ISSN 0965-545X, Polymer Science, Ser. A, 2013, Vol. 55, No. 12, pp. 778–783. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.P. Tyutnev, R.Sh. Ikhsanov, A.R. Tameev, V.S. Saenko, 2013, published in Vysokomolekulyarnye Soedineniya, Ser. A, 2013, Vol. 55, No. 12, pp. 1480–1485.

Bimolecular Recombination of Charge Carriers in Pure and Molecularly Doped Branched Polyphenylenevinylenes

A. P. Tyutnev[a,*], R. Sh. Ikhsanov[a], A. R. Tameev[b], and V. S. Saenko[a]

[a] *National Research University Higher School of Economics, 20 Myasnitskaya ul., Moscow 101000, Russia*
[b] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, korp. 4, Moscow, 119071 Russia*
**e-mail: aptyutnev@yandex.ru*

Received March 6, 2013;
Revised Manuscript Received May 6, 2013

Abstract—General problems of bimolecular recombination of charge carriers in both pure and molecularly doped branched polyphenylenevinylenes are addressed. Experiments are performed via the nonstationary radiation-induced conductivity method. Transient-current curves are numerically calculated in terms of the multiple-trapping model. Good agreement between the calculated and experimental curves is attained. In the investigated polymers, the Langevin mechanism of bimolecular recombination is active.

DOI: 10.1134/S0965545X1309006X

Poly(*p*-phenylenevinylene) (PPV) is the most typical representative of π-conjugated photoconducting polymer semiconductors with hole conductivity. Presently, poly(2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) is widely used owing to its excellent solubility, which allows thin films to be obtained through various methods [1]. It was shown that, in a polymer composite film, the phototransfer of an electron from a donor MEH-PPV molecule to an acceptor fullerene C_{60} molecule is very fast: The upper limit for the transfer time is 300 fs [2]. This circumstance is important for the development of photoactive layers for organic solar energy converters. In particular, a donor–acceptor composite and a photoactive layer, in which a bulk heterojunction enhancing the efficiency of the polymer photoconverter is formed, are prepared from MEH-PPV molecularly doped with the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) [3].

In this context, the study of transport of holes and their bimolecular recombination in MEH-PPV and MEH-PPV:PCBM is of great interest not only for practical use but also for fundamental science.

In [4, 5], a universal method was suggested to investigate both the transport of charge carriers and their recombination in molecularly doped polymers (MDPs) on the basis of an electron-beam gun with a tunable energy of accelerated electrons [4, 5]. In the framework of this approach, it is possible to eliminate the primary restriction of the optical method, which is conventionally applied to investigate both processes: the subsurface character of charge-carrier generation with the use of intrinsic photogeneration and injection of charges from a special generation layer.

In contrast to photoexcitation, the radiation-induced generation almost always proceeds in bulk, and the aforementioned difficulties are easily removed. In particular, a similar situation is observed during irradiation of thin films with electrons having an energy on the order of 50 keV. Note that the radiation-induced version of the time-of-flight method based on an electron gun with a tunable electron-beam energy resulted in considerable progress in the field of electronic transport in MDPs [4].

In the present study, the radiation-induced version of the time-of-flight method with the bulk irradiation is used to examine the transport of holes and the bimolecular recombination of charge carriers in MEH-PPV and MEH-PPV:PCBM.

DESCRIPTION OF THE PROBLEM

For the investigated polymers, hole transport was analyzed similarly to that in [6, 7]. For completeness of analysis, multiple-trapping models with Gaussian (MTM-g) and exponential (MTM-e) energy distributions of traps were considered. Model parameters were adjusted through fitting of experimental transient-current curves measured via the time-of-flight method during bulk irradiation of the polymers with 20-μs electron pulses in the small-signal regime.

The bimolecular recombination of charge carriers was analyzed with the use of known theoretical parameters. The following one-dimensional problem (uniform irradiation of a semi-infinite sample under a constant electric field) was solved numerically: The radiation dose rate was constant and corresponded to the generation rate of charge carriers, g_0 ($m^{-3}\,s^{-1}$); the

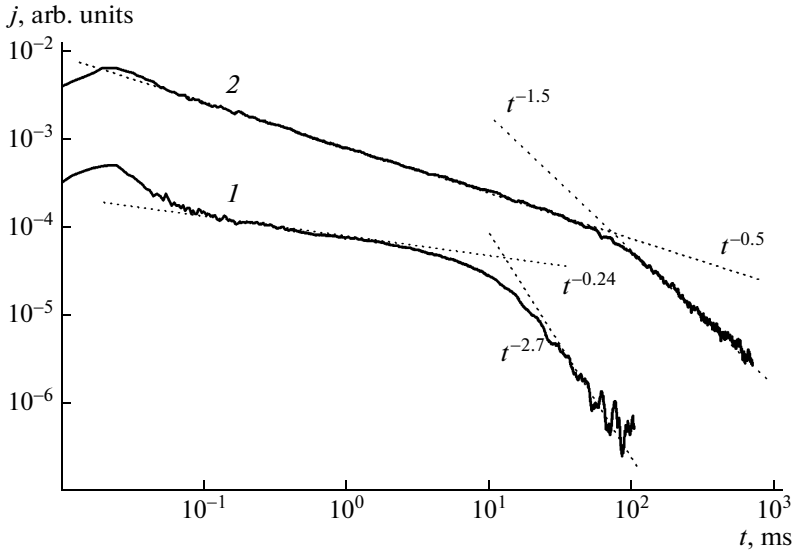

Fig. 1. Time-of-flight curves used to determine parameters of the multiple-trapping model: (*1*) MEH-PPV and (*2*) MEH-PPV:PCBM. The curves are deliberately shifted along the ordinate axis in order to better reveal their details; $RC = 4$ μs.

duration of a rectangular pulse, t_p; and the electric-field strength, F_0. The case of unipolar (hole) conductivity was addressed; electrons were regarded as immobile centers of recombination.

Naturally, the flight effects are absent, in accordance with the problem formulation (polymer-layer thickness $L \to \infty$). In this case, the system of equations is fully equivalent to that presented in the classical Rose–Fowler–Weisberg model [4] approved for investigation of the radiation-induced conductivity of ordinary polymers. In this approach, recombination rate $\Omega(t)$ is defined as

$$\Omega(t) = -k_r P_0(t) N(t). \quad (1)$$

Here, k_r is the rate constant (coefficient) of bimolecular recombination, $P_0(t)$ is the concentration of mobile holes, and $N(t)$ is the concentration of electrons at time t after the onset of irradiation. (Owing to quasi-neutrality, $N = P$, where P is the total concentration of holes.)

As is known, the Langevin recombination mechanism (diffusion–drifting) is described by the relationship

$$k_{rL} = \frac{e}{\varepsilon\varepsilon_0}\mu_0, \quad (2)$$

where e is the elementary electrical charge, ε is the relative dielectric permeability of the material, ε_0 is the dielectric constant, and μ_0 is the mobility of quasi-free holes accepted in the model.

The transient-current curves were calculated for several g_0 values in multiples of 10 covering the range of values for which the recombination effect in the time interval of interest (noticeably lower than the time of flight) is either practically absent or clearly pronounced. A comparison of the theoretical and experimental curves in the range of observation times makes it possible to determine k_r and to draw a conclusion about the recombination mechanism. It is natural to take the Langevin value of the recombination coefficient as a trial value.

OBJECTS AND METHODS OF TESTS

The polymer MEH-PPV (Organic Vision, Inc.) and the composition MEH-PPV:PCBM (Sigma-Aldrich) with a weight ratio of 1 : 1 were dissolved in chlorobenzene at a concentration of 10 mg/mL. Each solution was cast on a sheet of ethylated developing paper coated with PE film. The layer area was

Parameters of the theoretical models for the tested polymers

Model	σ (eV), α	μ_0, $m^2/(V\,s)$	ν_0, s^{-1}	τ_0, s
		MEH–PPV		
MTM-g	0.113 eV	1.5×10^{-5}	9×10^{10}	5×10^{-12}
		MEH–PPV : PCBM		
MTM-e	0.5	1.0×10^{-5}	6.0×10^{9}	3×10^{-11}
MTM-g	0.165 eV	1.0×10^{-5}	3.1×10^{12}	3×10^{-11}

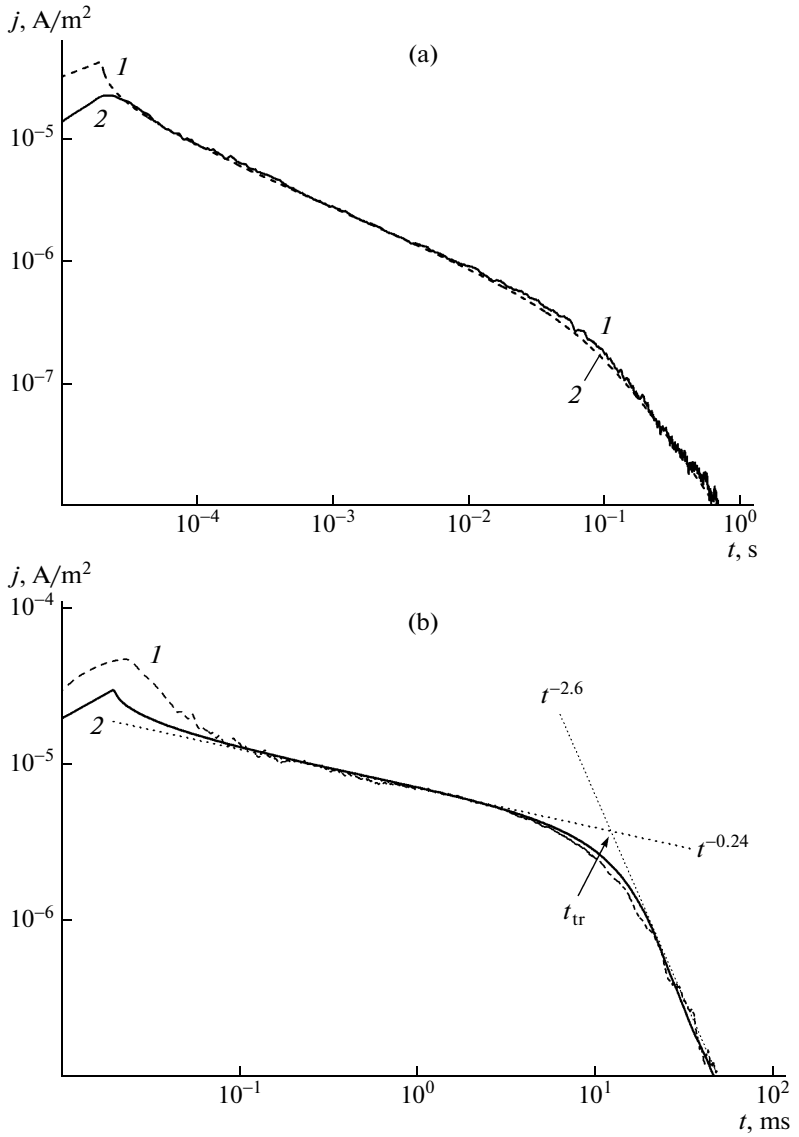

Fig. 2. (*1*) Experimental and (*2*) theoretical curves for (a) MEH-PPV:PCBM and (b) MEH-PPV: (a) MTM-e and (b) MTM-g.

restricted by a glass cylinder with an inner diameter of 40 mm preliminarily installed on the sheet. Formation of the polymer film (i.e., solvent removal from the solution) occurred at room temperature for a week in a mixture of air and solvent vapors because the 6-cm high cylinder was covered with an untightened lid on top. Afterward, the polymer film was separated from the developing paper. The thickness of the films selected for tests was about 13 μm. Electrodes with a thickness of about 40 nm and a diameter of 32 mm were deposited onto both sides of the samples via thermal evaporation of aluminum. The electric capacities of the samples were 3100 and 4300 pF at a frequency of 1 kHz. These values correspond to a relative dielectric permeability of 5.8 for MEH-PPV:PCBM and 8.0 for MEH-PPV. Note that the static dielectric constant is always higher than the optical dielectric constant, which is 3.61 for MEH-PPV [8].

Electric measurements were performed in a vacuum of 10^{-3} Pa at room temperature (295 ± 1 K) with an ELA-50 electron gun facility generating rectangular pulses of accelerated electrons with an energy of 50 keV and durations of 20 and 100 μs. During irradiation with electrons having an energy of 50 keV, the dose rate changes over sample thickness by no more than 20% of the average value (the regime of practically uniform irradiation).

The electron-current density in the method of nonstationary radiation-induced electric conductivity was controllably changed over three orders of magnitude, thereby providing its almost uniform distribution over the irradiated surface. The electron-pulse duration was set at 100 μs.

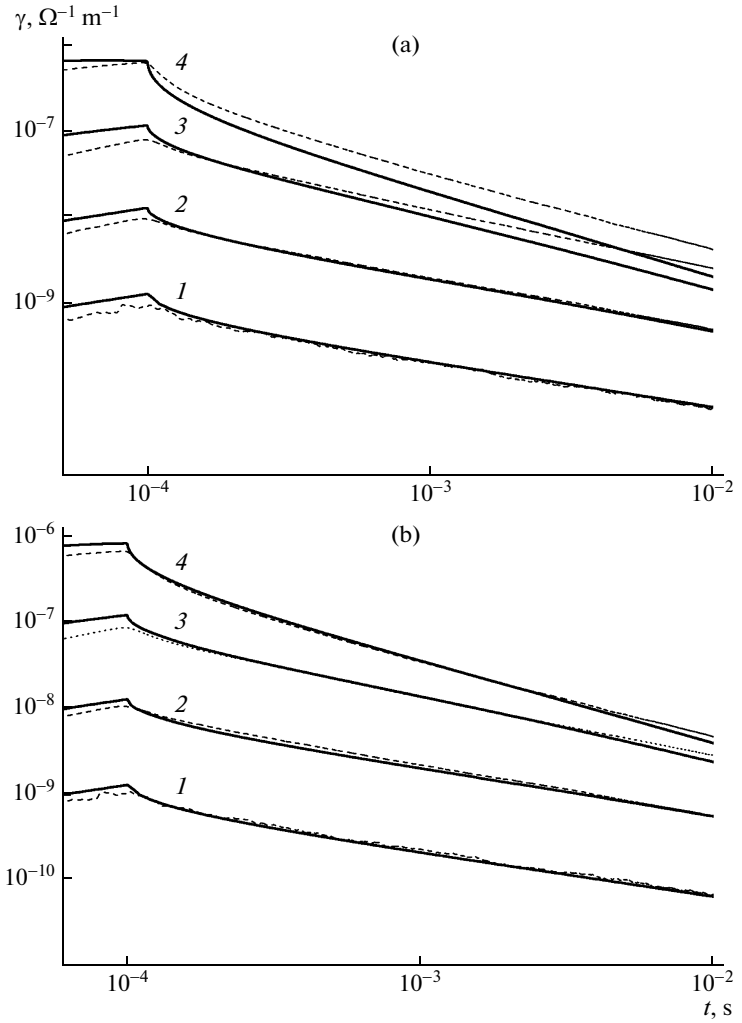

Fig. 3. Comparison of (solid lines, MTM-e) theoretical and (dashed lines) experimental curves for MEH-PPV:PCBM. The generation rates are (*1*) 5×10^{22}, (*2*) 5×10^{23}, (*3*) 5×10^{24}, and (*4*) 5×10^{25} m^{-3} s^{-1}. (a) The Langevin recombination and (b) $k_r = 0.5k_{rL}$.

The beam dosimetry was performed with a Faraday cup. The diameter of the collimator at the inlet of the measuring cell was 30 mm. The measured signal was registered with a universal device for inputting, outputting, and processing of analog and digital information supplemented with an electronic block of high-frequency cross-talk filtration [4].

EXPERIMENTAL RESULTS

The parameters of theoretical models were adjusted on the basis of the data presented in Fig. 1. The time-of-flight curves were registered during uniform irradiation of the samples. Therefore, these data were presented in $\log j$–$\log t$ coordinates. Times of flight t_{tr}, as determined from the intersection point of preflight and postflight asymptotes (shown by dashed lines in the figure), are 12.3 and 65.3 ms for curves *1* and *2*, respectively. Slopes β of asymptotes ($j \propto t^{-\beta}$) are shown for all four asymptotes.

Note that curve *2* is close to that predicted by the theory of strongly nonequilibrium dispersive transport for the dispersion parameter $\alpha = 0.5$ (MTM-e) [4]. This fact justifies the use of known analytical formulas for the time of flight. Moreover, MTM-g was used for both curve *2* and curve *1*. The degree of accordance of the theoretical model with the experimental data may be evaluated from Fig. 2. It is seen that the experimental curves are well reproduced by the calculated curves. As a rule, the fitting procedure requires five to seven cycles of adjusting calculations for each version of the model.

It should be stressed that the experiments were performed in the range of low electric-field strengths of 1–4 V/μm. (The standard value is 2 V/μm.) To provide a high time resolution, the measuring resistance was 1 kΩ, so that the time constant of the measuring circuit did not exceed 4 μs.

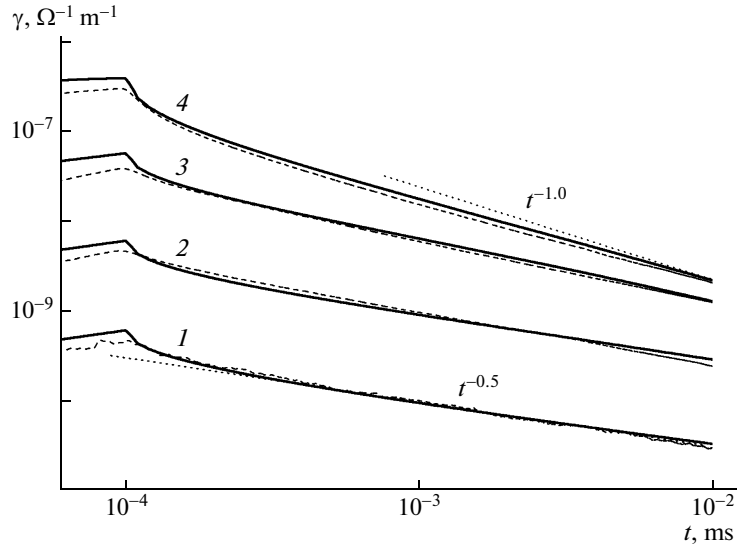

Fig. 4. Comparison of (solid lines, MTM-g) theoretical and (dashed lines) experimental curves for MEH-PPV:PCBM. The space-generation rates are (*1*) 5×10^{22}, (*2*) 5×10^{23}, (*3*) 5×10^{24}, and (*4*) 5×10^{25} m^{-3} s^{-1}. The Langevin recombination.

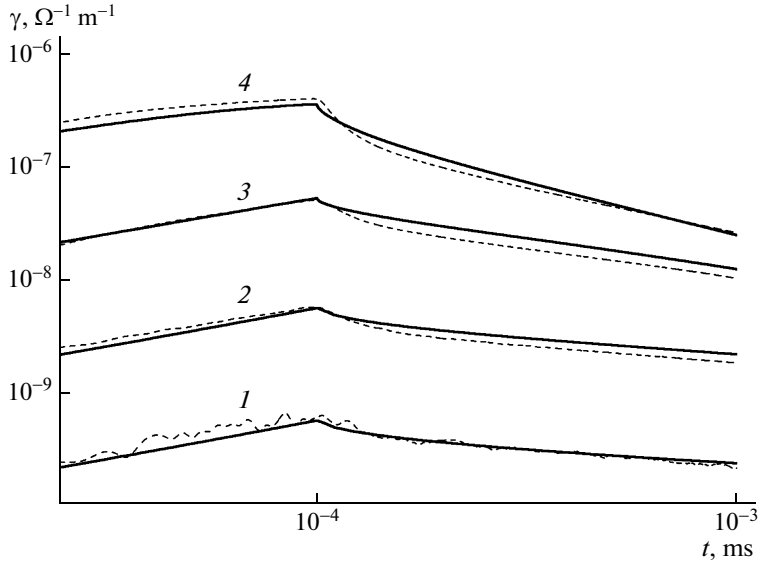

Fig. 5. Comparison of (solid lines, MTM-g) theoretical and (dashed lines) experimental curves for MEH-PPV. The space-generation rates are (*1*) 4.8×10^{22}, (*2*) 4.8×10^{23}, (*3*) 4.8×10^{24}, and (*4*) 4.8×10^{25} m^{-3} s^{-1}. For all calculated curves, $k_r = 2k_{rL}$.

For quantitative comparison of the experimental results with the theoretical results, it is necessary to determine the rate of space generation of charge carriers. Absolute measurements were performed through the method of time-of-flight current integration, while relative measurements were conducted through the method of voltage–ampere characteristics as described in [9].

At this stage, neither charge-carrier flight nor space-charge effects, which are inevitably exhibited in similar investigations in the large-signal regime, were taken into account in calculations. To minimize both effects, the interval of comparison of the theoretical and experimental curves is restricted by times $t \leq 0.1t_{tr}$, where t_{tr} is the time of flight.

The main experimental results are presented in Figs. 3–5. At the minimum dose rate, the current density value in each sample at 1 ms is somewhat lower (20% at most) than its calculated value. Transient-current curves at the minimum dose rate were matched at 100 μs and served as references for comparison of all remaining curves.

As shown in Fig. 3 for calculated curve *3*, an increase or decrease in the recombination coefficient

with respect to its Langevin value is accompanied by a change in the run of curves that far exceeds the differences between calculated and experimental curves. This result is evidence that the real recombination coefficient differs from k_{rL} by 30% at most.

DISCUSSION OF RESULTS

The question on the character of bimolecular recombination in disordered organic systems has been widely speculated [10]. In many papers, there were reports of non-Langevin recombination at which the effective recombination coefficient is much lower than its Langevin value. In the polymer MEH-PPV and the related composition, the recombination of charge carriers obeys the laws of diffusion-controlled processes, whereas the recombination-rate constant is described by the known Langevin formula up to a factor of 2. This conclusion is based on experiments designed according to the classical scheme: a practically uniform generation of charge carriers for a rectangular radiation pulse with changes in the generation rate by factors of 10, 100, and 1000 followed by comparison with model parameters estimated via independent measurements.

As was shown in [4] for a number of ordinary polymers, the non-Langevin recombination is observed also and the rate constant may be 100 times lower than its Langevin value (e.g., in high-pressure polyethylene). Note that this result was obtained via the same scheme as that applied in the present study. For the poly(3-hexylthiophene)–PCBM composition, this decrease in the rate constant may be as high as 10000 [10].

The approaches advanced for the theoretical description of the non-Langevin recombination are phenomenological, although an attempt to gain insight into the nature of this recombination [11, 12] requires further experimental verification.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 12-03-00604.

REFERENCES

1. F. Wudl and G. Srdanov, US Patent No. 5,189,136A (1993).
2. B. Kraabel, D. McBranch, N. S. Sariciftci, D. Moses, and A. J. Heeger, Phys. Rev. B: Condens. Matter **50**, 18543 (1994).
3. C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, Adv. Funct. Mater. **11**, 15 (2001).
4. A. P. Tyutnev, V. S. Saenko, E. D. Pozhidaev, and N. S. Kostyukov, *Dielectric Properties of Polymers in Ionizing Radiation Fields* (Nauka, Moscow, 2005) [in Russian].
5. A. P. Tyutnev, V. S. Saenko, E. P. Grach, and E. D. Pozhidaev, Polym. Sci., Ser. A **52**, 732 (2010).
6. A. P. Tyutnev, R. Sh. Ikhsanov, A. E. Abrameshin, and E. D. Pozhidaev, Polym. Sci., Ser. A **55**, 192 (2013).
7. A. P. Tyutnev, V. S. Saenko, and E. D. Pozhidaev, Chem. Phys. **415**, 133 (2013).
8. A. Boudrioua, P. A. Hobson, B. Matterson, I. D. W. Samuel, and W. L. Barnes, Synth. Met. **111**, 545 (2000).
9. A. P. Tyutnev, V. S. Saenko, R. Sh. Ikhsanov, V. N. Abramov, and E. D. Pozhidaev, High Energy Chem. **42**, 29 (2008).
10. A. Pivrikas, N. S. Sariciftci, G. Yuška, and R. Österbacka, Prog. Photovoltaics: Res. Appl. **15**, 677 (2007).
11. U. Albrecht and H. Bässler, Chem. Phys. **199**, 207 (1995).
12. Ye. Preezant and N. Tessler, J. Appl. Phys. **109**, 1 (2011).

Translated by A. Yakimanskii