Analytical approach towards transient phenomena in photoconductors

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A set of simultaneous, nonlinear, differential equations involved in the kinetics of the photoconductivity process has been solved analytically for the first time. On the basis of the results obtained the relaxation curves were simulated with the help of a computer. It has been found out that the experimentally observed relaxation curves agree very well with the simulated curves. It is worth mentioning that the form of the decay curve is explained with one single time constant rather than taking into account the sum of the reciprocals of various time constants. The relaxation time constant is also considered independent of photoexcited charge carriers.

I. INTRODUCTION

It is well known[1-5] that photoconductivity is one of the techniques for studying optically active traps in semiconductors and, in principal, transient curves recorded in such investigations contain a wealth of information about the kinetics of charge carriers together with the relevant parameters of the traps. Such information, however, has never been revealed experimentally in the true sense, simply because transient curves are not easy to interpret. Several models have been proposed[2,3,6,7] to explain the observed curves. Because of the complexity in the models and the presence of several simultaneous and competitive processes (such as separate contribution from surface and bulk time constants, undetermined constants in the process of diffusion of excess of charge carriers, etc.), meaningful analysis is really a difficult task.

The existing literature on the effects of kinetics of the charge carriers on the transient behavior of photoconductivity is really extensive. To understand the mechanism, it is necessary to set up the rate equations for the relevant impurity levels. This set of simultaneous equations turns out to be nonlinear, and an analytical solution is not possible[5] for a general case. This is a second serious impediment in realizing the form of the relaxation curves.

This problem is also treated with the help of phenomenological models.[4,2] In this case the rise and decay curves are explained with the help of multicomponent exponentials. The decay curve can be written as

$$I_{\rm ph}(t)=\sum_{i=1}^{M} A_i e^{-t/\tau_i}\,, \tag{1}$$

where $I_{\rm ph}(t)$ is the photocurrent and τ_i is a time constant. Summation generally goes up to 3 or 4 components.

Similar results have been obtained by Tureck[8] in semiconductors with M types of traps. It is worth mentioning that, in this particular case, the simultaneous set of equations was solved for impurity photoconductivity.

It is assumed that in Eq. (1), the various τ_i are considered as independents, such as surface and bulk lifetime constants.

Analysis of multicomponent exponential curves is a widely discussed problem, since it appears in a variety of experimental situations and several techniques have been suggested for analysis.[8-11] In some cases limited success have also been reported.[12-17]

Recently, Fleming[10] has developed a computer program to solve numerically the equations which govern transient photoconductivity in the presence of a continuous distribution of traps.

Because of the presence of several unknown parameters, complexity in the process, and difficulties in analyzing the relaxation curves, it is thought[5] that the solution of the set of nonlinear differential equations is an unrewarding task and because of this a rigorous attempt, probably, has not been carried out. The purpose of the present paper is to solve one aspect of the complicated phenomenon, namely, the solution of the set of nonlinear differential equations, and to analyze the relaxation curves with the help of an analytical solution. This might assist us in understanding up to what degree and in what way several competitive processes play a role in the relaxation phenomenon.

II. BACKGROUND

The basic theory for the time-dependence photoconductivity has been carried out in about thirty years. When the radiation, with an energy greater

than the band-gap energy of the semiconductor, is incident, electron-hole pairs are continually generated and continually recombined. (Transport of the charges through the impurity state is not considered here.) The excess of charge carriers formed in this process is transported to the electrode and the transient photocurrent is observed. The typical forms of the time-dependent photocurrent are reported in the literature.[2,3] It is worth mentioning that only in an ideal situation (such as the small contribution from the traps, a negligible role of surface states in the recombination process, etc.), the rise and decay curves can be explained satisfactorily with the help of

$$I_{\rm ph}(t)=I_{\rm max}(1-e^{-t/\tau}) \ \text{(rise)} ,$$

$$I_{\rm ph}(t)=I_{\rm max}e^{-t/\tau} \ \text{(decay)} ,$$

where $I_{\rm max}$ is a maximum photocurrent and τ is a lifetime of the majority charge carriers. (The word "lifetime" is used in different sense by different authors. Here we mean the time required to reduce the value of the photocurrent to its 0.3679 maximum value.) In practice, however, the experimentally observed curves deviate from the exponential nature.

Toward the understanding of the origin of this deviation, several models are proposed.[2–4] The basic fundamental principles are, nevertheless, the same and involve the existence of active traps where the charged particles spend some time either before recombination or before returning to the conduction band. Details of the mechanism depend on the nature of interaction but the basic principle is well known.

In a real system, there exist several types of traps and/or recombination centers available for both electrons and holes. This means that, in practice, a wide variety of situations occur depending upon related parameters of traps and recombination centers. We, however, assume that the system has only one type of predominant traps and the density of the luminescence centers is negligible. Further we consider that the recombination takes place through those traps. These assumptions are made only for simplicity in the calculations; however, they can be generalized to a system with more trap systems and with presence of recombination centers also.

The mechanisms of the formation of photoexcited charge carriers are well understood.[5] When the incident radiation with an energy greater than the energy of the band gap is incident, the electrons $n(t)$ are ejected in the conduction band and holes $p(t)$ are formed in the valence band. Fractions of the excess of electrons from the conduction band are then captured by the traps; the probability of the capture is given by $\alpha_1(N_t-n_c)$, where (N_t-n_c) is the number of unoccupied traps. Some of the electrons are reejected to the conduction band by thermal agitation with probability r_1 while others are captured through nonradiative recombination. The well-known rate equations under non-steady-state conditions are therefore given by[5]

$$\frac{dn}{dt}=G-\alpha_1 n(N_t-n_c)+r_1 n_c , \tag{1a}$$

$$\frac{dn_c}{dt}=\alpha_1 n(N_t-n_c)-\delta_0 n_c p-r_1 n_c , \tag{1b}$$

$$\frac{dp}{dt}=G-\delta_0 n_c p , \tag{1c}$$

where G is a rate of electron-hole pairs per unit time produced by the flux of incident photons of energy $(h\nu)$ greater than the band-gap energy. N_t is a total number of traps per unit volume, $n_c(t)$ is a number of occupied traps per unit volume, and δ_0 is a nonradiative recombination time constant. Equations (1a)–(1c) are valid if we assume that the traps are not distributed near the valence band and, hence, holes are not captured. According to the different experimental conditions, similar sets of differential equations appeared in the literature dealing with the kinetics of the charge carriers in the photoconductivity process and they are solved in the restricted domain with certain assumptions.

Very recently Chen *et al.*[18] have solved a similar set of differential equations with a numerical technique using a Runge-Kutta sixth-order predictor-corrector method for a given set of relevant parameters. But no attempt has been made so far to solve these equations in a more general form, permitting us to take into account a variety of experimental details.

The transient photocurrent originated from the diffusion process is small and hence is neglected at present. Moreover, it is also necessary to consider that the whole plane is uniformally illuminated and the contacts are Ohmic.

In fact, all the details of the transient phenomena are explicitly explained with the help of a set of first-order-differential equations [(1a)–(1c)]. The system carries all the information not only about the variation of the photocurrent as a function of time but also about important parameters involving traps in the kinetics processes. In spite of this importance, the present system of differential equations was never completely solved. More attempts in this direction are not carried out, as one of the models proposed by Rose[3] always explains the form of the relaxation curves, or in limited approximated situations, where the initial conditions are known, the form can be simulated with numerical methods.[19,20]

III. AN ANALYTICAL APPROACH TOWARDS TRANSIENT BEHAVIOR

It is clear that basic aspects of transient behavior are hidden in Eqs. (1a)–(1c) and it is important to solve this system of equations. The present system of nonlinear differential equations can be solved by series solutions. Let

$$n = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + \cdots , \tag{2a}$$

$$n_c = b_0 + b_1 t + b_2 t^2 + b_3 t^3 + \cdots , \tag{2b}$$

$$p = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + \cdots . \tag{2c}$$

The coefficients $a_0, a_1, a_2, \ldots, a_n$, $b_0, b_1, \ldots, b_n$, and $c_0, c_1, c_2, \ldots, c_n$ can be obtained by the usual method and the expressions for a_n are given below,

$$\begin{aligned} a_1 &= G - \alpha_1 a_0 (N_t - b_0) + r_1 b_0 , \\ 2a_2 &= -\alpha_1 a_1 (N_t - b_0) + \alpha_1 a_0 b_1 + r_1 b_1 , \\ n a_n &= -\alpha_1 a_{n-1} (N_t - b_0) \\ &\quad + \alpha_1 \sum_{i=0}^{(n-1)} a_i b_{(n-1)-i} + r_1 b_{n-1} \cdots . \end{aligned} \tag{3}$$

The values of a_0, b_0, c_0 are determined by the initial conditions. Meanwhile the constants $b_1, \ldots, b_n$ and $c_1, \ldots, c_n$ are determined in a similar way as $a_1, \ldots, a_n$. However, they are not of importance for the time being.

Now let us consider for simplicity the decay of the photocurrent. This also helps in understanding the importance of the various terms involved in the present discussion. The photoconductor is illuminated and after reaching a steady state of photocurrent, the radiation is turned off, i.e., G, the rate of photogeneration of charge carriers, is 0. Then, using Eqs. (2a)–(2c) one can obtain $a_0 = N_{\max}$, $b_0 = n_{c_{\max}}$, and $c_0 = P_{\max}$, and hence for these initial conditions the solution $n(t)$ takes the following form (see the Appendix):

$$\begin{aligned} n(t) &= [N_{\max} - r_1 n_{c_{\max}} \tau + (\alpha_1 N_{\max} b_1 + r_1 b_1)\tau^2] e^{-t/\tau} \\ &\quad + r_1 n_{c_{\max}} \tau - (\alpha_1 N_{\max} b_1 + r_1 b_1) \\ &\quad \times \tau^2 (1 - t/\tau) + \cdots , \end{aligned} \tag{4}$$

where

$$\tau = [\alpha_1 (N_t - n_{c_{\max}})]^{-1} .$$

Generally, the lifetime τ is small, i.e., of the order of milliseconds or microseconds, and hence the contribution arising from higher powers of τ is not taken into account in Eq. (4).

The present analytical approach gives a new significant result. Even in the presence of optically active traps, the decay curves can be explained satisfactorily with the help of only one time constant. Deviation from the exponential nature is easily understood from the last terms of Eq. (4).

IV. COMPARISON WITH EARLIER THEORIES

Equation (4) is a solution of a set of differential equations given by (1a)–(1c) and shows how the number of excess charge carriers varies with time as the radiation is cut off. If τ is reasonably small, Eq. (4) is reduced to the well-known decay equation[4]

$$n(t) = N_{\max} e^{-t/\tau} , \tag{5}$$

which, in fact, is a solution of Eq. (1a) in the case when electrons are not reinjected in the conduction band through the traps, and is generally known as a simple classical form of transient photocurrent. It can be understood from Eq. (4) that when the lifetime is not small, the relaxation curves should deviate from the exponential nature which is also an observed fact. In large energy-band-gap semiconductors, the dominating mechanism for electron-hole recombination is carried out via traps or flaws, and a time constant for electrons is given by[21]

$$(\tau_n)^{-1} = (N_t - N_c)\langle c_n \rangle ,$$

where $\langle c_n \rangle$ is the average capture coefficient. It is worth mentioning that with our present analysis the same expression for the time constant is obtained.

Zitter[7] has analyzed the behavior of the traps in the photoconduction process and has classified the effects in two distinct ways. Electrons from the conduction band are captured by the traps and immediately recombine with holes from the valence band. Since the electrons do not spend much time in the traps, the population of occupied traps remains constant and it is concluded that the decay will be exponential. In the second case, electrons remain a reasonable time in the traps and, naturally, the decay will not be exponential. In this case the decay curves are explained by taking the sum of the exponential components. The first conclusion is a direct consequence of Eq. (4). Since the number of occupied traps is constant, b_1, b_2, b_3, etc., $=0$, and electrons are not thermally ejected, therefore $r_1 = 0$, and so Eq. (4) reduces to the well-known classical equation (5). In the second case the number of occupied traps is a function of time, b_1, b_2, b_3, etc., are nonzero terms, and the deviation of the exponential nature will be explained by (4). Moreover, the above equation suggests in what way the form of the relaxtion curves depend on the relative values of b_1, b_2, b_3, etc., and r_1.

The majority of the decay curves are satisfactorily

explained with the help of three or four prominent decay modes. However, the present analysis explains the same form for the curves with a single time constant. Thus, it is very difficult to distinguish between the higher-order decay modes and the deviation caused by the second and third terms of Eq. (4). It is, therefore, suggested that the deviation from the exponential nature could be due to the simultaneous nature of the differential equations and this possibility should be considered before carrying out any analysis.

As the shape of the relaxation curve depends on several parameters, the form of the curve cannot be understood easily and therefore the shape is simulated from Eq. (4). Figure 1 shows such simulated decay curves. Physical parameters used for simulation purposes are given in Tables I and II. In order to maintain generality in the discussion, the form of the relaxation curve is not compared with any particular experimental result.

A large number of experimental data shows that, usually, photocurrent does not decay exponentially.[4] The general trend of the observed shape agrees very well with the curves obtained by simulation. Figure 2 shows a plot of $\log_{10} I_p$ vs time for the simulated curves which appear in Fig. 1. Such types of curves are generally plotted to separate time constants which are involved in a multiexponential model. The deviation of the photocurrent obtained from the second and third terms of Eq. (4) is reflected in the latter part of the curves. The logarithm's scale reduces the magnitude of the deviation and hence the latter part of the curves look nearly like a straight line with different slopes. When considering the experimental results, displacement of the points from the straight line is attributed to the ex-

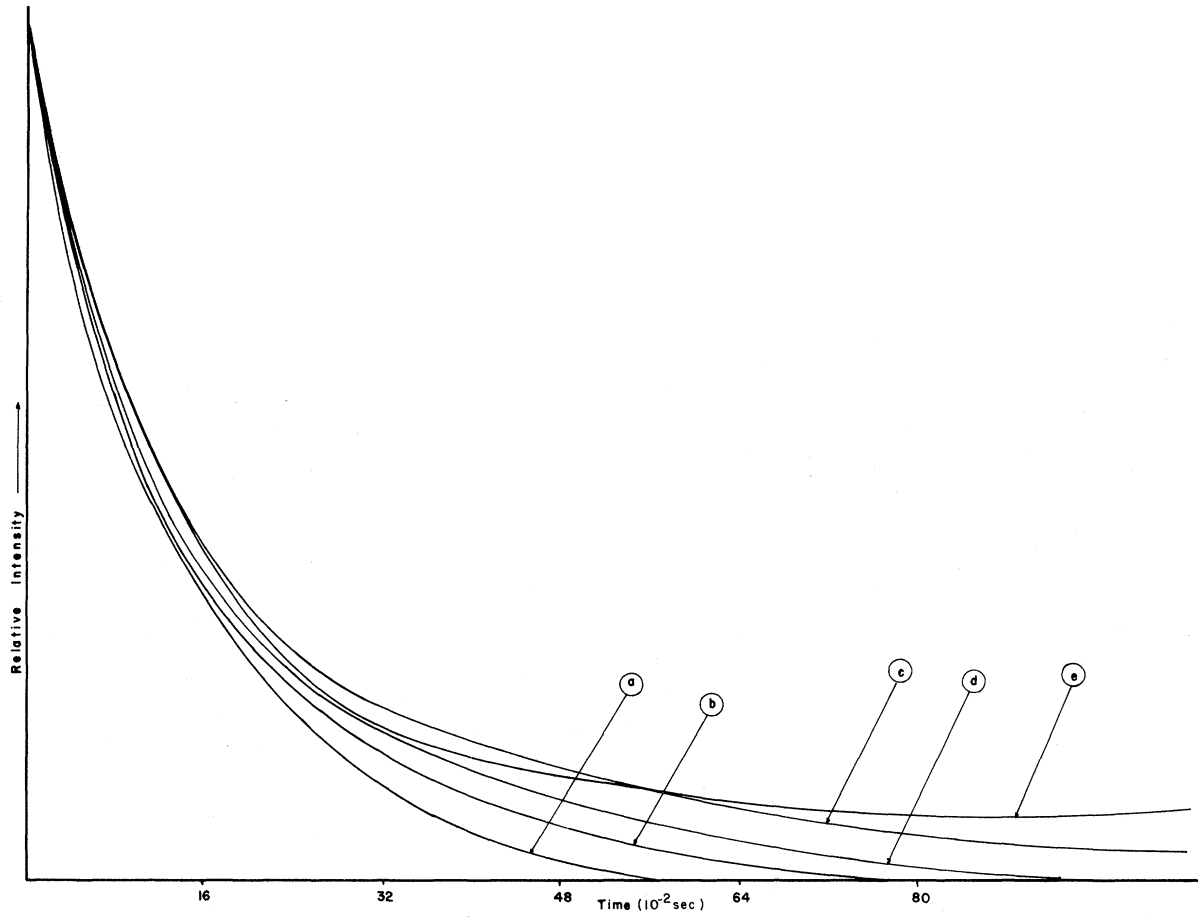

FIG. 1. Relaxation curves simulated using Eq. (5) and with only one time constant. Other parameters used here are given in Table I.

TABLE I. Physical parameters used for simulation purposes.

Photoexcited electron-hole pairs (low-level photo injection)	6.5×10^{8} cm^3/sec
Capture cross section for a particular type of traps at a given temperature	1.5×10^{-9} cm^3/sec
Total number of traps	10^{10} cm^3
Total number of occupied traps when the photocurrent reached its saturated value	0.33×10^{10} cm^3
Lifetime $\tau=[\alpha_1(N_t-n_{c_{max}})]^{-1}$	$=0.1$ sec

perimental error. Thus again, this is a confusing situation for supporting the multicomponent model.

The shape of the relaxation curve is used[2,16] several times for rapid determination of the type of recombination (linear, quadratic, etc.) and/or type of traps (α or β type), the variation of traps, etc., but the present analysis suggests a word of caution before using the form of the relaxation curve for further information.

TABLE II. Variable parameters used for different simulated relaxation curves. Even though b is related to the other constants in the expansion, it is considered as a parameter for the present model.

Curve	r_1	b_1
A	0.4	2.367×10^{9}
B	0.4	1.183×10^{9}
C	0.4	9×10^{9}
D	0.5	7×10^{9}
E	0.2	7×10^{9}

V. CONCLUDING REMARKS

A simultaneous set of nonlinear differential equations is solved in a series form. This gives a new outlook towards understanding the form of the relaxation curves and at the same time takes into account earlier established theories. The new approach might help to separate the contributions of the different mechanisms. For further conclusions and for getting more information from relaxation curves, more experimental work is being carried out in this direction.

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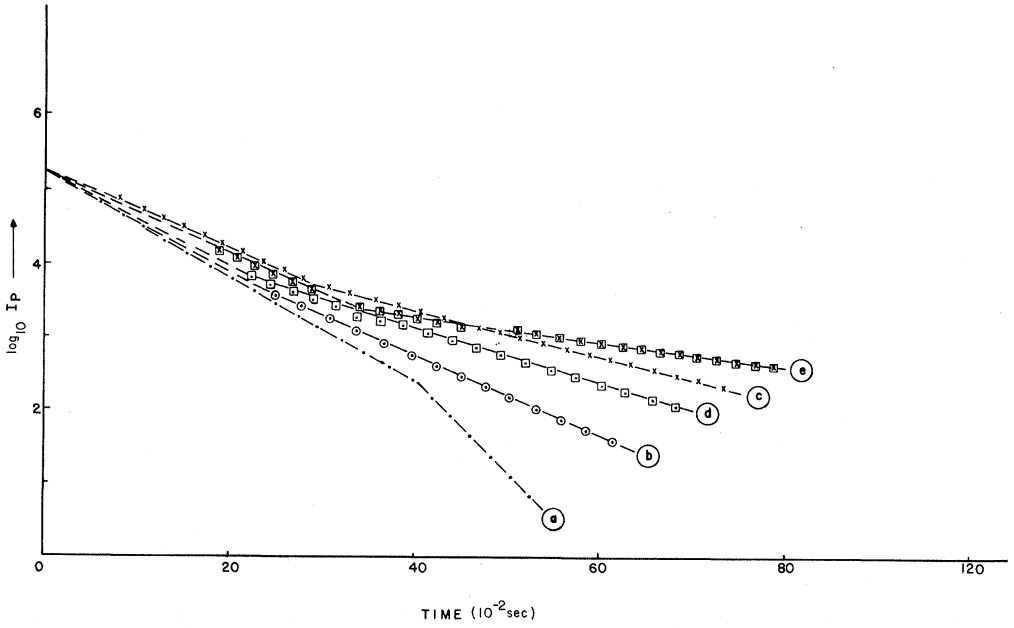

FIG. 2. A plot of log of photocurrent vs time for the simulated curves which appear in Fig. 1.

APPENDIX

The values of a_0, b_0, and c_0 are evaluated using initial conditions; at $t=0$, Eq. (2) gives

$$a_0=n_{\max}=N_{\max},$$

the number of photoexcited electrons;

$$b_0=n_{c_{\max}},$$

the maximum number of occupied traps during the photoexcitation;

$$C_0=P_{\max},$$

the number of photoexcited holes. The behavior of $n(t)$ can be understood if the constants $a_1 \cdots a_n$ are evaluated and this can be done by using Eq. (3),

$$a_1=-\alpha_1 N_{\max}(N_t-n_{c_{\max}})+r_1 n_{c_{\max}},$$

$$2a_2=-\alpha_1(N_t-n_{c_{\max}})[-\alpha_1 N_{\max}(N_t-n_{c_{\max}})+r_1 n_{c_{\max}}]+\alpha_1 N_{\max} b_1+r_1 b_1$$

$$=\frac{\alpha_1^2 N_{\max}(N_t-n_{c_{\max}})^2}{2!}-\frac{\alpha_1(N_t-n_{c_{\max}})r_1 n_{c_{\max}}}{2!}+\frac{\alpha_1 N_{\max} b_1+r_1 b_1}{2},$$

$$3a_3=-\alpha_1(N_t-n_{c_{\max}})\left[N_{\max}\frac{\alpha_1^2(N_t-n_{c_{\max}})^2}{2!}-\frac{\alpha_1(N_t-n_{c_{\max}})}{2!}r_1 n_{c_{\max}}+\frac{\alpha_1 N_{\max} b_1+r_1 b_1}{2}\right]$$

$$+\alpha_1 a_1 b_1+\alpha_1 N_{\max} b_2+r_1 b_2,$$

$$a_3=-\left[N_{\max}\frac{\alpha_1^3(N_t-n_{c_{\max}})^3}{3!}-\frac{\alpha_1^2(N_t-n_{c_{\max}})^2}{3!}r_1 n_{c_{\max}}+\frac{(\alpha_1 N_{\max} b_1+r_1 b_1)\alpha_1(N_t-n_{c_{\max}})}{3.2}\right]$$

$$+\frac{\alpha_1 a_1 b_1+\alpha_1 N_{\max} b_2+r_1 b_2}{3},$$

and so on. Equation (2.1), therefore, can be written as

$$n(t)=N_{\max}+[-N_{\max}\alpha_1(N_t-n_{c_{\max}})+r_1 n_{c_{\max}}]t$$

$$+\left[\frac{N_{\max}(N_t-n_{c_{\max}})^2\alpha_1^2}{2!}-\frac{\alpha_1(N_t-n_{c_{\max}})r_1 n_{c_{\max}}}{2!}+\frac{\alpha_1 N_{\max} b_1+r_1 b_1}{2}\right]t^2$$

$$+\left[\frac{-N_{\max}(N_t-n_{c_{\max}})^3\alpha_1^3}{3!}+\frac{\alpha_1^2(N_t-n_{c_{\max}})^2 r_1 n_{c_{\max}}}{3!}-\alpha_1\frac{(\alpha_1 N_{\max} b_1+r_1 b_1)(N_t-n_{c_{\max}})}{3.2}\right.$$

$$\left.+\frac{(\alpha_1 r_1 b_1+\alpha_1 N_{\max} b_1+r_1 b_2)}{3}\right]t^3$$

$$=N_{\max}\exp[-\alpha_1(N_t-n_{c_{\max}})t]-\frac{r_1 n_{c_{\max}}}{\alpha_1(N_t-n_{c_{\max}})}\exp[-\alpha_1(N_t-n_{c_{\max}})t]$$

$$+\frac{\alpha_1 N_{\max} b_1+r_1 b_1}{\alpha_1^2(N_t-n_{c_{\max}})^2}\exp[-\alpha_1(N_t-n_{c_{\max}})t]+\frac{r_1 n_{c_{\max}}}{\alpha_1(N_t-n_{c_{\max}})}$$

$$-\frac{\alpha_1 N_{\max} b_1+r_1 b_1}{\alpha_1^2(N_t-n_{c_{\max}})^2}(1-t/\tau)+\cdots.$$

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