Time-delayed four-wave mixing in a localized state + band system

M. N. Belov and É. A. Manykin

I. V. Kurchatov Institute of Atomic Energy

(Submitted 8 August 1991)
Zh. Eksp. Teor. Fiz. **101**, 344–351 (January 1992)

The conditions under which time-delayed four-wave mixing (photon echo effect) occurs in the local state + band quantum-mechanical system are determined. It is shown that if the bands are sufficiently narrow, a time-delayed pulse is observed, whose response time and temporal shape are different from those of the photon echo in completely localized systems. The possibility of using echo spectroscopy (É. A. Manykin and V. V. Samartsev, *Optical Echo Spectroscopy* [in Russian], Nauka, Moscow, 1984) to measure the characteristic width of narrow bands is discussed.

1. In the last ten years significant progress has been made in the technique of compression, amplification, and generation of optical pulses. In addition, it should be especially noted that this pertains not only to the visible region of the spectrum, but it also encompasses, in principle, a wavelength range of five orders of magnitude (from 10^3 to 10^{-2} μm). Picosecond pulses are now widely employed in experimental physics, and methods based on the use of femtosecond pulses are also appearing. As a result, research into coherent interactions, when the duration of the excitation pulses is shorter than the characteristic relaxation times of the medium, continues to grow steadily. The shortest pulse durations are observed for the condensed state of matter, especially in the case of electron–electron and electron–phonon interactions in solids.

In 1973 Manykin and Zakharov studied photon echoes in semiconductors and dielectrics for direct interband transitions.[2] However, investigations of this type could not be performed with the experimental technique existing at that time. A number of experimental and theoretical papers on the coherent interactions of ultrashort pulses with semiconductors in the picosecond and subpicosecond ranges have by now been published.[3-14] Modern experimental techniques employing femtosecond pulses are significantly extending the possibilities of using coherent time-delayed four-wave mixing (photon echo) for the investigation of fast relaxational processes in matter. This is confirmed by a recent experiment in which the characteristic relaxation times in a GaAs film, where the time-delayed response was the result of coherent interband transitions induced by an external field, were measured.[15] Time-delayed four-wave mixing in delocalized systems was also studied in the recently published of theoretical Refs. 16 and 17.

It is timely in view of the above to examine the problem of time-delayed four-wave mixing with coherent excitation of electrons from localized centers into a band. It turns out that in this case the echo effect is significantly modified and additional conditions must be satisfied in order for a time-delayed response to appear in the "localized state + band" quantum-mechanical system.

2. We choose the Hamiltonian describing the coherent interaction of light pulses with a semiconductor under conditions of resonant excitation of electrons from impurity centers into a band in the following form:

$$H=H_0+H_{int}, \tag{1}$$

where

$$H_0=\sum_j E_{0j}a_j^+a_j+\sum_{\mathbf{k}} E_1(\mathbf{k})a_{\mathbf{k}}^+a_{\mathbf{k}}, \tag{2a}$$

$$H_{int}=-\sum_j\sum_{\mathbf{k}}\mu_{\mathbf{k}j}E(\mathbf{R}_j,t)a_{\mathbf{k}}^+a_j+\mu_{\mathbf{k}j}^*E^*(\mathbf{R}_j,t)a_j^+a_{\mathbf{k}}, \tag{2b}$$

where a_j^+ (a_j) is the creation (annihilation) operator of an electron in the localized ground state, with a corresponding radius vector $\mathbf{R}_j$; $a_{\mathbf{k}}^+$ ($a_{\mathbf{k}}$) is the operator for creation (annihilation) of a band electron into a band in a state with wave vector $\mathbf{k}$; $\mu_{\mathbf{k}j}$ is the matrix element of the dipole moment operator; E_{0j} is the energy of an electron localized in the ground state near a site with the coordinate $\mathbf{R}_j$; $E_1(\mathbf{k})$ is the dispersion relation in the band. The intensity of the electric field of the optical wave is defined by the expression

$$E(\mathbf{r},t)=\mathscr{E}_1(t)\exp(-i\omega_0t+i\varkappa_1\mathbf{r})+\mathscr{E}_2(t-\tau)\exp(-i\omega_0t+i\varkappa_2\mathbf{r})+\mathscr{E}_3(t-T)\exp(-i\omega_0t+i\varkappa_3\mathbf{r})+\text{c.c.} \tag{3}$$

The expression (3) for the point $\mathbf{r}=\mathbf{R}_j$ was substituted here into Eq. (2b) and the following notation was employed: $\mathscr{E}_1$, $\mathscr{E}_2$ and $\mathscr{E}_3$ are the slowly varying amplitudes of three pulses separated in time; τ is the time delay between the first and second pulses and T is the time delay between the first and third pulses; $\varkappa_1$, $\varkappa_2$ and $\varkappa_3$ are the corresponding wave vectors; and, ω_0 is the frequency of the optical wave. The coordinate dependence of the amplitudes is omitted, since it is assumed that the conditions $\lambda\ll L\ll ct_p$ [where $\lambda=2\pi c/\omega_0$, L is the length of the specimen in the direction of propagation of the pulses, t_p is the pulse duration, and c is the velocity of light] are satisfied.

Choosing the external field in the form (3) makes it possible to study time-delayed four-wave mixing in the system localized state + band. For this it is necessary to determine how the following quantum-mechanical averages evolve in time:

$$n(\mathbf{k})=\langle a_{\mathbf{k}}^+a_{\mathbf{k}}\rangle, \tag{4a}$$

$$n_j=\langle a_j^+a_j\rangle, \tag{4b}$$

$$p_j^*(\mathbf{k})=\langle a_{\mathbf{k}}^+a_j\rangle, \tag{4c}$$

where the first two quantities (4a) and (4b) determine the populations of the $\mathbf{k}$th state in the band and the localized ground state, respectively, while Eq. (4c) makes it possible to calculate from the following expression the macroscopic polarization induced in the medium by the external field:

 0038-5646/92/010182-04$05.00

$$P(t)=\sum_{\mathbf{R}_j}\sum_{\mathbf{k}}\delta(\mathbf{r}-\mathbf{R}_j)\,\mu_{\mathbf{k}j}p_j^*(\mathbf{k})+\text{c.c.} \tag{5}$$

The temporal evolution of the obtained quantum-mechanical averages follows from Heisenberg's general equation of motion

$$i\hbar\frac{\partial}{\partial t}\langle A\rangle=\langle AH-HA\rangle, \tag{6}$$

where A is an arbitrary operator. Substituting into Eq. (6) the operators indicated above and using the Hamiltonian (1), we obtain

$$\frac{\partial}{\partial t}\rho_j^*(\mathbf{k})=-i\Delta_j(\mathbf{k})\rho_j^*(\mathbf{k})+2i\hbar^{-1}\mu_{\mathbf{k}j}^*\{\mathscr{E}_1^*(t)\exp(-i\varkappa_1\mathbf{R}_j)+\mathscr{E}_2^*(t-\tau)\exp(-i\varkappa_2\mathbf{R}_j)+\mathscr{E}_3^*(t-T)\exp(-i\varkappa_3\mathbf{R}_j)\}n_j(\mathbf{k}), \tag{7a}$$

$$\frac{\partial}{\partial t}n_j(\mathbf{k})=-\sum_{\mathbf{k}'}\sum_{j'}\{\delta_{\mathbf{k}\mathbf{k}'}+\delta_{jj'}\}\times 2\,\mathrm{Im}[\hbar^{-1}\mu_{\mathbf{k}'j'}\{\mathscr{E}_1(t)\exp(i\varkappa_1\mathbf{R}_{j'})+\mathscr{E}_2(t-\tau)\exp(i\varkappa_2\mathbf{R}_{j'})+\mathscr{E}_3(t-T)\exp(i\varkappa_3\mathbf{R}_{j'})\}\rho_{j'}^*(\mathbf{k}')], \tag{7b}$$

where $p_j^*(\mathbf{k})=\rho_j^*(\mathbf{k})\exp(i\omega_0 t)$, $n_j(\mathbf{k})=n(\mathbf{k})-\mathrm{n}_j$, $\Delta_j(\mathbf{k})=\omega_0-\hbar^{-1}[E_1(\mathbf{k})-E_{0j}]$.

Solving the system of equations of motion (7a) and (7b) with the help of perturbation theory in the external field, and substituting the solution into the expression for the macroscopic polarization (5), we can separate the nonlinear part that produces the response in the direction $\varkappa_3+\varkappa_2-\varkappa_1$, and it is precisely for this direction that a time delay should be expected. Thus we obtain

$$P^{(3)}(t)=P_1^{(3)}(t)+P_2^{(3)}(t). \tag{8}$$

where

$$P_1^{(3)}(t)=K\exp[-i\omega_0 t+i(\varkappa_3+\varkappa_2-\varkappa_1)\mathbf{r}]\int dE_{0j}\,g_{\mathrm{imp}}(E_{0j})\times\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\mathscr{E}_1^*(\Delta_j(\mathbf{k}'))\mathscr{E}_2(\Delta_j(\mathbf{k}'))\mathscr{E}_3(\Delta_j(\mathbf{k}))\times\exp[i\Delta_j(\mathbf{k})(t-T)]\times\exp[-i\Delta_j(\mathbf{k}')\tau]+\text{c.c.}, \tag{9a}$$

$$P_2^{(3)}(t)=K\exp(-i\omega_0 t+i\varkappa_3\mathbf{r})\times\int dE_{0j}g_{\mathrm{imp}}(E_{0j})\sum_{\mathbf{k}}\sum_{j'}\mathscr{E}_1^*(\Delta_{j'}(\mathbf{k}))\times\mathscr{E}_2(\Delta_{j'}(\mathbf{k}))\mathscr{E}_3(\Delta_j(\mathbf{k}))\exp[i(\varkappa_2-\varkappa_1)\mathbf{R}_{j'}]\exp[i\Delta_j(\mathbf{k})(t-T)]\times\exp[-i\Delta_{j'}(\mathbf{k})\tau]+\text{c.c.} \tag{9b}$$

Here $g_{\mathrm{imp}}(E_{0j})$ is the density of states, which characterizes the inhomogeneous broadening of the impurity level and is normalized to unity. This function arises when the summation over $\mathbf{R}_j$ is replaced by integration over the transition frequencies. Next, $\mathscr{E}_1(\Delta_j(\mathbf{k}))$, $\mathscr{E}_2(\Delta_j(\mathbf{k}))$ and $\mathscr{E}_3(\Delta_j(\mathbf{k}))$ are the spectral forms of the first, second, and third pulses, respectively. We neglected the $\mathbf{k}$ and j dependence in the matrix element of the dipole moment operator $\mu_{\mathbf{k}j}$. Here and below we designate by K the constant factor that is not important for the analysis. In addition, in deriving the expression (8) we assumed that the inequalities $\tau_p<\tau$ and $t_p<|T-\tau|$ are satisfied.

3. We shall now analyze the expression (8) derived above for nonlinear polarization. If $\varkappa_1\neq\varkappa_2$, which, as a rule, is realized in an experiment in order to be able to resolve spatially the echo response, then in view of the sum over the sites $\Sigma_{j'}\exp[i(\varkappa_2-\varkappa_1)R_{j'}]$ expression (9b) vanishes and does not contribute to the polarization (8). It is then obvious from Eq. (9a) that if the band is sufficiently narrow, the time-delayed four-wave mixing response exists and its temporal envelope is determined by the distribution function $g_{\mathrm{imp}}(E_{0j})$ as well as by the spectra of the excitation pulses. Thus, assume that when the summation is replaced by integration according to the rule

$$\sum_{\mathbf{k}}\to\int d\Delta_j g(\Delta_j) \tag{10}$$

the density of states in the band has a form close to a delta-function $g(\Delta_j)\propto\delta(\Delta_j-\Delta_0)$, where the peeled-off layer Δ_{0j} no longer depends on $\mathbf{k}$ and characterizes the inhomogeneous impurity broadening according to the distribution $g_{\mathrm{imp}}(E_{0j})$. Then Eq. (8) gives for the polarization of the echo response

$$P^{(3)}(t)=K\exp[-i\omega_0 t+i(\varkappa_3+\varkappa_2-\varkappa_1)\mathbf{r}]\times\int d\Delta_{0j}g_{\mathrm{imp}}(\Delta_{0j})\mathscr{E}_1^*(\Delta_{0j})\times\mathscr{E}_2(\Delta_{0j})\mathscr{E}_3(\Delta_{0j})\exp[i\Delta_{0j}(t-\tau-T)]+\text{c.c.} \tag{11}$$

This expression is a well-known result for the polarization of a photon echo. Thus, if the distribution function $g_{\mathrm{imp}}(\Delta_{0j})$ and the spectral shapes of the pulses in Eq. (11) are Gaussian exponentials with respective characteristic half-widths δ_{imp} and $2/t_p$, then Eq. (11) can be rewritten in the form

$$P^{(3)}(t)=K\exp[-i\omega_0 t+i(\varkappa_3+\varkappa_2-\varkappa_1)\mathbf{r}]\times\exp[-(t-T_e)^2/t_e^2)+\text{c.c.} \tag{12}$$

Here the following notation was employed for the maximum of the response (echo) and its duration:

$$T_e=T+\tau, \tag{13a}$$

$$t_e=2[3/(2/t_p)^2+1/\delta_{\mathrm{imp}}^2]^{1/2}. \tag{13b}$$

In the other limiting case, which occurs also for transitions from an impurity level into a band of the semiconductor, the density of states in the band varies slowly compared with the spectral shape of the pulses. Then the inhomogeneity of the impurity level can be neglected, $g_{\mathrm{imp}}(\Delta_{0j})$ can be replaced with a delta function, and the density of states in the band can be assumed to be approximately constant. Under the above assumptions the polarization (8) can be represented in the form

$$P^{(3)}(t)=K\exp[-i\omega_0 t+i(\varkappa_3+\varkappa_2-\varkappa_1)\mathbf{r}]\mathscr{E}_3(t-T)\times\int_{-\infty}^{+\infty}dt'\,\mathscr{E}_1^*(t')\mathscr{E}_2(t'-\tau)+\text{c.c.} \tag{14}$$

This result shows that in the case of a semiconductor a photon echo is not formed by excitation from an impurity center into a band. The maximum of the diffraction signal (14) is also the maximum of the third pulse and it decreases with increasing time delay τ. Thus a response with a peak at the moment $t=T+\tau$ does not arise.

4. In order to determine the conditions under which time-delayed four-wave mixing occurs in the localized state + band quantum-mechanical system we study a specific band whose density of states can also be approximated by a Gaussian exponential with characteristic half-width δ. Then the following expression can be derived for the polarization (8):

$$P^{(3)}(t)=K\exp[-i\omega_0 t+i(\varkappa_3+\varkappa_2-\varkappa_1)\mathbf{r}]\times\exp\left[-\frac{(t-T)^2+\gamma\tau^2}{t_p^2+(2/\delta)^2}\right]\exp\left[\frac{-(t-T_e)^2}{t_e^2}\right]+\text{c.c.}, \tag{15}$$

where

$$\gamma=\frac{1+\alpha}{1+2\alpha},\qquad \alpha=\left[\frac{\delta}{2/t_p}\right]^2.$$

In addition, the following notation was introduced:

$$T_e=T+\gamma\tau, \tag{16a}$$

$$t_e=2(1+\alpha)\left[\frac{1+2\gamma}{(2/t_p)^2+\delta^2}+\frac{1}{\delta_{\text{imp}}^2}\right]^{1/2}. \tag{16b}$$

In the limiting case of a narrow band, as $\delta\to 0(\alpha\to 0)$, the expressions (15), (16a), and (16b), as expected, converge to the previously obtained expressions for the polarization of the photon echo (12), (13a), and (13b). In the other limit $\delta\to\infty$ we obtain the instantaneous response after the third pulse in the form (14), into which the expression for the field in the form $\mathscr{E}(t)\propto\exp(-t^2/t_p^2)$ must be substituted, i.e., an echo-type effect does not occur for a wide band.

From Eqs. (15), (16a), and (16b) follows the condition under which time-delayed four-wave mixing occurs with transitions from an inhomogeneously broadened localized state into a band. It is obvious that the maxima of the exponentials in Eq. (15) occur at different times: The first exponential has a maximum at $t=T$ and the second at $t=T_e$. For this reason, we shall take the inequality

$$P^{(3)}(t=T_e)>P^{(3)}(t=T) \tag{17}$$

to be the criterion for the existence of an echo response, i.e., a time-delayed response. We obtain then from Eq. (15)

$$\beta<\frac{1-\alpha(1+4\alpha)}{(1+\alpha)(1+2\alpha)}, \tag{18}$$

where $\beta=(\delta/\delta_{\text{imp}})^2$. The range of values of the parameters α and β satisfying the requirement (18) is illustrated in Fig. 1 and it shows the ratios of the quantities δ, δ_{imp}, and $(2/t_p)$ for which an echo-type signal exists in the localized state + band system.

Thus, if the condition (18) is satisfied, a time-delayed four-wave mixing response can be observed and its maximum is determined by the expression

$$P^{(3)}(t=T_e)=K\exp\{-[\gamma(1+\gamma)\tau^2]/[t_p^2+(2/\delta)^2]\}, \tag{19}$$

It is obvious that even though there are no relaxational processes the amplitude of the echo response decreases with increasing time delay between the first and second excitation pulses. Thus, if the band is sufficiently narrow and the inequality $\alpha\ll 1$ is satisfied, then Eq. (19) assumes the form

$$P_e(t=T_e)=K\exp(-\tau^2\delta^2/2). \tag{20}$$

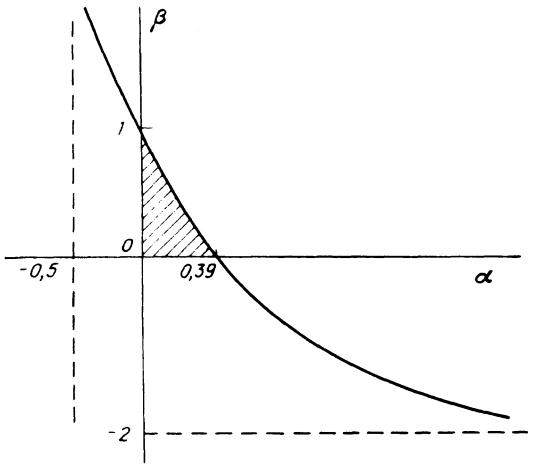

FIG. 1. The range of values of the parameters α and β (hatched region) for which a time-delayed response exists in the localized state + band system.

This means that in the case under study the time-delayed four-wave mixing permits measuring the characteristic width of the narrow band. We note that the traditional spectroscopy does not give the correct result, since the ground state is inhomogeneous ($\beta<1$ or even $\beta\ll 1$), which can result in significant broadening of the spectrum. If the characteristic width of the narrow band is $\delta\approx 10^{13}\ \text{s}^{-1}$ and for the inhomogeneous ground state $\delta_{\text{imp}}\approx 10^{14}\ \text{s}^{-1}$ (the case $\beta\ll 1$), then femtosecond pulses must be employed to satisfy the condition $\alpha\ll 1$. It follows then from Eq. (20) that by scanning the time delay between the first two pulses from $\tau=0$ up to $\tau\sim 10^{-13}$ s it is possible to obtain information about the value of δ (it is assumed that in the time scale under study relaxational processes can still be neglected).

It turns out that a time-delayed response should also exist in a system with a band for which a condition analogous to the inequality (18) is not satisfied but the density of states $g(\Delta)$ of the band has a singular point at which divergence is observed. In order to explain this effect we approximate $g(\Delta)$ by a function of the form

$$g(\Delta)=g_0(\Delta)+C\delta(\Delta-\Delta_0), \tag{21}$$

where $g_0(\Delta)$ is the density of states, for which $\alpha\gg 1$ and which has no singularities; C is a constant factor. After substituting Eq. (21) into the expression (8) for the polarization of four-wave mixing, where only the term (9a) is different from zero as before, we obtain two terms: The first is determined by the function $g_0(\Delta)$ and its form is analogous to Eq. (14) for the polarization for instantaneous response after the third pulse. The second term is identical to the expression (11) for the polarization of the photon echo. Thus in the case of a band whose density of states has a singular point there exists at the moment $t=T+\tau$ a response whose duration, as in the case of an extremely narrow band, is characterized solely by the distribution function of the inhomogeneous ground state and the spectral shape of the pulses, and an additional condition of the type (18) is not required.

5. In the analysis of the general expression for the nonlinear polarization (8) on the basis of the assumption that $\varkappa_1\neq\varkappa_2$ the term (9b), which includes the sum over sites

$\Sigma_{j'} \exp[i(\varkappa_2 - \varkappa_1)\mathbf{R}_{j'}]$, was omitted. If, however, $\varkappa_1 = \varkappa_2$, then this term remains, and in the case of a homogeneous localized state ($g_{\text{imp}}(E_{0j}) = \delta(E_{0j} - E_0)$) it makes a contribution of the following form to the polarization of the photon echo:

$$P_2^{(3)}(t) = K \exp(-i\omega_0 t + i\varkappa_3 \mathbf{r}) \times \sum_{\mathbf{k}} \mathscr{E}_1^*(\Delta_j(\mathbf{k}))\mathscr{E}_2(\Delta_j(\mathbf{k}))\mathscr{E}_3(\Delta_j(\mathbf{k})) \times \exp[i\Delta_j(\mathbf{k})(t - T - \tau)] + \text{c.c.} \quad (22)$$

This result means that in the case when the first two pulses are directionally degenerate ($\varkappa_1 = \varkappa_2$) the photon-echo effect, i.e., time-delayed response, exists in the system state + band localized even with a homogeneous ground state and a wide band, while the energy spectrum of the band plays the role of inhomogeneous broadening. Thus in the case of excitation from impurity centers into a semiconductor band it follows from Eq. (22) that

$$P^{(3)}(t) = K \exp(-i\omega_0 t + i\varkappa_3 \mathbf{r}) \exp[-(t - T_e)^2/t_e^2] + \text{c.c.}, \quad (23)$$

$$T_e = T + \tau, \quad (24a)$$

$$t_e = 3^{1/2} t_p, \quad (24b)$$

where it was assumed that the pulses are Gaussian with a corresponding spectral width $2/t_p$.

From Eq. (23) it is obvious that there exists a time-delayed response described by the term (9b) in the nonlinear polarization (8), while the term (9a) does not contribute to an echo effect in this case, since the condition (18) is not satisfied (a wide band and a homogeneous ground state is studied). It should be noted, however, that the requirement $\varkappa_1 = \varkappa_2$ makes it difficult to investigate the time-delayed four-wave mixing effect experimentally. In this case the response propagates in the direction of the third pulse and can be separated only in time. This is why this situation is not encountered in experiment. If, however, $\varkappa_1$ and $\varkappa_2$ are sufficiently different, so that the photon echo signal can be separated spatially from the excitation pulses, then the term (9b) does not occur in the polarization (8) and there is only the response determined by the relation (9a). Then, as shown above, a condition analogous to the inequality (18) must be satisfied in order for time-delayed four-wave mixing to exist in the localized state + band system.

In conclusion we note that the approach employed in this work is, in our opinion, the preferred approach, because it makes it possible to extend the problem of coherent interaction of light with the quantum-mechanical system localized center + band to the case when electron-electron and electron-phonon interactions are taken into account, which can be done by simply adding the corresponding terms to the starting Hamiltonian.

[1] É. A. Manykin and V. V. Samartsev, *Optical Echo Spectroscopy* [in Russian], Nauka, Moscow (1984).
[2] É. A. Manykin and S. M. Zakharov, Izv. Akad. Nauk SSSR, Ser. Fiz. **37**, 2171 (1973).
[3] A. Mysyrowiz, D. Hulin, A. Antonetti *et al.*, Phys. Rev. Lett. **56**, 2748 (1986).
[4] A. von Lehman, D. S. Chemla, J. E. Zucker, and J. P. Heritoege, Opt. Lett. **11**, 609 (1986).
[5] S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. **57**, 2752 (1986).
[6] M. Lindberg and S. W. Koch, Phys. Status Solidi B **150**, 379 (1988).
[7] B. Fluegel, N. Peyghambarian, G. Olbright *et al.*, Phys. Rev. Lett. **59**, 2588 (1987).
[8] S. W. Koch, M. Peyghambarian, and M. Lindberg, J. Phys. C **21**, 5229 (1988).
[9] E. O. Gobel, K. Leo, T. C. Damen *et al.*, Phys. Rev. Lett. **64**, 1801 (1990).
[10] M. Lindberg and S. W. Koch, Phys. Rev. B **38**, 3342 (1988).
[11] S. Schmitt-Rink, D. S. Chemla, and H. Haug, Phys. Rev. B **37**, 941 (1988).
[12] M. Lindberg and S. W. Koch, J. Opt. Soc. Am. B **5**, 139 (1988).
[13] L. W. Molenkamp and D. A. Wiersma, Phys. Rev. B **32**, 8108 (1985).
[14] L. Schultheis, M. D. Sturge, and T. Hegarty, Appl. Phys. Lett. **47**, 995 (1985).
[15] P. C. Becker, H. L. Fragnito, C. H. Brito Cruz *et al.*, Phys. Rev. Lett. **61**, 1647 (1988).
[16] M. N. Belov and E. A. Manykin, Preprint IAE-4826/10, Institute of Atomic Energy, Moscow (1989).
[17] D. Bennhardt, P. Thomas, A. Weller *et al.*, Phys. Rev. **43**, 8934 (1991).

Translated by M. E. Alferieff