K for two different wavelengths. Shown in Fig. 10 on a semilog scale are similar data obtained for another deep impurity (gold in germanium) for three wavelengths. The quantities $\sigma_i$ and $\sigma_d$ are the sample conductivities under illumination and in the dark, respectively. Since the pump pulse duration is shorter than the nonequilibrium-carrier trapping time, recombination during the excitation can be disregarded. Therefore the experimentally determined relative change in conductivity, $\Delta \sigma/\sigma_d = (\sigma_i - \sigma_d)/\sigma_d$, corresponds to the relative change in the free-carrier concentration, which, in its turn, is proportional to the change in the impurity ionization probability. Deep-impurity photoionization by light with $h\Omega < e_T$ and the strong nonlinear dependence of this process on pump intensity can be related to several mechanisms of nonequilibrium carrier generation, such as multiphoton-assisted ionization, tunneling ionization involving photon absorption, light-induced impact ionization, and multiphonon-assisted or direct tunneling in the electric wave field. These processes depend differently on the radiation frequency. An increase in radiation frequency boosts the rate of nonequilibrium carrier generation through multiphonon absorption and tunneling ionization involving pho-
ton absorption, and reduces the probability of light-induced impact ionization.\textsuperscript{34} By contrast, tunneling ionization occurring in the field of an optical wave does not depend on frequency.

Measurements showed that at temperatures of about 70 K photocconductivity does not depend on radiation wavelength above 90 \( \mu \text{m} \) throughout the intensity range covered. This is demonstrated by Figs. 9 and 10, which show that the curves for all wavelengths coincide within the measurement accuracy. The signal is also independent of the radiation polarization, which is evident from Fig. 11, where the photocurrent signal in Ge:Au is presented as a function of intensity for linearly and circularly polarized light with a wavelength \( \lambda = 90.5 \mu \text{m} \). The observed independence of the signal of radiation frequency (Figs. 9 and 10) permits a conclusion that the free-carrier generation is due here to the tunneling processes,\textsuperscript{60} with the FIR–SBM radiation acting as a dc field. The ionization probability is determined in this case by the electric field of the radiation rather than by the magnitude and number of the photons. It is in these conditions that most experiments were made whose results are discussed in detail and compared with the theory for a dc field in Sec. 4. An increase in frequency or decrease in temperature result in the onset of a frequency dependence of the ionization probability, which corresponds to increasing tunneling probability. The corresponding experimental results and the mechanisms responsible for the appearance of this frequency dependence are treated in Sec. 4.5.

4. IONIZATION OF DEEP-IMPURITY CENTERS BY HIGH-INTENSITY FIR-SBM RADIATION

4.1. Multiphonon-assisted tunneling ionization

The multiphonon tunneling ionization is characterized by an exponential dependence on the squared electric wave-field amplitude: \( e(E) = e(0)\exp(E^2/E_c^2) \) (see 1.3). Such an increase in the photoconductive signal was observed for all samples within a broad range of fields and temperatures. The experimental dependences of \( \ln(\sigma_I/\sigma_d) \) on squared amplitudes of the electric wave field are shown in Fig. 12 for Ge:Au and in Fig. 13 for Al\(_{0.5}\)Ga\(_{0.5}\)Sb. The measurements were performed at different temperatures and wavelengths.

We see that there exists a field interval for each temperature within which the probability of photoionization depends on electric field amplitude as \( \exp(E^2/E_c^2) \). A comparison of experimental data on FIR ionization of the Au impurity in Si at \( T = 300 \text{ K} \) with earlier studies of the dependence of thermal ionization probability on dc electric field, \( e(E) \), made by capacitive spectroscopy\textsuperscript{91,92} showed that \( e(E)\exp(E^2/E_c^2) \) in both cases, with the values of \( E_c \) differing by a factor 1.5–2 (Fig. 14). This may be considered a good agreement between the results obtained by such different methods, if we take into account the field inhomogeneities present in a sample studied by DLTS.

Figures 12–14 also show with solid-lines plots the \( A\exp(E^2/E_c^2) \) relation calculated with the fitting parameter \( E_c^2 \). As follows from Eqs. (23) and (36), the slope of the experimental curves in the field region where \( \ln(\sigma_I/\sigma_d) \cong \exp(E^2/E_c^2) \) permits one to determine the tunneling times \( \tau_2 \). In order to extract \( \tau_2 \) from experimental data, one has to know the effective carrier mass, which determines the tunneling process. In Fig. 15, the tunneling time \( \tau_2 \) is shown as

\[
\ln(\sigma_I/\sigma_d) = A - B \exp(E^2/E_c^2)
\]
a function of reciprocal temperature for a number of deep impurities studied. In the case of deep acceptors in germanium, the light-hole mass was used. Figure 15 demonstrates the good agreement of the experimental values of $\tau_2$ with Eq. (12). One may thus conclude that carriers bound to a deep acceptor tunnel into the light-mass subband. This is due to the fact that the symmetry of substitutional impurities corresponds to the point group $T_d$, and that the ground state of a deep impurity represents a superposition of the light- and heavy-hole states. Thus an acceptor-bound hole can be associated with neither the light nor the heavy mass. It was shown theoretically that tunneling depends essentially on the wave-function tail distant from the center, and that it is the light holes that provide a major contribution to this tail. For comparison, Fig. 15 shows also a plot of $h/2k_BT$. We see that $\tau_2$ is of the order of $h/2k_BT$. Note, however, an essential point. As evident from the experimental data presented in Fig. 15, for any temperature $\tau_2$ is larger than $h/2k_BT$ for substitutional impurities, but less than $h/2k_BT$ for self-trapped DX centers. This result is in excellent agreement with theory [see Eq. (12) in Sec. 1.1)]. Thus, by determining the tunneling time from data on multiphonon tunneling ionization in a high-frequency electric field, one can unambiguously identify the type of the deep-impurity adiabatic potential. The temperature-independent tunneling times $\tau_1 = \tau_2 - h/2k_BT$ are given in the caption to Fig. 15 for different impurities.

We note in conclusion that the existence of persistent photoconductivity in Al$_{0.5}$Ga$_{0.5}$Sb samples permitted one to observe, besides the multiphonon tunneling ionization of DX centers, stimulated carrier trapping by the center. In this case preliminary illumination of the sample in the visible region at low temperatures ($T<100$ K) results in electron detachment from DX centers and, respectively, in an increase of the sample conductivity. Due to the persistent photoconductivity, this state persists for a long time. Subsequent illumination of the sample with FIR pulses produces a negative photoresponse signal (Sec. 2, Fig. 8b) caused by the multiphonon-stimulated carrier capture by the center in the high-frequency radiation field. This provides an additional argument for the ionization being due to multiphonon-assisted tunneling transitions.

### 4.2. Direct tunneling ionization

In strong electric fields, one observes transition to direct tunneling that does not involve phonons. As evident from Fig. 12, photoconductive signals in strong fields are less than expected in the case of multiphonon tunneling ionization. This is seen also from Figs. 16–18, where $\ln(\sigma/\sigma_0)$ is plotted as a function of squared electric field $E$ for Ge:Au and Ge:Hg for different wavelengths and temperatures. For fields in excess of $E_0$ the ionization probability grows slower with increasing $E$ than that in the multiphonon tunneling region. As shown in Sec. 1, multiphonon tunneling in an electric field gives only a correction to multiphonon-assisted thermal emission. The emission probability proportional to $\exp(E^2/E_0^2)$ was obtained taking into account the fact that the electron tunneling energy $E_m$ is less than the optimum defect-tunneling energy $E_0$ (13). The electron tunneling energy grows with electric field, thus reducing $E_0$. The multiphonon tunneling approximation becomes invalid when $E_m$ becomes equal to $E_0$. The critical value of the electric field
FIG. 16. Log conductivity ratio under illumination and in the dark, \( \ln(\sigma_i/\sigma_d) \), of Au-doped germanium samples (\( \varepsilon_i = 150 \) meV) vs squared electric field amplitude of \( \lambda = 90.5 \) \( \mu \)m radiation. The three sample temperatures are specified at the curves. The dashed straight lines are plots of the relation \( e(E) \propto A \exp(E/E_c) \) constructed with the experimental values of \( \tau_2 \), and the solid lines relate to the calculations made using Eqs. (28)–(32). The calculations made use of the experimental values of \( \tau_2 \) and of the localized vibrational frequency \( \omega = 2 \times 10^{13} \) s\(^{-1}\).

The ionization probability in the field domain defined by inequality (58), according to Ref. 96, is characterized by weaker field dependences [see Eqs. (26) and (27)]. The experimentally observed change in the character of the field dependence for fields corresponding in order of magnitude to the calculated values of \( E_0 \) permits a conclusion that for \( E \gg E_0 \) the mechanism of direct tunneling ionization becomes dominant. 108

A general expression describing the limiting cases of both multiphonon and direct tunneling was obtained within the Huang–Rhys model (see Sec. 1.4). Consider the results of calculating the field dependence of emission probability performed by using Eqs. (28)–(32) (see 1.4). The calculation makes use of three phenomenological parameters, namely, thermal ionization energy \( \varepsilon_T \), localized vibrational frequency \( \omega \), and the nondimensional electron-phonon coupling constant \( \beta = \Delta \varepsilon / \varepsilon_T \). The value of thermal ionization energy \( \varepsilon_T \) was taken from literature. The tunneling times \( \tau_2 \) (Fig. 15) were then used to determine the tunneling time \( \tau_1 \) which, according to Eqs. (2) and (15), relates parameter \( \beta \) to the localized vibrational frequency \( \omega \). Thus the problem reduces to finding the only fitting parameter, for which the localized vibrational frequency was taken. Its value (\( \omega = 2 \times 10^{13} \) s\(^{-1}\)) determined for one temperature and one impurity was not changed in the subsequent treatment of the data obtained for other temperatures and other impurities in the same material, in other words, there were no fitting parameters after that. Figure 19 shows the calculated probabilities of emission in an electric field \( e(E) \) normalized to that of thermal emission \( e(0) \) for different localized vibrational frequencies \( \omega \). We see that the emission probability depends noticeably on \( \omega \) for fields \( E \gg E_0 \) and, thus, \( \omega \) can indeed be used as a fitting parameter.

Figures 16–18 compare the calculations made using Eqs. (28)–(32) (Sec. 1.4) with experimental data. We readily see that while the deviation from the \( e(E) \propto \exp(E/E_c) \) relation observed for \( E > E_0 \) is described satisfactorily by theory, the latter gives a stronger dependence on intensity than the one measured in experiment. We note also that the characteristic electric field \( E_0 \) as a function of temperature and thermal ionization energy is in a good agreement with theory for all

FIG. 17. Log conductivity ratio under illumination and in the dark, \( \ln(\sigma_i/\sigma_d) \), of Hg-doped germanium samples (\( \varepsilon_i = 90 \) meV) vs squared electric field amplitude of \( \lambda = 90.5 \) \( \mu \)m radiation. The three sample temperatures are specified at the curves. The dashed lines are plots of the relation \( e(E) \propto A \exp(E/E_c) \) constructed with the experimental values of \( \tau_2 \), and the solid lines relate to the calculations made using Eqs. (28)–(32). The calculations made use of the experimental values of \( \tau_2 \) and of the localized vibrational frequency \( \omega = 2 \times 10^{13} \) s\(^{-1}\).

FIG. 18. Log conductivity ratio under illumination and in the dark, \( \ln(\sigma_i/\sigma_d) \), of germanium samples doped with Au and Hg, obtained at \( T = 46 \) K vs squared electric field amplitude of \( \lambda = 90.5 \) \( \mu \)m radiation. The dashed lines are plots of the relation \( e(E) \propto A \exp(E/E_c) \) constructed with the experimental values of \( \tau_2 \), and the solid lines relate to the calculations made using Eqs. (28)–(32). The calculations made use of the experimental values of \( \tau_2 \) and of the localized vibrational frequency \( \omega = 2 \times 10^{13} \) s\(^{-1}\).
the studied impurities exhibiting weak electron-phonon coupling.

One of the reasons for the discrepancy between theory and experiment in the high electric-field domain may be the scattering of tunneling carriers under the barrier, which sets an upper bound for the tunneling probability. This process was considered for carrier tunneling through Schottky barriers, where the observed tunneling probability was also smaller than that predicted by theory. The energy of the tunneling electron and the length of the under-barrier tunneling trajectory increase with electric field to the extent where the scattering processes place a limit on the emission.

4.3. Charge effect and the Poole–Frenkel effect

In the region of relatively weak electric fields one also observes deviations from the \( \exp(E^2/\epsilon) \) behavior, clearly seen in Fig. 20 displaying the \( \ln(\sigma_i/\sigma_d) vs E^2 \) relation for Ge:Hg. The dominant mechanism in this ionization process is the Poole–Frenkel effect (see Sec. 1.5), which is seen in the onset of an exponential dependence of photosresponse signal on the square root of electric field, \( e(E) \approx \exp(\sqrt{E/E_{PF}}) \). Data for the weak-field region are shown in Figs. 21 and 22, where \( \ln(\sigma_i/\sigma_d) \) is plotted as a function of the square root of the high-frequency electric-field amplitude, \( \sqrt{E} \). In the low-field domain, the ionization probability is seen to grow strongly with decreasing temperature, following closely the \( e(E) \approx \exp(\sqrt{E/E_{PF}}) \) relation. The square-root dependence of \( \ln(\sigma_i/\sigma_d) \) on \( E \) and its temperature behavior are in good agreement with Eqs. (33) and (34) describing the Poole–Frenkel effect.

At the same time the theory of Frenkel does not provide an adequate description of the dependence of conductivity on the high-frequency electric field. The slope of the dependence of \( \ln(\sigma_i/\sigma_d) \) on the square root of electric field is about one half that calculated from Eqs. (33) and (34), which may also be considered as an argument for the presence of multiphonon processes (Sec. 1.5). For low fields, the conductivity does not vary at all (Fig. 22). The same deviations from Eqs. (33) and (34) are observed also in the case of dc fields and accord with published data.

The charge effect manifests itself also in multiphonon tunneling ionization, resulting, according to Eq. (36), in an additional factor in the ionization probability. This is seen...
from extrapolation of the straight lines corresponding to the region of multiphonon tunneling ionization to zero electric field. We see that \( \ln(\sigma_i/\sigma_d) \) does not vanish for \( E=0 \) (Figs. 12 and 20), which implies that \( \sigma_i \) is not equal to \( \sigma_d \), as this followed from Eq. (23) which does not take into account the charge effect.

4.4. Effects due to the high-frequency of FIR radiation

As shown in the preceding Sections, ionization of deep impurity centers by FIR-SBM radiation is a result of tunneling processes occurring in the wave electric field. The ionization probability here does not depend on radiation frequency, and the action of the high-frequency field is equivalent to application of a strong electric field across the sample. As pointed out in Sec. 1.6, however, an increase in radiation frequency or decrease of sample temperature, i.e. transition to the condition \( \Omega \tau_2 = \Omega (\hbar/2k_BT + \tau_1) > 1 \), should result in the ionization probability becoming dependent on frequency. The frequency dependence of ionization probability was measured in Ge:Hg samples (\( \varepsilon_T = 90 \) meV).

The results obtained at \( T = 40 \) K and at wavelengths from 35 to 280 \( \mu \)m are presented graphically in Fig. 23. It is seen that the photoresponse signal grows substantially with radiation frequency while retaining at the same time the character of the field dependence \( \ln(\sigma_i/\sigma_d) \propto \exp(E^2/E_{c0}^2) \). The same sample does not exhibit any frequency dependence at higher frequencies (Fig. 9).

Experiments showed that within this frequency range the \( \ln(\sigma_i/\sigma_d) \propto \exp(E^2/E_{c0}^2) \) relation, which is typical of multiphonon tunneling, occurs above 30 K. For lower temperatures, the frequency dependence becomes stronger, and the electric field dependence of the photoresponse signal changes its character.

The field dependence of the ionization probability measured for Ge:Hg within the temperature range \( T = 35 - 80 \) K and at wavelengths \( \lambda = 35 - 280 \) \( \mu \)m was used to derive the effective tunneling time \( \tau_2^* \) (see Sec. 1.6). Figure 24 displays the dependence of the ratio \( \tau_2^*/\tau_2 \), where \( \tau_2 \) is the tunneling time in a dc electric field, as a function of parameter \( \Omega \tau_2 \) which is dominant in the frequency effects. The tunneling time \( \tau_2 \) was derived from measurements at the longest wavelengths, where no frequency dependence is observed. We see that \( \tau_2^*/\tau_2 \) up to \( \Omega \tau_2 = 1 \), in support of the conclusion that the radiation field acts in this region as a dc field (all the experiments quoted here before were done with this condition met). An increase of \( \Omega \tau_2 \), which corresponds to an increase of frequency or decrease of temperature [see Eq. (12)], brings about a substantial increase in the effective tunneling time compared to the tunneling time \( \tau_2 \). Figure 24 presents also the \( \tau_2^*/\tau_2 \) ratio as a function of \( \Omega \tau_2 \) calculated using Eq. (56). The theory of multiphonon-assisted tunneling (Sec. 1) is seen to agree well with experimental data.

As already pointed out, the theory of multiphonon tunneling in dc and high-frequency fields is valid provided electron tunneling contributes little to thermal emission. This is true if the electron tunneling energy \( \varepsilon_m \) is much smaller than the energy of defect tunneling, \( \varepsilon_0 \), and that of thermal ionization, \( \varepsilon_T \). At low temperatures this condition breaks down because of the smallness of the optimum defect-tunneling energy, and, hence, the existing theory is inapplicable already for very low electric fields. Presented in Fig. 25 is a calculated dependence of the boundary beyond which the theory of multiphonon tunneling energy is no longer valid, as determined by the condition \( \varepsilon_0/e_m = 1 \), on electric field...
strength $E$, temperature $T$, and radiation frequency $\Omega$ for Ge:Hg.

5. KINETIC STUDIES OF THE LONG-LIVED COULOMB EXCITED STATES OF A SHALLOW IMPURITY CENTER

Development of sources capable of generating short FIR-SBM pulses permitted study of the dynamics of non-equilibrium processes in semiconductors and semiconductor quantum-well structures.\textsuperscript{21,40,123–126}

In the case of interest to us here, using short pulses for the ionization of impurities also makes possible the use of tunneling ionization in the FIR-SBM field to study carrier trapping by impurities. As pointed out in Sec. 2, the kinetics of the photoresponse observed are in agreement with the capture cross sections by an impurity which were obtained by other techniques for the materials under study.

Studies of the kinetics of the extrinsic photoconductivity occurring under multiphonon tunneling ionization of a shallow donor center (tellurium) in GaP in an electric field of pulsed laser radiation in the FIR range revealed specific features in the kinetics of carrier trapping and buildup in the valley-orbit split $1s(E)$ state of the shallow donor level.\textsuperscript{127} Such long-lived excited electronic states were discovered earlier in simple substitutional impurities in Ge and Si from modulation of the microwave absorption.\textsuperscript{128,129}

We also consider here carrier buildup in the excited Te level in GaP under ionization of the impurity by short FIR-SBM pulses.

5.1. Experimental investigation of the trapping kinetics into shallow donor states of Te in GaP

Submillimeter photoconductivity measurements were carried out on GaP samples, which were doped heavily by tellurium to concentrations of $3 \times 10^{17}$ and $7 \times 10^{17}$ cm$^{-3}$ and lightly compensated. The samples were maintained in an optical cryostat with the temperature variable from 20 to 150 K, where most of the carriers at thermal equilibrium are frozen out onto the ground-state impurity.

Illumination of a sample by FIR-SBM pulses increased its conductivity. Measurements of the photoresponse signal vs wavelength, radiation intensity, and temperature show that the ionization probability does not depend on wavelength and grows nonlinearly with the electric field $E$ of the radiation as $\exp(E^2/E_c^2)$ while the characteristic field $E_c^2$ decreases with decreasing temperature as $T^3$, which implies that the ionization is produced by multiphonon-assisted tunneling in the electric field of the laser radiation.\textsuperscript{127}

Figures 26 and 27 present typical photoresponse pulse shapes obtained in different time intervals. Shown in Fig. 26 is the photoresponse of the sample measured during the laser pulse and immediately after its completion, to be compared with the laser pump pulse registered by a photon-drag detector.
The first fast photoresponse component is clipped to demonstrate more clearly the unusual behavior of the response after the radiation pulse. The response is seen to grow during the radiation pulse and subsequently drop to zero in times shorter than 40 ns. After the end of the pulse, however (for $t > t_0$), the signal starts to grow again and reaches a maximum in one microsecond, to finally fall off exponentially to zero (Fig. 27). The signal growth after the end of the pulse can be fitted well by the function $a [1 - \exp((t - t_0)/\tau_1)]$, with a characteristic time $\tau_1$ of the order of $10^{-7}$ s. The characteristic time of the subsequent slow exponential decay $\tau_1$ does not depend on the intensity and frequency of the radiation but is strongly temperature dependent, increasing by nearly three orders of magnitude with the temperature decreasing from 150 K (6 $\mu$s) to 35 K (3 ms). Figure 28 presents the reciprocal decay time, $1/\tau_1$, as a function of inverse temperature. This strong temperature dependence can be well fitted in a first approximation by the function $1/\tau_1 = 1/\tau_0 \exp(-\Delta \varepsilon/kT)$ with $\Delta \varepsilon = 28$ meV.

The fast component of the signal is accounted for by ionization and fast capture into the excited Coulomb states of tellurium. $^{130,131}$ The main difficulty consists here in explaining the growth and decay of the signal after the end of the radiation pulse.

The heating of the electron gas or of the sample as a whole can be excluded as possible formation mechanisms of the photoconductive signal. It was shown $^{132,133}$ that at 70 K and higher the electron mobility and, hence, conductivity in GaP decreases with increasing temperature. Thus observation of positive photoconductivity excludes electron gas heating by radiation as a possible cause of the photoresponse. Besides, heating of the sample cannot account for the complex time behavior of the slow signal component and the detected increase of the exponential decay time constant by three orders of magnitude with the temperature changing by five times only.

Presence of additional deep impurities, for instance, of oxygen, which has a small capture cross section ($10^{-22}$ cm$^2$, Ref. 134) cannot explain the observed kinetics of the photoresponse signal. To obtain the measured long decay time by this mechanism, one would have to assume that the concentration of oxygen in the sample is comparable to that of tellurium, $5 \times 10^{17}$ cm$^{-3}$, which contradicts the low level of light compensation in the material under study.

5.2. Kinetic model of the relaxation process in the presence of a long-lived excited state

The initial fast decay of the photoconductive signal is due to the fast cascade trapping of free carriers into high excited states, which subsequently relax to the ground state. The latter stage requires essentially a longer time because of the large energy gap between the excited Coulomb states and the ground state. In the case of deep centers $^{1}$ it usually occurs through multiphonon-assisted processes or optical transitions. The dynamic time consists in this case of two components, namely, a fast and a slower one. The slow decay time is, however, either temperature-independent or grows with temperature, which is at odds with experiment. $^{75}$ Thus the cascade trapping model, unless it is modified properly, cannot account for the increase of the photoconductive signal after the end of the pulse, and the observed temperature behavior of the slow signal decay.

We are going to show that the assumption of the existence of a long-lived excited state characterized by an extremely small transition probability to the ground state permits one to describe adequately the kinetics of the observed signal. The carriers build up in this state and return later by thermal activation to an array of closely spaced Coulomb
states located near the bottom of the conduction band, thus increasing the carrier concentration in the conduction band accordingly.

The inset to Fig. 28 shows a characteristic camel-back-shaped structure of the conduction-band bottom and the position of the ground state and of a number of the lowest excited states of Te in GaP, constructed in accordance with Ref. 135. We readily see that valley-orbit coupling splits the $1s$ state in GaP into two states [$1s(E)$ and $1s(A)$] separated by a gap of 40.7 meV. Cascade trapping was shown to occur primarily over the $s$ states by one-phonon acoustic transitions. Since the energy gap between the $1s(E)$ and the ground state exceeds by far the maximum energy of the acoustic phonon (31.5 meV, Ref. 135) while being less than that of the optical phonon (51 meV by Ref. 135), the electrons promoted to the $1s(E)$ level cannot transfer to the ground state by one-phonon processes, which results in their buildup in this level. The most probable relaxation channel from this state is one-phonon excitation into the next, higher lying $s$ state, $2s(A)$, separated from $1s(E)$ by 28 meV. Note that the exponential dependence of the slow-decay time $\tau_s$ on temperature is characterized by an energy of 28 meV. One may thus conjecture that electrons build up in the $1s(E)$ state, are promoted by thermal excitation to the $2s(A)$ state, and transfer to the closely lying $p$ states through absorption and emission of acoustical phonons, to relax finally via optical (infrared) transitions to the ground state. The kinetic model based on these assumptions is presented schematically in the upper right corner of Fig. 28.

For $t > t_0$, when there is no generation of nonequilibrium carriers, the rate equations determining the electron concentrations $n$ in the conduction band and the concentrations $n_2$ and $n_E$ in the $2s(A)$ and $1s(E)$ states can be written

$$\frac{dn}{dt} = - \frac{n}{\tau_{c2}} + e_{2c}n_2,$$

$$\frac{dn_2}{dt} = \frac{n}{\tau_{c2}} - e_{2c}n_2 - \frac{n_2}{\tau_{2E}} + e_{E2}n_E - \frac{n_2}{\tau_{2A}},$$

$$\frac{dn_E}{dt} = \frac{n_2}{\tau_{2E}} - e_{E2}n_E - \frac{n_E}{\tau_{EA}}. \tag{59}$$

We have neglected here the thermal population of the states and introduced the following characteristic transition times: $\tau_{c2}$-from the conduction band to the $2s(A)$ level, $\tau_{2E}$ and $\tau_{2A}$-from $2s(A)$ to the $1s(E)$ and $1s(A)$ level, respectively, and $\tau_{EA}$-from the $1s(E)$ to $1s(A)$ level. The probabilities of the reverse processes, $e_{2c}$ and $e_{E2}$, are related through the principle of detailed balance to the $\tau_{c2}$ and $\tau_{2E}$ times, respectively. For instance, for the transition probability $e_{E2}$, which is essential for the model, we obtain

$$e_{E2} = \frac{1}{\tau_{2E}} \exp(-\Delta e_{2E}/k_B T), \tag{60}$$

where $\Delta e_{2E}$ is the energy separation between the $1s(E)$ and $2s(A)$ levels.

The first of Eqs. (59) shows that for $t > t_0$, $\tau_{c2}$ a quasi-equilibrium is set in between the electrons in the conduction band and those populating the $2s(A)$ state, i.e. $n = e_{2c} \tau_{c2} n_2$.

In these conditions, concentration $n_2$ determines the concentration $n$ of nonequilibrium free carriers in the conduction band and, thus, the photoresponse signal. Substituting $n = e_{2c} \tau_{c2} n_2$ in Eq. (59) reduces the set of three equations to a set of the two latter equations for $t > t_0$. Then the electron concentration in the $2s(A)$ state as a function of time can be written

$$n_2(t) = \frac{1}{\left(1 / \tau_{d1} - 1 / \tau_{d2}\right)} \left[\frac{n_2^{(0)}}{\tau_{2A}} + \frac{1}{\tau_{2E}} - \frac{1}{\tau_{EA}} - e_{2c} \left(\frac{\tau_{2E}}{\tau_{2A} + \tau_{2E}}\right) - e_{E2} n_E^{(0)} \exp\left(-\frac{(t-t_0)}{\tau_{d1}}\right) + e_{E2} n_E^{(0)} \exp\left(-\frac{(t-t_0)}{\tau_{d2}}\right) \exp\left(-\frac{(t-t_0)}{\tau_{d1}}\right) \right], \tag{61}$$

where $n_2^{(0)}$ and $n_E^{(0)}$ are the concentrations in states $2s(A)$ and $1s(E)$ at time $t = t_0$, respectively, and $\tau_{d1}$ and $\tau_{d2}$ are the dynamic relaxation times defined by

$$\frac{1}{\tau_{d1}} = \frac{1}{\tau_{2A}} + \frac{1}{\tau_{2E}} + e_{E2} \left(\frac{\tau_{2A}}{\tau_{2A} + \tau_{2E}}\right), \tag{62}$$

$$\frac{1}{\tau_{d2}} = e_{E2} \left(\frac{\tau_{2E}}{\tau_{2A} + \tau_{2E}}\right) + \frac{1}{\tau_{EA}}. \tag{63}$$

Assuming $\tau_{2E} \approx \tau_{2A}$ we come to the inequality $n_2^{(0)} \approx n_E^{(0)}$. Neglecting in Eq. (61) terms proportional to $n_2^{(0)}$ compared to those proportional to $n_E^{(0)}$ one obtains

$$n_2(t) \approx \frac{e_{E2} n_E^{(0)}}{\left(\frac{1}{\tau_{d1}} - \frac{1}{\tau_{d2}}\right)} \left[\exp\left(-\frac{(t-t_0)}{\tau_{d1}}\right) - \exp\left(-\frac{(t-t_0)}{\tau_{d2}}\right)\right]. \tag{64}$$

For $\tau_{d1} < \tau_{d2}$, Eq. (64) shows $n_2$ to vary nonmonotonically with time, namely, after the removal of illumination $n_2$ exhibits a growth followed by an exponential decay. Figures 26 and 27 compare the evolution of carrier concentration in the conduction band, which determines the photoresponse kinetics and was calculated using Eq. (61), with experiment. The times $\tau_{d1}$ and $\tau_{d2}$ were taken as fitting parameters. Since these times differ by at least two orders of magnitude, one actually used only one fitting parameter in each time interval. The dynamic times determined in this way are: $1/\tau_{d1} = 10^7$ s$^{-1}$ and $1/\tau_{d2} = 1.6 \times 10^6$ s$^{-1}$, 1.44 $\times 10^5$ s$^{-1}$ (for $\Delta e_{2E} = 28$ meV). Figure 28 presents calculated $\tau_{d2}$ times (solid line) to be compared with the experimentally determined slow decay time as a function of temperature. The results of a numerical calculation are seen to be in good agreement with experiment.

It can be shown that, within the temperature interval under consideration, the last term in Eq. (62) is much smaller than the sum of the first two terms, $1/\tau_{2A} + 1/\tau_{2E}$. Neglecting it in Eq. (62), we find from the experimentally measured dynamic times and the temperature dependence of $\tau_{d2}$ the three characteristic times introduced earlier: $\tau_{2E} = 10^{-7}$ s,
These values accord with the condition \( \tau_{2A} < \tau_{2A} \leq \tau_{EA} \) used in the calculation.

Thus investigation of the kinetics of FIR–SBM-induced photoconductivity in GaP:Te permitted observation of the buildup of electrons in the excited state of a shallow donor level in times up to a few milliseconds, and its identification as a valley-orbit split \( 1\varepsilon(E) \) state. Electrons are promoted from this state by thermal excitation into the higher-lying \( \psi \) and \( \varphi \) states, with subsequent relaxation to the ground state occurring primarily by radiative transitions. The existence of radiative transitions was established here through observation of infrared luminescence.\(^{127}\)

6. CONCLUSIONS

Photoionization of deep impurity centers in semiconductors stimulated by high-intensity submillimeter laser radiation having photon energies much smaller than the impurity ionization energy has been discovered and studied within a broad range of intensities, wavelengths, and temperatures, and for a variety of impurities. A comprehensive comparison of experimental data with the theory of multiphonon-assisted and direct deep-impurity ionization in an electric field has shown that terahertz radiation acts frequently like a dc field.

Within a broad electric-field range, the carrier emission probability can be described in terms of multiphonon-assisted tunneling. Thermally activated emission of carriers from the ground state to continuum is usually accompanied by thermal excitation of the system followed by tunneling of the defect from the configuration corresponding to a bound electron state to that of an ionized impurity. Electric field enhances defect tunneling by the electrons tunneling through the barrier produced by the electronic potential and the electric field. This enhancement of carrier emission was detected from the photoconductive signal. The field dependence of the photoconductive signal is well approximated by a simple expression

\[
\frac{\Delta \sigma}{\sigma} = \frac{1}{\mu} \left. \frac{\partial \mu}{\partial T_e} \right|_{T_e=T_0} \Delta T_e, \quad (A2)
\]

where \( T_0 \) is the lattice temperature.

We readily see that the sign of the photoconductive signal is determined by that of the derivative \( \partial \mu / \partial T_e \). It is well known that this sign can be positive (for instance, if scattering from charged impurities is dominant) or negative (in the case where scattering occurs predominantly from acoustical phonons, optical phonons, etc.).\(^{141,143}\)

The main experiments of deep-impurity ionization were performed using germanium samples. To reveal the role heating processes play in the submillimeter-range photoconductivity observed in samples having deep impurities, a study was carried out of the electron gas heating in Ge doped with shallow impurities (Ga, Sb) at close to liquid-nitrogen temperature, where the impurities are ionized, i.e. under the conditions most favorable for the heating. The concentrations were chosen close to those of deep impurities in the samples considered in this work.

Free-carrier heating in Ge in the temperature interval of interest results in negative photoconductivity, since the major part here is played by scattering by acoustic phonons, which brings about a decrease of the mobility with increasing electron-gas temperature. The kinetics of the photoconductivity caused by the free-carrier heating is dominated by

\[ \tau_{2A} = 5 \times 10^{-7} \text{ s}, \quad \tau_{EA} = 0.7 \times 10^{-2} \text{ s}. \]
the short times of the free-carrier energy relaxation, which lie usually in the range $10^{-9} - 10^{-13}$ s. Accordingly, the signals generated by electron heating either repeat the radiation pulse in shape or exhibit a more complex behavior in time, but do not exceed in duration the nanosecond-range excitation pulses.

Thus observation of positive photoconductivity in samples containing less than $5 \times 10^{14}$ cm$^{-3}$ deep impurities at $T \approx 77$ K during times longer than the radiation pulse duration exclude electron gas heating as a possible cause of the photoresponse. This is accounted for by the suppression of heating in samples doped primarily by deep impurities and maintained at sufficiently low temperatures by carrier freeze-out at the impurity and, hence, a practically complete absence of absorption.

Note that the free-carrier concentration in Al$_x$Ga$_{1-x}$Sb and Al$_x$Ga$_{1-x}$As samples in which DX centers were studied was high enough for the heating effects to provide a substantial contribution to photoresponse. The strong difference between the relaxation times of the heating-induced photoconductivity and of the photoconductivity due to the ionization of the DX centers permitted, however, easy separation of these contributions.

In the conditions of strong nonlinear carrier heating by high-intensity radiation one can observe also photoionization of deep impurities with light of $h \Omega < \varepsilon_T$ in the course of light-induced impact ionization, first discovered in InSb.\textsuperscript{34} In this case one detects, in addition to the prevailing fast $\mu$ photoresponse signals, positive photoconductivity, whose kinetics are dominated by the nonequilibrium-carrier lifetime. Since the carriers are heated here by the high-frequency field, the probability of the light-induced impact ionization falls off exponentially with increasing radiation frequency. The opposite frequency-dependence patterns of behavior exhibited by tunneling (multiphoton) and impact ionization permit one to identify the processes. Thus the absence of the fast negative component of $\mu$ photoconductivity in the positive photoresponse signal observed under high-intensity FIR illumination in samples having deep impurities, as well as the independence of probability on wavelength, or its decrease with the latter, gives us grounds for an unambiguous exclusion of light-induced impact ionization from among the processes which could be responsible for the deep-impurity ionization discussed in the present work.

In conclusion, consider the possible effect of lattice heating. Similarly to the case of electron gas heating, heating of the lattice by radiation should affect the conductivity. In this case, the sign of the photoconductivity is determined by both the variation of mobility (the carriers are ionized) and an increase of carrier concentration in the band (the carriers are frozen out at the impurity). The kinetics of photoconductivity are dominated in this case by the slow cooling of the sample as a whole (on a time scale substantially longer than microseconds). Observation in samples containing deep impurities of signals with characteristic times of the order of a few microseconds and shorter gives one grounds to exclude the heating of the sample as a whole as the cause of the photoresponse. We also note that no lattice heating effects were observed in the bulk semiconductors illuminated by short (100 ns) radiation pulses having energies not in excess of a mJ, even at high free-carrier concentrations (see, for instance, Refs. 39–41, 43, 114).

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