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Two-photon spectroscopy of shallow donor states in semiconductors

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We analyze the possibility of observing parity-forbidden transitions of shallow-donor electrons by means of a two-photon absorption. We consider two energy levels of an impurity, coupled by a two-photon transition and interacting with the crystal. To describe the dynamics of the system, we introduce the master equation for the reduced density matrix. In this equation, the two-photon interaction is computed with the help of the Coulomb-Green's function, while the interaction with the crystal is phenomenologically taken into account by appropriate damping constants. The numerical calculations for GaAs and CdTe show that the observation of two-photon absorption by shallow donors in semiconductors seems to lie within the present experimental possibilities of the photothermal ionization technique.

I. INTRODUCTION

Recent spectroscopic studies of the shallow impurities in semiconductors are usually performed with the help of the photothermal excitation of photoconductivity. In this method, introduced by Lifshits and Nad',[1] an electron is raised from the ground state to an excited state of an impurity by photon absorption. Then it can either fall back to the ground state or be thermally released into the conduction band, and thus the photon absorption between bound states of an impurity can manifest itself as a change in the conductivity. Transitions originating on both the ground and the excited states have been observed,[2,3] the chemical shifts of various donors have been measured,[4,5] and lines arising from the mutual interaction of impurity electrons have been reported.[6]

Investigation of the Zeeman splitting of impurity states in a magnetic field, combined with, e.g., far-infrared cyclotron resonance measurement of the appropriate band-edge effective mass, gives probably the most accurate values of the impurity Rydberg as well as the static dielectric constant of the host crystal. In this way Stillman *et al.*[7] precisely verified the effective-mass theory for shallow donors in GaAs.

Similar experiments performed by Simmonds *et al.*[3,5] and Skolnick *et al.*[8] for CdTe revealed that in this case both the effective Rydberg and static dielectric constant can be considerably affected by the so-called polaron effects. In a polar crystal, like CdTe, due to continuous emission and reabsorption of virtual optical phonons by a donor electron, its energy spectrum is considerably modified relative to that of a purely hydrogenic one. The problem of an electron bound in a Coulomb potential and weakly interacting with optical phonons has not been solved exactly. The various theoretical treatments disagree markedly on the magnitude of the polaron corrections to the impurity energies calculated on the effective-mass approximation.[9]

In this paper we wish to propose an experiment which should give useful information on the problem of the magnitude of polaron corrections. Our theoretical analysis shows that the photothermal-ionization technique should allow one to observe, by means of a two-photon excitation of impurity electrons, parity-forbidden transitions to s and d states. It seems that investigation of the $1s$-$2s$, $1s$-$3s$, and $1s$-$3d$ transitions will allow the measurement of the phonon-induced "Lamb shift" of the $n=2$ and $n=3$ energy levels, and thus the polaron contribution to the hydrogenlike impurity energy levels. Bassani *et al.*[10] have recently made a remark that observation of such two-photon transitions can provide a useful source of information about shallow-impurity states in semiconductors.

The weak lines corresponding to the parity-forbidden impurity transitions have been observed on certain occasions by means of conventional one-photon spectroscopy. Such transitions were identified for the first time for shallow donors in silicon by Kleiner and Krag.[11] Violation of electric-dipole selection rules was attributed to the effects of polarization of the donor by other charged defects and to the breakdown of the effective-mass approximation. The electric fields of randomly distributed ionized impurities are also believed to be responsible for the appearance of the $1s$-$2s$ photoconductivity line in GaAs.[2] Recently, the $1s$-$2s$ transition has also been identified in CdTe.[8] Unfortunately, for a hydrogenic donor this transition can be distinguished from the $1s$-$2p$ line only in an external magnetic field, whereas the influence of a magnetic field on the polaron effects remains as yet unknown.

Semiconductors, like CdS, in which the LO phonon energy is of the same order as the effective Rydberg, are infrared active. In these materials donors and acceptors have to be studied by means of visible spectroscopy, e.g., by the so-called two-electron transitions in which an exciton bound to a neutral donor decays, leaving the donor in an excited state.[12] Rossi *et al.*[13] have observed, in this way, transitions involving the 2*s* state of a hydrogenic donor. It seems that the two-photon infrared spectroscopy proposed in this work can offer another approach to study of impurities in these materials.

As will be shown, investigation of the parity-forbidden transitions can also give some information about the various decay rates of the otherwise inaccessible states.

II. MASTER EQUATION AND TRANSITION PROBABILITY

We consider an uncompensated *n*-type semiconductor with N_D donors per unit volume. To avoid complications due to the multilevel character of the donor spectrum, we introduce the following approximate model: We take into account two energy levels coupled by the two-photon transition and interacting with the remaining part of the crystal. Thus, we can treat the latter as a heat reservoir and describe the system by means of the reduced density matrix ρ. This matrix gives the dynamics of the two-level subsystem, whereas the presence of the heat reservoir is manifested by the appropriate damping constants appearing in ρ.

All interesting physical quantities can be expressed in terms of ρ. In particular, one can easily find the increase of the conduction-band electron concentration N_B due to an incoherent two-step process, namely, the two-photon excitation of a donor followed by the thermoionization of an excited state. In our approach, neglecting possible population of the remaining bound donor states, it is given by the following formula:

$$N_B = N_D(1 - \mathrm{Tr}\rho) \ . \tag{1}$$

Due to the random electric fields of ionized impurities and other charged defects in the crystal, the energy levels of neutral impurities are spread out in energy and the impurity lines are inhomogeneously broadened.[14] Thus, to excite as many neutral donors as possible one should use a laser with large spectral width, much larger than the width of the investigated impurity level. The whole formalism used below is applicable only to the case of a broad line excitation.

Denoting the ground and excited states of an impurity electron by $|g\rangle$ and $|e\rangle$, respectively, we can introduce the 2×2 reduced-density matrix ρ. Its diagonal elements ρ_{ee} and ρ_{gg} satisfy the following master equation (see Appendix for a derivation):

$$\begin{aligned}\dot{\rho}_{ee} &= -\Gamma_1\rho_{ee} - \Gamma_2\rho_{ee} + \Gamma_3(1-\rho_{ee}-\rho_{gg}) \\ &\quad + (\rho_{gg}-\rho_{ee})/T_I \ , \\ \dot{\rho}_{gg} &= \Gamma_1\rho_{ee} + \Gamma_4(1-\rho_{ee}-\rho_{gg}) - (\rho_{gg}-\rho_{ee})/T_I \ .\end{aligned} \tag{2}$$

Γ_1 is the rate of spontaneous emission from the excited state to the ground state, Γ_2 is the excited-state thermoionization rate, Γ_3 is the conduction-band-to-excited-state recombination rate, and Γ_4 is the conduction-band-to-the ground-state recombination rate. Thus, Γ_2, Γ_3, and Γ_4 express the interaction of our two-level subsystem with the heat reservoir. T_I is the pumping time, and terms proportional to $1/T_I$ describe the interaction with the light beam. The stationary solution of Eq. (2), together with the formula in Eq. (1), gives the following expression for the concentration N_B of thermoionized electrons:

$$N_B = N_D \frac{1}{T_I}\frac{\Gamma_2}{\Gamma_1(\Gamma_3+\Gamma_4)+\Gamma_2\Gamma_4} \ . \tag{3}$$

The physical meaning of the pumping time is the following: in the absence of damping (i.e., interaction with the remaining part of the crystal) it is the inverse of the ground-state-to-excited-state transition rate. In the case of two-photon transitions T_I is given by the formula (derived in the Appendix)

$$1/T_I = 2(2\pi/\hbar^2\Delta)\,|\langle\psi_e|H_I(E-H_0)^{-1}H_I|\psi_g\rangle|^2 \ , \tag{4}$$

where Δ is the laser line spectral width, assumed to be much larger than the natural width of the excited state. H_0 is the effective-mass Hamiltonian of a donor electron, Ψ's are its eigenfunctions, and H_I is the Hamiltonian of electron-photon interaction (in the dipole approximation)

$$H_I = e\vec{\mathrm{r}}\cdot\vec{\mathcal{E}}(t) \ ,$$

where $\vec{\mathcal{E}}(t)$ is the electric vector of radiation.

For hydrogenic donors, H_0 is the hydrogenlike effective-mass Hamiltonian, and one can compute the matrix element appearing in Eq. (4) with the help of the Coulomb Green's function

$$|\langle\psi_e|H_I(E-H_0)^{-1}H_I|\psi_g\rangle|^2 = \left| e^2\mathcal{E}^2 \int \psi_e^*(\vec{\mathrm{r}})\vec{\mathrm{r}}\cdot\vec{\mathrm{e}}G(\vec{\mathrm{r}},\vec{\mathrm{r}},'E)\vec{\mathrm{r}}'\cdot\vec{\mathrm{e}}'\psi_g(\vec{\mathrm{r}}')\,d\vec{\mathrm{r}}\,d^3\vec{\mathrm{r}}'\right|^2 ,$$

where $\vec{e}$ and $\vec{e}\,'$ are photon polarization vectors.

$$G(\vec{r},\vec{r}\,',E)=\sum_n \frac{\psi_n(\vec{r})\psi_n^*(\vec{r}\,')}{E_n-E}$$

is the Green's function of the Schrödinger equation for a hydrogen atom.[15] Integrations which appear in the above formula can be performed with the method given by Zon *et al.*[16] Since the calculations are rather extensive, we shall only quote the final result:

$$|\langle\psi_e|H_I(E-H_0)^{-1}H_I|\psi_g\rangle|^2=16\pi^2\alpha^2m^2a^8I^2A_e/\epsilon\hbar^2\ , \tag{5}$$

where m is the conduction-band effective mass, a is the effective Bohr radius, and α is the fine-structure constant. I is the radiation intensity, and ϵ is the dielectric constant at radiation frequency, which we approximate by the static dielectric constant of the host crystal. A_e is a rather complicated dimensionless numerical factor depending on the final state of the two-photon transition—the initial state is, in our case, the ground state—and on the photon polarization. Its numerical values are $A_{2s}=61.68$, $A_{3s}=3.65$, $A_{3d}^{l}=34.61$, and $A_{3d}^{c}=51.91$.[17] The superscripts l and c denote the linear and circular light polarization, respectively.

Thus, from Eqs. (4) and (5) we obtain for the pumping time T_I the formula

$$T_I^{-1}=64\pi^3(\hbar c)^{-2}a^6\epsilon I^2A_e/\Delta\,. \tag{6}$$

Finally, Eqs. (3) and (6) give the following expression for the concentration of thermoionized electrons

$$N_B=N_D 64\pi^3(\hbar c)^{-2}a^6\epsilon(I^2A_e/\Delta)\times\Gamma_2[\Gamma_1(\Gamma_3+\Gamma_4)+\Gamma_2\,\Gamma_4]^{-1}. \tag{7}$$

III. NUMERICAL RESULTS AND DISCUSSION

Numerical calculations have been performed for two typical direct band-gap III-V and II-VI compounds, GaAs and CdTe. In both materials the hydrogenlike effective-mass approximation for shallow-donor electrons is valid. Table I gives the values of material parameters used.

TABLE I. Material parameters.

	Ry (cm^{-1})	a (Å)	ϵ
GaAs	46.1[a]	100	12.56[a]
CdTe	106[b]	55	9.9[b]

[a] Reference 7.
[b] Reference 3.

It is evident from Eq. (7) that in order to compute the concentration of thermoionized electrons it is necessary to know the values of damping constants Γ_1, Γ_2, Γ_3, and Γ_4 appearing in Eqs. (2) and (7). Unfortunately, even for so intensively studied a material as GaAs, only one of them has been measured as yet. Due to the fact that both the carrier recombination with ionized impurities and the thermal ionization of impurity levels lack a satisfactory theoretical description, one can only attempt to estimate these values. Thus, we are looking here for reasonable but the most unfavorable values of damping constants, i.e., a lower bound for Γ_2 and an upper bound for the others.

Ulbrich[18] has recently studied the capture of thermalized electrons into shallow donors in GaAs. Using the time-resolved spectroscopy of donor-related luminescence he estimated the rate at which electrons enter the donor ground state: $\Gamma_4 \cong 5\times10^8$ sec^{-1}, over the temperature range of experiment (1.9–10 K). Ulbrich's results, as well as earlier observations of Norton *et al.*[19] for silicon, are in significant quantitative disagreement with the existing theories of electron capture.[20,21] The present authors made an attempt to improve the model, which considers initial capture of an electron into one of the excited s states followed by a cascade of one-phonon transitions to either the impurity ground state or back to the conduction band, taking into account two-phonon transitions.[22] However, these calculations were performed for the direct "continuum → 1s donor state" transition so far, and thus, they are not useful in the present case where we are looking for the "continuum → excited donor state" and "excited state → ground state" recombination rates (Γ_3 and Γ_1). Thus, we have assumed Γ_3 to be equal to Γ_4, whereas Γ_1 has been estimated by the rate of transition accompanied by emission of one LA phonon, computed in the deformation potential approximation. For the 2s → 1s transition in GaAs its numerical value is $\Gamma_1=1.6\times10^6$ sec^{-1}.[18]

The thermal-ionization probability of electrons from the 2p excited states of GaAs has been shown, by Stillman and co-workers,[23] to be about unity for temperatures greater than 3 K. For temperatures below about 2 K, the thermal-ionization probability decreases exponentially with decreasing temperature. Thus, at temperature $T\cong3$ K an electron in the 2p excited state has equal chance to be released into the conduction band or to go back to the donor ground state. Therefore, assuming that the electron relaxes its energy by photon emission,[24] we can estimate the 2p excited-state thermoionization rate at $T\cong3$ K by the photon-assisted 2p → 1s transition rate,[25]

$$\Gamma^{\mathrm{ph}}_{2p\to 1s} = 2^9\alpha^2\epsilon_\infty^{3/2}/3^8\epsilon\ \mathrm{Ry}\ . \tag{8}$$

Since the experimental results of Stillman *et al.*[2] suggest that the thermal-ionization probability of an electron in the $2s$ state is considerably greater than for an electron in the $2p$ state, we expect that $\Gamma^{\mathrm{ph}}_{2p\to 1s}$ provides a reasonable lower bound for Γ_2 at $T \cong 3$ K. Thus, for the excited $2s$ state in GaAs we assume, from Eq. (8), $\Gamma_2 \cong 6.2\times 10^4$ sec^{-1}, where the high-frequency dielectric constant $\epsilon_\infty = 11.1$ as given by Marshall and Mitra,[26] has been used. One can expect that Γ_2 increases with increasing temperature.

Finally, we can estimate the conduction-band concentration N_B of photoexcited electrons. For the two-photon excitation of the $2s$ donor state in GaAs we obtain, from Eq. (7), the formula

$$N_B = N_D 1.9\times 10^{-4} I^2\ ,$$

where I is the total power (in W/cm^2) of the laser-radiation line of peak frequency $1/\lambda = \frac{3}{8}$ Ry $= 17.3$ cm^{-1} and width $\Delta = 0.2$ cm^{-1}. Thus, in a sample with $N_D = 10^{15}$ cm^{-3}, a laser line of power 1 W/cm^2 can excite about 2×10^{11} cm^{-3} electrons into the conduction band. At $T = 3$ K that number exceeds by a few orders of magnitude the concentration of thermal electrons, and seems to be detectable in the dc conductivity.[27]

For other excited states, $3s$ and $3d$, the values of Γ_1, Γ_3, and Γ_4 should be, roughly speaking, of the same order as for the $2s$ state, while the thermoionization rate Γ_2 seems to be much higher. Thus, the corresponding two-photon transitions should be much easier to observe.

As far as we know, for CdTe none of the transition rates have been measured as yet. Thus, in order to estimate N_B we put in Eq. (7) $\Gamma_3 = \Gamma_4 = 10^9$ sec^{-1} and approximate Γ_1 by the $2s\to 1s$ one-phonon transition rate, $\Gamma_1 \cong 8\times 10^5$ sec^{-1}.[28]

Just as for GaAs, we have estimated Γ_2 for the $2s$ state by the $2p$ state thermoionization rate. To obtain the latter we have referred to an earlier paper[25] where we computed the probability of the $2p$-state thermal ionization by LO-phonon absorption. Thus, with the help of Eq. (3) of Ref. 25, we get $\Gamma_2 = 7.2\times 10^{16}\times e^{-\hbar\omega_{\mathrm{LO}}/kT}$, where the LO phonon angular frequency, $\omega_{\mathrm{LO}} = 31.9$ THz.[29]

Therefore, we estimate from Eq. (7) that the two-photon excitation of the $2s$ state with the laser beam of frequency $1/\lambda = \frac{3}{8}$ Ry $= 39.75$ cm^{-1}, linewidth $\Delta = 0.5$ cm^{-1}, and a total power I W/cm^2 gives

$$N_B = N_D 1.9\times 10^{-5} I^2$$

and

$$N_B = N_D 3.6\times 10^{-5} I^2$$

of conduction electrons at $T = 10$ and 15 K, respectively. At 10 K, N_B is equal to the concentration of thermal electrons for radiation power of about 100 mW/cm^2. As in the case of GaAs, much higher values of Γ_2 and roughly the same values of Γ_1, Γ_3, and Γ_4 are expected for the $n = 3$ states compared to the $2s$ state. This should allow one to observe these transitions at lower radiation intensities. At this point, we wish to remark that for $n = 3$ and higher states our model of thermoionization as due to LO-phonon absorption[25] breaks down since multi-LA-phonon processes probably dominate.

IV. CONCLUSIONS

We conclude that the observation of two-photon absorption by shallow donors in semiconductors should be possible using the photothermal-ionization technique. It is known that an external static magnetic field, or uniaxial stress, splits and shifts hydrogenlike impurity energy levels.[30] One can expect that, at least in the low-field region, the damping constants appearing in Eqs. (2), (3), and (7) do not change drastically when a magnetic field is applied, while the separation of the energy levels can, to a certain extent, be adjusted to the frequency of laser radiation. We expect that the two-photon spectroscopy proposed here should provide a useful tool for the investigation of shallow donors in semiconductors.

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APPENDIX

In this appendix we shall sketch briefly how the master equation (2) and the expression (4) for the pumping time T_I can be derived by a simple generalization of the usual one-photon approach.[31]

We assume that the two-photon process is described by the effective Hamiltonian H_I^{eff} as given by Happer[32]:

$$\langle f|H_I^{\mathrm{eff}}|i\rangle = \langle \psi_f(\vec{r})|\, e\vec{\mathcal{E}}\cdot\vec{r}\, G(\vec{r},\vec{r}\,',E_i+\hbar\omega)\, e\vec{\mathcal{E}}\cdot\vec{r}\,'\,|\psi_i(\vec{r}\,')\rangle,$$

where $\vec{\mathcal{E}}$ is the electric field of angular frequency ω, E_i is the initial-state energy, and the remaining symbols have their usual meaning. For our system, consisting of two levels $|e\rangle$ and $|g\rangle$, the above Hamiltonian is a 2×2 matrix. The diagonal elements of this matrix give rise to energy shifts of $|e\rangle$ and $|g\rangle$ states. However, the shifts are negligible in comparison to the inhomogeneous linewidths, and can be neglected.

Our system is described by the density matrix ρ satisfying the equation of motion $i\hbar\dot{\rho}=[\rho,H]$, where $H=H_0+H_I^{\mathrm{eff}}+H_{\mathrm{rad}}$, H_0 being the effective-mass Hamiltonian of donor electrons, and H_{rad} is the free-field Hamiltonian. From this equation of motion we shall derive the master equation, assuming that the spectral width Δ of the laser beam is much larger than the width of the inhomogeneously broadened impurity level.

Let Δt be much shorter than the time T_p, characterizing the evolution of ρ, and being simultaneously much longer than the coherence time of the laser beam, $1/\Delta$

$$T_p \gg \Delta t \gg 1/\Delta .$$

We shall calculate the coarse-grained rate of variation of ρ, $\rho(t+\Delta t)-\rho(t)$. Since Δt is small, the latter can be calculated by perturbation theory, and in the interaction representation one obtains

$$\rho(t+\Delta t)-\rho(t)=\frac{1}{i\hbar}\int_t^{t+\Delta t} dt'[H_I^{\mathrm{eff}}(t'),\rho(t)]-\frac{1}{\hbar^2}\int_t^{t+\Delta t} dt' \int_t^{t'} dt''[H_I^{\mathrm{eff}}(t'),[H_I^{\mathrm{eff}}(t''),\rho(t)]]. \qquad \text{(A1)}$$

Dealing with the broad-line excitation we have to compute the mean value of ρ over the electric field of the radiation. In Eq. (A1), $H_I^{\mathrm{eff}}(t'')$ and $\rho(t)$ are correlated only within the time of the order of $1/\Delta$ Therefore, in the integration over a time interval much larger than $1/\Delta$, factorization of the mean values introduces only a negligible error. Thus, we approximate $\langle H_I^{\mathrm{eff}}(t')\rho(t)\rangle$ by $\langle H_I^{\mathrm{eff}}(t')\rangle\langle\rho(t)\rangle$, and $\langle H_I^{\mathrm{eff}}(t')H_I^{\mathrm{eff}}(t'')\rho(t)\rangle$ by $\langle H_I^{\mathrm{eff}}(t')H_I^{\mathrm{eff}}(t'')\rangle\langle\rho(t)\rangle$. Making the usual assumption that the laser beam consists of many statistically independent modes, we obtain that the first term on the right-hand side of Eq. (A1) vanishes while the second one gives a linear combination, with real coefficients, of the diagonal elements of ρ. Denoting these coefficients by the inverse of the pumping time T_I, one obtains the formula (4), and the radiation-dependent part of the master equation (2). The other terms in Eq. (2) are introduced phenomenologically and their origin is intuitively clear.

In the above considerations we have assumed that the laser radiation modes are statistically independent. If they are not, a factor of 2 appearing in Eq. (4) has to be replaced by a numerical factor of value between 1 and 2.

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