Instability in nonautocatalytic ionization-recombination processes

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(Received 11 October 2006; revised manuscript received 22 November 2006; published 22 January 2007)

Variational analysis of ionization-recombination processes shows that instability in gas- or solid-state plasmas is possible only if the sign symmetry of the Jacobian matrix of the dynamical system is broken. Well-known autocatalytic processes like impact ionization of impurities in semiconductors provide only one of the possible mechanisms achieving this effect. Electron exchange between atoms in metastable states, level inversion in multiply ionized centers, and impact excitation from free electrons or holes are here proved to be good candidates as well, due to the competition between two or more mutually dependent recombination channels. These instability patterns are employed to model photoconduction in a semiconductor suitably doped with a two-level impurity, obtaining a bistable behavior driven either by the light irradiance alone or by the electric field too.

DOI: 10.1103/PhysRevB.75.024305 PACS number(s): 05.65.+b, 72.20.Jv, 72.40.+w, 82.20.Db

I. INTRODUCTION

Self-generated dynamical instability in ionization-recombination processes has been attributed in the past, almost without exception, to the occurrence of some kind of autocatalytic reaction. In 1957 Robertson[1] explained oscillations in the striations of the positive column of dc discharges by means of impact ionization of a metastable state. Since then, evidence has been accumulated about negative differential conductivity regimes in lightly doped semiconductors, mostly explained as instable states of equilibrium between ionization and recombination, driven by impact ionization of impurities.[2–5] Experimental findings on spatiotemporal complexity in recombination processes have also been reported until now, all involving impurity breakdown.[6–10] As a matter of fact, ionization and recombination are not the only mechanisms leading to negative-resistance regimes: multiple solutions of the energy balance between the electron gas and the lattice (superheating mechanism[11]) and effective-mass effects in two-valleys semiconductors (Ridley-Watkins-Hilsum mechanism[11]) are also capable of causing conductance multistability in semiconductors. Nevertheless, ionization-recombination processes are the most intensively studied mechamisms leading to instability in a solid-state plasma, due to the multiplicity of the effects involved. For instance, not less than five different causes have been investigated, accounting for an increase of carrier mobility once the impact ionization of the impurities is initiated (see Ref. 5 and related references). The screening effect, due to the shielding of charged scatterers by free electrons or holes, is probably the most significant one, intensively investigated by several authors.[12–14] Schöll, on the other hand, proposed a different, very versatile instability mechanism based on the two-stage impact ionization of a two-level dopant, which has prevailed as an interpretation of bistability and chaos caused by the impact-ionization avalanche in semiconductors.[6,15] Other mechanisms based on self-enhanced charge generation were modeled too, like hole-assisted autocatalysis of electrons[16] and autocatalytic generation of excitons.[17]

Other works report on possible instability mechanisms in ionization-recombination processes due to field-dependent effects other than autocatalytic charge generation: namely, field-enhanced trapping[18] and Poole-Frenkel emission.[19,20] But if we exclude these exceptions, due to field-enhanced modification of the trapping potential, autocatalytic charge generation is the only well-assessed mechanism in the field of recombination instability.[21–23]

As a matter of fact, instability patterns other than those due to autocatalysis are available, as I will show in this article, involving competition between different, mutually dependent recombination channels, but they were never studied in the past.

In this work, I develop a model of ionization-recombination processes in gas- or solid-state plasmas with an arbitrary number of chemical species, in the absence of chemical reactions. Within this framework a sufficient condition for asymptotic stability is clearly identified in the sign symmetry of the Jacobian matrix of the rate equations (nonnegative sign of the off-diagonal entries). This condition has been enounced in the past for linear compartmental systems[24] and applied to evolving plasmas in nonlocal termodinamic equilibrium[25] but the possibility of asymptotic divergencies due to zero characteristic exponents has not been discussed thoroughly, in my opinion. In this article, the theoretical apparatus of M matrices[26,27] is applied to the problem and a rigorous conclusion about the stability of sign-symmetric systems is reached. As a consequence of this criterion, instability is found to be compatible only with a limited amount of physical situations, which include, but are not limited to, the well-known autocatalytic mechanisms.

In Sec. II a necessary condition for dynamical instability is stated, based on the sign symmetry of the Jacobian matrix. In Sec. III this criterion is followed to identify the three possible mechanisms driving to instability without the intervention of autocatalytic processes. In Sec. IV these patterns are followed to build models based on the competition of two different recombination channels in a semiconductor doped with a two-level impurity.

II. NECESSARY CONDITION FOR DYNAMICAL INSTABILITY

Let $\{N_i\}$ be the set of the electron occupation numbers of a system of (generally) degenerate energy levels, describing the state of a homogeneous gas- or solid-state plasma in

which no chemical transformation occurs. The index i labels both the atomic specie and the energy level. Let

$$\dot{N}_i = f_i(\{N_k\}) \tag{1}$$

be the rate equations of such a system, and let $\{\delta N_i(t)\}$ be a small perturbation of a solution $\{N_i(t)\}$ of system 1, satisfying the neutrality condition

$$\sum_i \delta N_i = 0. \tag{2}$$

The perturbation evolves in time according to the equations

$$\delta\dot{N}_i = \sum_j \boldsymbol{T}_{ij}\delta N_j + o(\{\delta N_k\}) \quad \text{with } \boldsymbol{T}_{ij} = \frac{\partial f_i}{\partial N_j}. \tag{3}$$

We will state some sufficient conditions under which any perturbation $\{\delta N_i(t)\}$ vanishes for time approaching infinity (asymptotic stability). Preliminarily, we assume that no rearrangement of the indexes exists such that $\boldsymbol{T}_{ij}=0$ for all $i \leqslant k$ and $j > k$ for a convenient k (irreducibility for permutations). In this way we exclude that the system can be divided into two or more noninteracting parts. In this case, the following, equivalent statements hold.

(i) Non-negativity of the off-diagonal entries of $\boldsymbol{T}_{ij}$ implies stability of the system.

(ii) Dynamical instability requires as a necessary condition the negative sign of some off-diagonal entry of $\boldsymbol{T}_{ij}$.

This condition was enounced in the past[24,25] as a direct consequence of the Gershgorin theorem,[28] which states that all the eigenvalues of the matrix $\boldsymbol{T}_{ij}$ (characteristic exponents of the system) belong to some of the disks in the complex plane having centers in $\boldsymbol{T}_{jj}$ and radii $r_j \equiv \Sigma_{i\neq j}|\boldsymbol{T}_{ij}|$. Now, the conservation of the number of electrons implies vanishing of the sum of all the entries of a same column of $\boldsymbol{T}_{ij}$—in fact,

$$\sum_i \boldsymbol{T}_{ij} = \frac{\partial}{\partial N_j}\sum_i f_i, \quad \text{with } \sum_i f_i = \frac{d}{dt}\sum_i N_i = 0. \tag{4}$$

Consequently, if the off-diagonal entries of $\boldsymbol{T}_{ij}$ are non-negative, each diagonal term $\boldsymbol{T}_{jj}$ equals $-r_j$, and thus all the Gershgorin disks lie on the side of the complex plane corresponding to numbers with a negative or null real part. Moreover, the Gershgorin disks all cross the origin and are tangent to the immaginary axis. Consequently, all the *non-null* eigenvalues of $\boldsymbol{T}_{ij}$ have a negative real part. Now, it is well known that the negative real part of *all* the characteristic exponents of the system could be a sufficient condition for dynamic stability.[29] Nevertheless, Eq. (4) implies singularity of the matrix $\boldsymbol{T}_{ij}$; then, at least one of the roots of the characteristic equation is null and an asymptotic divergence of the solutions of Eq. (3) cannot be excluded, due to the higher-order terms in Eq. (3).

The key for the solution is to notice that the space S of the sets $\{\delta N_i\}$ satisfying condition (2) is closed with respect to the matrix $\boldsymbol{T}_{ij}$, as can easily be seen by application of Eq. (4). Therefore, it will be sufficient to test the sign of the eigenvalues of $\boldsymbol{T}^S$: the restriction to the space S of the linear operator defined by $\boldsymbol{T}_{ij}$. For this aim, we recall two conclusions concerning sign-symmetric and irreducible matrices, reached by Hearon[24] and more recently surveyed in the context of general M-matrix theory (see Chap. 6 of Ref. 26).

(a) An eigenvector of the zero eigenvalue exists, such that all its components are positive.

(b) The multiplicity of the zero characteristic exponent is 1.

For statement (a), the eigenspace S_0 corresponding to the zero eigenvector is not included in the space S spanned by the solutions of Eq. (3), because its vectors do not satisfy condition (2). Thus, S and S_0 both being closed with respect to the matrix $\boldsymbol{T}_{ij}$, a similarity transformation A_{ij} exists such that

$$A^{-1}\boldsymbol{T}A = \left(\begin{array}{c|c} 0 & 0 \\ \hline 0 & \boldsymbol{T}^S \end{array}\right), \tag{5}$$

where $\boldsymbol{T}^S$ operates in the space S.

For statement (b), only one of roots of the characteristic equation of $\boldsymbol{T}_{ij}$ vanishes, so that the eigenvalues of $\boldsymbol{T}^S$ are all nonzero and equal the non-null eigenvalues of $\boldsymbol{T}_{ij}$, which have a negative real part. Since $\boldsymbol{T}^S$ is the restriction of $\boldsymbol{T}_{ij}$ to the space spanned by the solutions of system (3), the negative real part of its eigenvalues implies asymptotic stability.[34]

Of course, the negativity of some off-diagonal entry of the Jacobian matrix is not a sufficient, but only a necessary condition for instability; nevertheless, it is a very simple tool to greatly restrict the field of investigation in the study of nonequilibrium phase transition in ionization-recombination processes. Moreover, we will verify that within every class of systems with a broken sign symmetry of T_{ij}, a nonempty subset of systems can be found exhibiting multistability.

III. DYNAMICAL INSTABILITY IN IONIZATION-RECOMBINATION REACTIONS

If r_{ik} represents the number of electrons that, in unit time, change their state from k to i, the functions f_i in Eq. (1) have the form

$$f_i = \sum_{k\neq i}(r_{ik} - r_{ki}). \tag{6}$$

The transition rates r_{ik}, in their turn, depend on the occupation numbers N_l in one of the following two ways:

$$\text{excitation-relaxation} \quad r_{ik} = R_{ik}(\{N_l\})N_k^{\mathrm{A}}, \tag{7}$$

$$\text{ionization-recombination} \quad r_{ik} = S_{ik}(\{N_l\})N_k^{\mathrm{A}}N_i^{\mathrm{F}}, \tag{8}$$

where N_k^{A} is the number of electrons in the state k which are available to make a transition to another state, while N_i^{F} is the number of free places in the state i. Transition probabilities S_{ik} and R_{ik} depend on the externally imposed physical parameters relevant in the process (e.g., temperature, electric field, light irradiance, and wavelenght). Moreover, they may depend or not on the occupation numbers $\{N_l\}$, according to the nature of the reactions involved. For example, in impact ionization and in Auger recombination, S_{ik} depends on the number of free electrons. N_k^{A} and N_i^{F}, on the other hand, depend

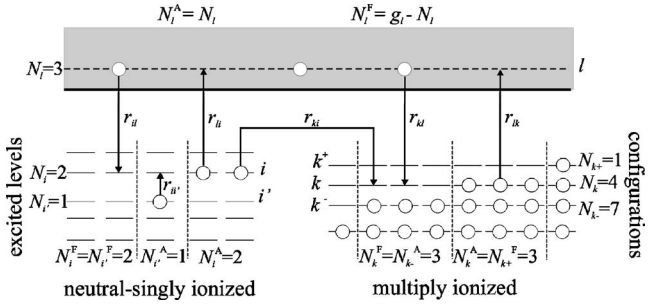

FIG. 1. A schematics of the model represented by Eqs. (7) and (8). On the left side, a set of atoms of a given specie is represented, each with its Grotrian diagram; three of these atoms are neutral and two singly ionized. On the right side, a set of neutral, singly, or multiply ionized atoms are represented. In this case, the excited levels of each configuration are not considered, presuming that the population of the excited levels is ruled by lattice or free electrons temperature. The upper side represents the unbound state.

on the nature of the state labeled by the index. Figure 1 gives a schematics of the various cases involved in neutral and singly ionized atoms (left side of the figure), multiply ionized atoms (right side), and free states (top of the figure).

Neutral or singly ionized atoms. Since all the valence electrons can be excited or extracted from the atoms, the number N_k^{A} of electrons available to make a transition is simply N_k. On the other hand, the number of "free places" for an electron to recombine is given by the number of ions; then,

$$N_k^{\mathrm{A}} = N_k,$$

$$N_i^{\mathrm{F}} = g_i - \sum_l \Delta_{il} N_l, \tag{9}$$

where g_i is the number of atoms of the specie labeled by i, while Δ_{il} is equal to 1 only if i and l refer to states of a same atomic specie and otherwise is zero (notice that the index labels both the atomic specie and the energy level).

Multiply ionized atoms. Let the indices k^-, k, and k^+ indicate three adjacent energy levels in a given atomic configuration. An electron in the state k can make a transition in low-energy processes only if no other electrons occupy the state k^+ in the same atom. Analogously, a free state k can be reached by an unbound electron only if the state k^- is occupied in its turn. Consequently, we have

$$N_k^{\mathrm{A}} = N_k - N_{k^+},$$

$$N_i^{\mathrm{F}} = N_{i^-} - N_i. \tag{10}$$

Free states. If g_i is the degeneration of an unbound state, we can obviously state

$$N_k^{\mathrm{A}} = N_k,$$

$$N_i^{\mathrm{F}} = g_i - N_i. \tag{11}$$

It is worth noting that, if we formally state $N_{k^+}=0$ and $N_{i^-}=g_i$, the present case reduces to the previous one, which will be useful in the following discussion.

Once the expressions for the transition probabilities r_{ik} are determined by Eqs. (7)–(11), the entries of the matrix $\boldsymbol{T}_{ij}$ are calculated from their derivatives with respect to the occupation numbers, as given in Eq. (3), and can be then expressed as a sum of two contributions:

$$\boldsymbol{T}_{ij} = \boldsymbol{T}_{ij}^{\mathrm{nc}} + \boldsymbol{T}_{ij}^{\mathrm{c}} \quad \text{with}$$

$$\boldsymbol{T}_{ij}^{\mathrm{nc}} = \sum_{k\neq i} \left(S_{ik} \frac{\partial N_k^{\mathrm{A}} N_i^{\mathrm{F}}}{\partial N_j} - S_{ki} \frac{\partial N_i^{\mathrm{A}} N_k^{\mathrm{F}}}{\partial N_j} \right) + \left(R_{ik} \frac{\partial N_k^{\mathrm{A}}}{\partial N_j} - R_{ki} \frac{\partial N_i^{\mathrm{A}}}{\partial N_j} \right),$$

$$\boldsymbol{T}_{ij}^{\mathrm{c}} = \sum_{k\neq i} \left(\frac{\partial S_{ik}}{\partial N_j} N_k^{\mathrm{A}} N_i^{\mathrm{F}} - \frac{\partial S_{ki}}{\partial N_j} N_i^{\mathrm{A}} N_k^{\mathrm{F}} \right) + \left(\frac{\partial R_{ik}}{\partial N_j} N_k^{\mathrm{A}} - \frac{\partial R_{ki}}{\partial N_j} N_i^{\mathrm{A}} \right). \tag{12}$$

The apices "nc" and "c" refer, respectively, to "noncatalytic" and "catalytic" processes. In fact, $\boldsymbol{T}_{ij}^{\mathrm{c}}$ is nonzero only if the transition probabilities S_{ik} and R_{ik} depend explicitly on $\{N_l\}$—that is, if the transition of an electron from state k to i is catalyzed or somewhat influenced by the presence of electrons in some specific quantum state. If this is not case, only the $\boldsymbol{T}_{ij}^{\mathrm{nc}}$ (noncatalytic) term is nonzero. In this last case, the equations of the system (1) are of the second degree in $\{N_i\}$. Indeed, nonlinearity of the second order has been known to be a cause of instability in dynamical systems since the very beginning of chaos studies.[30,31] Nevertheless, up to now, only catalytic processes have been considered as possible mechanisms leading to instability in ionization-recombination processes, in both theoretical and experimental studies.

We will first study noncatalytic processes, in the case of single or multiple ionization, in order to identify sufficient conditions for asymptotic stability.

Noncatalytic processes: neutral or singly ionized atoms. The rate equations assume the form [from Eqs. (6), (9), and (12)]

$$\dot{N}_i = \sum_{l\neq i} \left\{ \left[S_{il} \left(g_i - \sum_k \Delta_{ik} N_k \right) + R_{il} \right] N_l \right\} - \left\{ \sum_{l\neq i} \left[S_{li} \left(g_l - \sum_k \Delta_{lk} N_k \right) + R_{li} \right] \right\} N_i, \tag{13}$$

while the off-diagonal entries of the matrix $\boldsymbol{T}_{ij}$ are

$$\boldsymbol{T}_{ij} = \boldsymbol{T}_{ij}^{\mathrm{nc}} = S_{ij} \left(g_i - \sum_l \Delta_{il} N_l \right) + S_{ji} N_i + R_{ij} - \Delta_{ij} S_{ij} N_j + \sum_{l\neq i,j} (\Delta_{lj} S_{ki} N_i - \Delta_{ij} S_{il} N_l). \tag{14}$$

Observing Eq. (14), we notice that the only way for the off-diagonal entries to assume a negative value is to admit transitions involving several excited states of the same atomic specie, corresponding to the terms $-\Delta_{ij} S_{ik} N_k$ and $-\Delta_{ij} S_{ij} N_j$. These transitions may be free electron capture or emission, or also electron exchange between atoms, during collisions

in a gas or by tunneling between impurities in solid state plasmas. Tunneling requires impurity centers which are comparatively close to each other, and this could be true in the case of localized states related to low-dimensional structural defects (dislocations or twinnings) or also in clusters of impurities. Regarding this, interatomic Coulombic decay[32] has been recently identified as a decay or ionization mechanism due to correlation between electrons in different atoms of a same cluster. Even in these cases, however, the negative contributions of the expression can be overwhelmed if the exchange contributions are lesser than the collisional or radiative rates R_{ij}, which are always positive. In conclusion, instability, if any, requires electron exchange between metastable states and low excitation-relaxation rates.

Noncatalytic processes: multiply ionized atoms. Sufficiently high collisional rates involve stability in the case of single ionization, as just shown. This is not necessarily true for multiple ionization. If the collisional rates are high enought to thermalize the distribution of the excited levels of each electronic configuration, the transition probabilities S_{ij} between configurations depend on temperature, and the rate equations can be written in the following form [from Eqs. (6), (10), and (12)]:

$$\dot{N}_i = \sum_{k \neq i} [S_{ik}(N_{i^-} - N_i)(N_k - N_{k^+}) - S_{ki}(N_{k^-} - N_k)(N_i - N_{i^+})]. \tag{15}$$

This equation describes not only electronic exchange between singly or multiply ionized atoms, but also ionization or recombination toward or from an unbound state k, formally stating $N_{k^+}=0$ and $N_{k^-}=g_k$.

For $i \neq j, j^{\pm}$, the off-diagonal terms of the Jacobian matrix $\boldsymbol{T}_{ij}$ assume the simple form

$$\boldsymbol{T}_{ij} = \boldsymbol{T}_{ij}^{\mathrm{nc}} = (S_{ji} - S_{j^+i})(N_i - N_{i^+}) + (S_{ij} - S_{ij^-})(N_{i^-} - N_i) \tag{16}$$

Since N_i and N_{i^-} are always not less than N_{i^+} and N_i, respectively, sufficient conditions for the non-negativity of Eq. (16), and then for the stability of the dynamic system, are $S_{ij} \geqslant S_{ij^-}$ and $S_{ji} \geqslant S_{j^+i}$ for every i and j. That is, non-negativity of $\boldsymbol{T}_{ij}$ is assured if any further ionization of less ionized atoms is more favored than the more ionized ones and recombination of the more ionized atoms is more probable compared with the less ionized. This is effectively true for shallow states of the band gap of semiconductors, but for deeper states the opposite can hold, due to the momentum transfer: Nickel impurities in germanium, for instance, act as double acceptors that capture electrons with a probability about 6 times higher in the charged state than in the neutral one.[33]

Catalytic processes. If $\boldsymbol{T}_{ij}^{\mathrm{nc}}$ is sign symmetric, only catalytic processes can break the sign symmetry of the matrix $\boldsymbol{T}_{ij}$ and possibly reverse the real part of some of its eigenvalues. In this case, we have to distinguish *autocatalytic from nonautocatalytic* reactions, according to the dependence of S_{ij} and R_{ij} on the occupation numbers N_k:

Autocatalytic reactions. S_{ij} or R_{ij} depend on N_i or N_j, or both. This is the typical case of impact ionization by free electrons, or holes in a solid, or positive ions. Therefore, if N_j is the number of free electrons, the impact transition probability S_{ji} from bound to free state depends on the concentration of free electrons itself. In this case, $\frac{\partial S_{ji}}{\partial N_j}$ is likely to be positive and the off-diagonal entries $\boldsymbol{T}_{ij}^{\mathrm{c}}$, given by Eq. (12), equal $-\frac{\partial S_{ji}}{\partial N_j} N_i^{\mathrm{A}} N_j^{\mathrm{F}}$, which is negative and can break the sign symmetry of $\boldsymbol{T}_{ij}$.

Nonautocatalytic reactions. S_{ij} or R_{ij} depend on N_k, with $k \neq i, j$. This could be the case of impact excitation or relaxation by free electrons, depending on the number of free electrons N_k. In this case, R_{ij} does not contribute to the diagonal components of $\boldsymbol{T}_{ij}^{\mathrm{c}}$ and the other entries are positive or negative according to which states tend to be populated or depopulated by the impact events. In any case, a possible break of the sign symmetry of $\boldsymbol{T}_{ij}$ is left open.

In conclusion, we have shown that dynamical instability in ionization-recombination processes requires the occurring of one or more of the following conditions: (i) electronic exchange between metastable states with low excitation-relaxation rates, (ii) inversion of transition probability in multiply ionized atoms, and (iii) catalytic processes, even if nonautocatalytic.

IV. MODELS OF NONAUTOCATALYTIC INSTABILITY

In order to assess the possibility of a bistable behavior in *nonautocatalytic processes*, determined by the violation of the stability conditions stated in the preceding section, we have to build some particular, possibly simple models exhibiting a first-order phase transition under the control of an external parameter. For this aim, we will study intrinsic photoconduction in a semiconductor in which a two-level deep donor impurity, partially compensated if necessary, provides two different recombination channels. The two levels may consist of the first and second states of ionization of a double-donor impurity (*noncatalytic* process), also of a ground and an excited state of the valence electron, whose transitions are triggered by tunneling between metastable levels of different atoms (again a *noncatalytic* process), or impact excitation (*catalytic but nonautocatalytic* reaction). The dynamical variables of the system are the populations of: the conduction (c) band n, the first and second levels (0 and 1) of the deep donor impurity n_0 and n_1, the deep acceptor (r) level n_r, and the hole population of valence (v) band p. Of course, according to the formalism previously developed, the population p has to be understood as the difference between the number of states of the valence band and its electron population.

As long as thermal rates are negligible and intrinsic photoconduction is involved—that is, no thermal or photoexcitation occurs between delocalized bands and localized levels—the rate equations of the system are the following (with the rates r_{ik} having the significance specified in Sec. III):

TABLE I. The dependence of the transition rates r_{ik} on the dynamical variables are displayed in the case that the two-level impurity is provided by a double donor (second column) or by a ground and an excited state, triggered by tunneling (third column) or impact excitation (fourth column).

	Double ionization	Ground and metastable state (tunneling)	Ground and metastable state (impact excitation)
r_{cv}	g (generating factor)	g	g
r_{vr}	$S_{vr}pn_r$	$S_{vr}pn_r$	$S_{vr}pn_r$
r_{rc}	$S_{rc}n(M-n_r)$	$S_{rc}n(M-n_r)$	$S_{rc}n(M-n_r)$
r_{0c}	$S_{0c}n(N-n_0)$	$S_{0c}n(N-n_0-n_1)$	$S_{0c}n(N-n_0-n_1)$
r_{1c}	$S_{1c}n(n_0-n_1)$	$S_{1c}n(N-n_0-n_1)$	$S_{1c}n(N-n_0-n_1)$
r_{v0}	$S_{v0}p(n_0-n_1)$	$S_{v0}pn_0$	$S_{v0}pn_0$
r_{v1}	$S_{v1}pn_1$	$S_{v1}pn_1$	$S_{v1}pn_1$
r_{01}	0	$S_{01}n_1(N-n_0-n_1)+R_{01}n_1$	$R_{01}n_1$ with $R_{01}=\Sigma_{01}\times n+\rho_{01}$
r_{10}	0	$S_{10}n_0(N-n_0-n_1)+R_{10}n_0$	$R_{10}n_0$ with $R_{10}=\Sigma_{10}\times n+\rho_{10}$

$$\dot{n} = r_{cv} - r_{1c} - r_{0c} - r_{rc},$$

$$\dot{p} = r_{cv} - r_{v1} - r_{v0} - r_{vr},$$

$$\dot{n}_0 = r_{0c} + r_{01} - r_{10} - r_{v0},$$

$$\dot{n}_1 = r_{1c} + r_{10} - r_{01} - r_{v1},$$

$$\dot{n}_r = r_{rc} - r_{vr}. \tag{17}$$

These five equations are not independent, as seen, verifying that $\dot{n}_0+\dot{n}_1+\dot{n}_r+\dot{n}-\dot{p}=0$; in fact, charge conservation imposes the condition

$$n_0 + n_1 + n_r + n - p = N \text{ or } 2N, \tag{18}$$

according to the single or double nature of the deep donors, whose concentration is N (while the deep acceptor compensating centers have concentration M). The transition rates in system (17) have different forms according to the nature of the two-level impurity and the kind of transition which it undergoes, as shown in Table I. Imposing equilibrium—that is, the vanishing of the time derivatives in system (17)—and solving the algebraic system obtained by inserting the continuity equation (18), we can have either single or multiple solutions, depending on the values of the generating factor g and on the transition probabilities. In case of multiple solutions, these are three, two stable, corresponding to stable nodes in the phase space, and one instable, corresponding to a saddle point.

Before entering into some detail about the calculation of equilibrium states, Fig. 2 tries to give some evidence of how a multistable behavior can emerge in the simplest case of impact excitation (*without* ionization) of state 1. Suppose the ground state has capture cross sections such that it provides a recombination channel faster both of the metastable and of the deep acceptor state. At a given rate of production of electron-hole couples, we can have two stable equilibrium states. In the first, a few electrons are in the conduction band, in a way that the frequency of their impacts with the electrons in the ground state are not sufficient to depopulate the ground level. Thus, the fast recombination channel provided by the ground state remains open and the number of the electrons in the conduction band remains small. On the contrary, at the same rate of production of e-h couples, if the number of the electrons in the conduction band is high, their impacts on the donor centers determine a complete de-

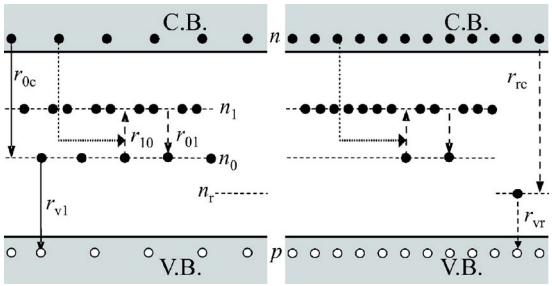

FIG. 2. (Color online) On the left side, fast recombination via the 0 state is predominant, the population of the conduction band is low, and the 0 state is not completely depopulated by impact with the free electrons. On the right side, the high concentration of free electrons maintains lowly populated the 0 state, inhibiting the fast recombination channel and making the mean lifetime of the free carriers longer.

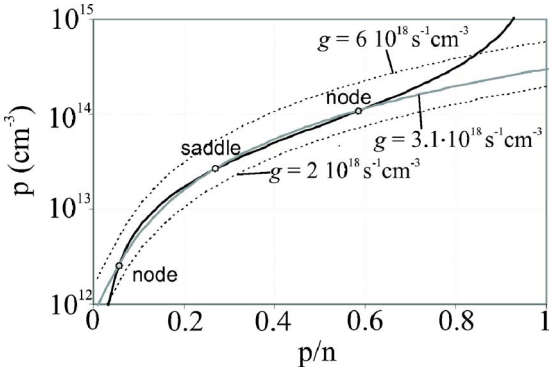

FIG. 3. (Color online) The curves of system (19) are shown for three values of the generating factor g. The values of the other parameters are $S_{0c}=2.5\times10^{-11}$ s^{-1} cm^3, $S_{v0}=5\times10^{-10}$ s^{-1} cm^3, $S_{1c}=5\times10^{-9}$ s^{-1} cm^3, $S_{v1}=1\times10^{-7}$ s^{-1} cm^3, and $N=4\times10^{13}$ cm^{-3}.

population of the ground level and privileges the slow recombination channel provided by the deep acceptors, maintaining a high concentration of the electrons in the conduction band. A similar bistable mechanism can take place also in case of tunneling between metastable states and in the case of double ionization, providing that the transition probabilities make the sign of some of the off-diagonal entries of the matrix $\boldsymbol{T}_{ij}$ negative. The solution of system (17) and (18) (imposing the vanishing of the time derivatives), both in the case of double ionization and in the case of metastable states (triggered by tunneling or impact excitation), reduces to the solutions of a system of two algebraic equations, which have the following form.

Double-donor deep impurity. Given $M=0$ (no compensation), $x=\frac{p}{n}$, $y=S_{v1}p$, and $s_{ij}=\frac{S_{ij}}{S_{1c}}$,

$$y=\frac{g}{N}\frac{1+s_{v1}x+(s_{v1}s_{v0}/s_{0c})x^2}{1+s_{v0}x},$$

$$y=NS_{v1}\frac{x}{1-x}\left(2-\frac{2+s_{v1}x}{1+s_{v1}x+(s_{v1}s_{v0}/s_{0c})x^2}\right). \quad (19)$$

Single-donor, ground and metastable level impurity, tunneling between impurity centers. Given $M=0$ (no compensation), $x=\frac{n_1}{n_0}$, $y=\frac{n_0+n_1}{N}$,

$$(1-y)y=\left(\frac{g}{N^2S_{01}}\right)\frac{1+x}{x-S_{10}/S_{01}}\left(\frac{1}{1+xS_{v1}/S_{v0}}-\frac{1}{1+S_{0c}/S_{1c}}\right),$$

$$\left(\frac{g}{N^2S_{0c}}\frac{1}{(1+S_{1c}/S_{0c})(1-y)}+y-1\right)y=\frac{g}{N^2S_{v1}}\frac{1+x}{S_{v0}/S_{v1}+x}. \quad (20)$$

Single-donor, ground and metastable level impurity, impact excitation. Given $x=\frac{p}{n}$, $y=\frac{R_{01}}{nS_{0c}}$, $s_{ij}=\frac{S_{ij}}{S_{0c}}$, $\sigma_{ij}=\frac{\Sigma_{ij}}{S_{0c}}$, $\rho_{10}=0$ (no photoexcitation),

$$\frac{(1+s_{1c})(s_{v1}s_{v0}x+s_{v0}y+\sigma_{01}s_{v0}+\sigma_{10}s_{v1})}{(s_{v0}x+1+\sigma_{10})(s_{v1}x+y+s_{1c}+\sigma_{01})-(1-\sigma_{01}-y)(s_{1c}-\sigma_{10})}+\frac{s_{vr}M/N}{1+xs_{vr}/s_{rc}}=\frac{gy}{\rho_{01}Nx},$$

$$\frac{(s_{v1}+s_{v0}s_{1c})x+(1+s_{1c})(y+\sigma_{01}+\sigma_{10})}{(s_{v0}x+1+\sigma_{10})(s_{v1}x+y+s_{1c}+\sigma_{01})-(1-\sigma_{01}-y)(s_{1c}-\sigma_{10})}+\frac{M/N}{1+xs_{vr}/s_{rc}}+\frac{\rho_{01}}{NS_{0c}}\frac{1-x}{y}=1. \quad (21)$$

The last three systems can be solved numerically and have multiple solutions for convenient values of the parameters. As an example, in Fig. 3, the curves representing the solutions of the system (19), for several values of the generating factor g, are shown; the values of the other parameters are given in the caption. Note that one of the conditions guaranteeing stability for multiply ionized atoms is not satisfied. In fact, $S_{1c}>S_{0c}$; that is, singly ionized atoms capture electrons more easily than the double ones. This could be true in case of capture by the ground of very low-lying states. In Fig. 4, the hysteresis curve for the population of the localized levels is shown for the bistability induced by tunneling between the ground and metastable states of different atoms [system (20)] and for the parameters specified in the caption.

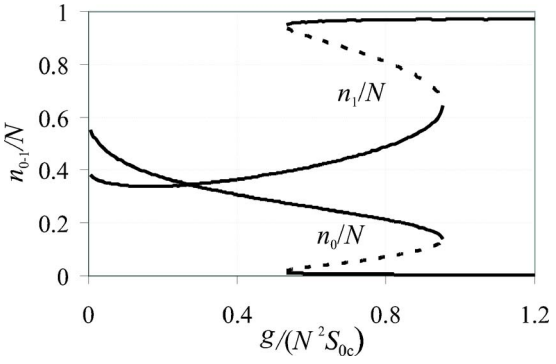

FIG. 4. (Color online) The hysteresis curve of the population of 0-1 levels for the bistability induced by tunneling between the ground and metastable states of different atoms [system (20)]. The values of the parameters are the following: $N=10^{17}$ cm^{-3}, $S_{10}=6\times10^{-9}$ s^{-1} cm^3, $S_{01}=4\times10^{-9}$ s^{-1} cm^3, $S_{v1}=2\times10^{-9}$ s^{-1} cm^3, $S_{v0}=2\times10^{-11}$ s^{-1} cm^3, $S_{1c}=2.5\times10^{-10}$ s^{-1} cm^3, and $S_{0c}=1\times10^{-9}$ s^{-1} cm^3.

In the case of impact excitation, bistability can be triggered not only by a variation of the light intensity, but also by the electric field, which enters in the term Σ_{ij} of Table I. In a more realistic modelization, Σ_{ij} should be also an increasing function of the free carrier density due to the shielding of charged impurities, an effect which has long been recognized as a possible instability mechanism in conjunction with impurity breakdown.[5] Here we neglect it, because we are interested in proving that the competition between different recombination channels could be sufficient alone to explain multistability. Figure 5 shows a three-dimensional section of the catastrophe manifold representing the solutions of system (21). The surface presents a pocket whose limbs, projected onto the control parameters plane $\Sigma_{10}-g$, form two cusps C_1 and C_2. Every pattern in the control parameter plane crossing the curves limited by the cusps involves a first-order transition of the system.

V. CONCLUSIONS

It has been proved in this article that every attempt to model multistability in ionization-recombination processes

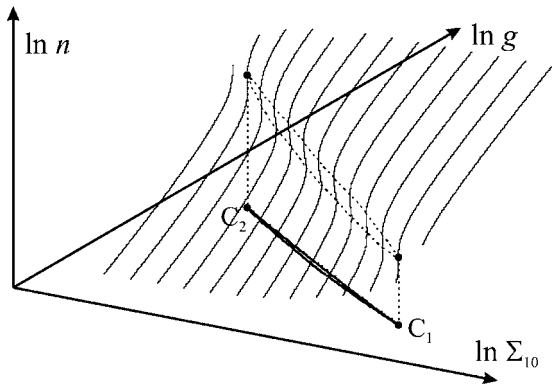

FIG. 5. A three-dimensional section of the catastrophe manifold representing the solutions of system (21) are shown in Σ_{10}-g-n space. C_1 and C_2 are the two cusps of the system. The position of the origin in the log-log-log space is taken arbitrarily. The other values of the parameters are $S_{0c}=1\times10^{-6}$ s^{-1} cm^3, $S_{1c}=1\times10^{-8}$ s^{-1} cm^3, $S_{v0}=6\times10^{-7}$ s^{-1} cm^3, $S_{v1}=1\times10^{-10}$ s^{-1} cm^3, $S_{rc}=2\times10^{-9}$ s^{-1} cm^3, $S_{vr}=5\times10^{-9}$ s^{-1} cm^3, $\Sigma_{01}=0$, $\rho_{01}=1\times10^4$ s^{-1}, $N=1\times10^{14}$ cm^{-3}, and $M=2\times10^{13}$ cm^{-3}.

has to manage some break of the sign symmetry of the Jacobian matrix of the system. Several physical situations have been proved to satisfy this condition without the intervention of any kind of autocatalytic reaction: namely, electronic exchange between metastable states, inversion of emission or capture probabilities in multiply ionized atoms, and impact excitation of metastable states (even without subsequent ionization). Moreover, a general theory has been developed showing why these are the only possible ways to obtain this effect. Finally, a modelization of a semiconductor suitably doped with a two-level deep-donor impurity has been utilized to obtain multistability in each of the three physical situations mentioned above, having a first-order nonequilibrium phase transition driven by light irradiation in conjunction or not with impact excitation by an electric field. Thus, a diffuse opinion about the uniqueness and the universality of the impact ionization mechanism in determining dynamical instability in ionization-recombination processes has been refuted on a theoretical basis.

Experimental investigation is worth doing to discriminate possible nonautocatalytic patterns in dynamical instability, especially in the case of intrinsic photoinduced charge generation in the absence of an electric field. Furthermore, the influence of the electric field on multistable photoconduction should be more deeply investigated to distinguish the weight of impact ionization from that of impact excitation. These two effects, indeed, determine the occurrence of two very different kinds of dynamic instability, the first based on a sort of auto enhanced charge generation, the other on the competition between different-speed recombination channels.

ACKNOWLEDGMENTS

I am indebted to Silvio Sciortino for useful and clarifying discussions and to Annalisa Ciampalini for her mathematical support.

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