

# Impurity recombination of Rydberg matter

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We consider the trapping of electrons by electronegative impurities from the conduction band for condensed systems of highly excited atoms (Rydberg matter). The trapping can occur both with photon emission and through a nonradiative mechanism. In both cases the transition of electrons from the conduction band of the condensate to impurity orbitals is possible in practice only in the regions where the electron motion is classically admissible. We show that the rate of radiative processes increases with an increase in the quantum-mechanical level of excitation of the atoms, whereas the rate of the nonradiative processes decreases rapidly. When the impurity density is comparable to the skeleton density of the Rydberg matter, the trapping of electrons by impurities leads to a fast decay of the condensate. At the same time, for low densities of the impurities, after electron trapping they will be incorporated into the structure of the Rydberg matter; as a result, the recombination of excitations is improbable.

## 1. INTRODUCTION

One can invoke condensed excited states (CES) to describe dense systems of excited centers (atoms, molecules, impurities in solids).<sup>1,2</sup> The well known electron-hole state, which occurs as the result of the condensation of excitons-elementary excitations in semiconductors—is an example of CES.<sup>3</sup> The interaction between separate excitations becomes more and more important as the density of excited centers increases. While for low densities the interaction leads merely to a renormalization of their spectrum, for sufficiently dense systems a qualitative change in the structure of the medium becomes possible, and the result of this is the formation of energetically more favorable condensates from the set of excited centers. The strong interaction between the electrons in the resulting condensate is conserved, but it is no longer related to the effective lifetime of the excited medium. Moreover, for highly excited atoms, the lifetime of the CES turns out to be macroscopically long.<sup>5</sup> A CES formed as the result of condensation of highly excited atoms or molecules is called a Rydberg substance, or Rydberg matter (RM).<sup>5,6</sup> If the density of the excitations is low, they can be considered an almost perfect gas, and renormalization of their spectrum reduces to a change in both the energy and the lifetime. As the density is increased, the damping of the excitations may become so large that the concept of an elementary excitation loses its meaning. The system of excitations must be considered a Fermi liquid, and the strong damping means only that we must look for elementary excitations near the limiting Fermi momentum, in complete accordance with Landau's theory of a Fermi liquid.<sup>4</sup> As regards the lifetime of the condensate (the excited medium), there is no reason whatever why it should necessarily always decrease.

In RM the external electrons form a Fermi liquid with the neutralizing ions immersed in it. Notwithstanding its low density-gaseous according to its parameters—RM is a solid metallic state of matter. It is possible to calculate the

equilibrium parameters of RM in the framework of a density functional theory using the concept of the pseudopotential of excited atoms from which the CES is formed.<sup>2</sup> For definiteness, we give briefly the numerical parameters of RM formed as the result of the condensation of cesium atoms excited in an  $s$  state. The spectrum of the excited states is well known for cesium atoms, which makes it possible to obtain estimates quantitatively, albeit with a certain amount of crudeness. The CES formed when excited cesium atoms condense were observed in Refs. 6–8. We restrict ourselves to excited states with principal quantum numbers  $n=12, 13$ , and  $14$ , which are of most interest to us. For smaller quantum numbers, the lifetime of the CES is less than a second, and for  $n > 14$  the binding energy is already comparable with room temperature.

In Table I we give the skeleton density of the RM of excited cesium atoms, the interionic distances, the binding energies (sublimation energies at zero temperature) per excited atom in the condensate, and an estimate of the lifetime. The lifetime of RM is calculated assuming it to be due to radiative recombination and nonradiative (Auger) processes.<sup>9</sup> At a low skeleton density, the collectivized valence electrons guarantee a sufficiently high binding energy for stability.<sup>2</sup>

At present, the theory of RM has been developed for the ideal case of zero temperature, assuming that there are no other recombination channels apart from just radiative recombination and Auger processes. The behavior of RM at a finite temperature and in the presence of impurities which can trap electrons from the CES requires a special analysis.

All the RM parameters given above were estimated neglecting temperature effects. The justification for normal metals is provided by the high Fermi energy of the electrons. However, in our case the electron density is too low to be a straightforward basis for neglecting the temperature. Moreover, if we start with a perfect Fermi gas model,

TABLE I.

Excitation level $n$	Skeleton density $\rho$ , $1/\text{cm}^3$	Interionic distance $L$ , $\text{\AA}$	Binding energy $B$ , K	Lifetime $\tau$ , s	Fermi energy $E_F$ , K
12	$1.1 \cdot 10^{18}$	120	1590	25	1700
13	$5.3 \cdot 10^{17}$	153	1310	5	1370
14	$2.8 \cdot 10^{17}$	189	1120	$3 \cdot 10^5$	1110

we see easily that the electron density below which they behave classically,

$$n_0 = \frac{1}{4\pi^3 \hbar^3} (2\pi m k_B T)^{3/2}$$

is, at room temperature, lower than the electron density in the RM considered.<sup>1)</sup> However, it was already noted in Ref. 2 that the free electron model is too crude for a CES of excited atoms, and it ceases to operate even for excitation levels only a few units above the ground state. This is connected with the strong inhomogeneity of the electron liquid of a CES, genetically connected with the sharply inhomogeneous electron distribution in a highly excited atom. In Table I we give estimates of the Fermi energy  $E_F$  of the electrons in the conduction band of RM. Since under normal conditions  $E_F$  is, as before, higher than  $k_B T$ , we shall no longer consider here temperature corrections, assuming that the electron liquid of the RM is degenerate.

## 2. IMPURITY RECOMBINATION

The decay of RM may be related not only to radiative and Auger transitions to low-lying and unoccupied levels of the ions of the intrinsic skeleton (intrinsic recombination), but also to the presence of molecules which have a high electron affinity. Electronegative molecules can trap electrons from RM states, forming negative ions. These can recombine when colliding with positive ions from the skeleton. As a result, the RM decays, and it turns out that the rate of such a process may be very high.

Electron affinity is observed in many molecules.<sup>10,11</sup> The affinity energy is small—of the order of 1 eV.<sup>2)</sup> The size of negative ions is a few angstroms. At the same time, the size of the elementary cells of RM, which is of the same order of magnitude as the size of highly excited atoms, is several hundred times larger. Comparing the affinity energy and the size of the negative ions with the RM parameters, we conclude that for a model of electronegative molecules, we can use local potential wells against a background of a slowly changing total electron potential for the electron. We show in Fig. 1 the interaction potential of a valence electron of RM inside an elementary cell of a condensate of cesium atoms excited to the 12-S state, containing a single electronegative water molecule. We model the potential of the latter by a well 3  $\text{\AA}$  in size with an electron binding energy of  $|E_e| = 0.9$  eV. As long as the electronegative molecule is far from the high electron density region, we can neglect screening effects.

The trapping of an electron by an electronegative center takes place through radiative and Auger processes. If

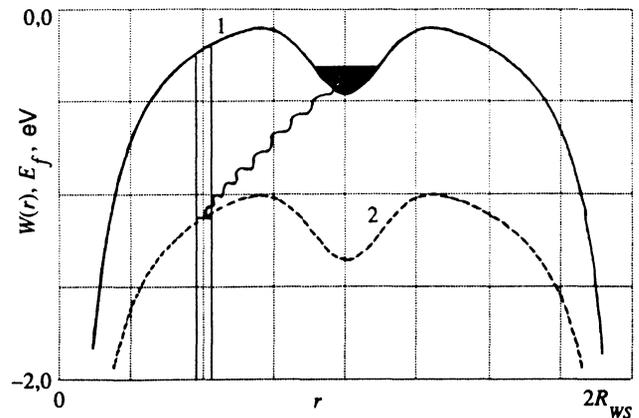


FIG. 1. 1) Effective single-electron potential  $W(r)$ . 2) Final energy  $E_f$  of an electron trapped by an impurity at different points of the elementary cells of a condensate of cesium atoms excited in the 12S state. The model of the electronegative impurity is a well of size 3  $\text{\AA}$  with a binding energy  $|E_e| = 0.9$  eV for the electron.

the electronegative molecule is in the Wigner–Seitz cell at a distance  $r < r_c$  from the central ion, where  $r_c$  determines the boundary of the region where the RM electrons are classically allowed to move, the trapping of an electron takes place when it tunnels through a potential barrier. This classically allowed region for the motion is for RM situated in a thin layer near the boundary of the elementary cell where the total potential has a local minimum (see Fig. 1). The probability for such a process is strongly suppressed due to the large width of the barrier. Direct capture processes are thus dominant when an electron is incident on an impurity in the region where the electron motion is classically allowed. It is therefore sufficient, when estimating the rate of decay of the RM due to electronegative components, to evaluate the electron trapping in that region. Generally speaking, screening effects, taking into account the relatively low binding energy of the electron in a negative ion, may play an important role in that region. For instance, the bound state of an electronegative molecule may completely disappear. Nonetheless, we shall neglect screening here. It is clear that this makes it possible to obtain only an upper limit for the decay rate.

## 3. RADIATIVE ELECTRON TRAPPING BY IMPURITIES

We consider the radiative trapping of an electron from the conduction band of RM. In that case, one of the RM electrons is trapped in an energetically more favorable state of a negative ion, which remains in the total field produced by all other electrons and the ions of the RM skeleton, and a photon is emitted with an energy

$$\hbar\omega \cong E_i - E_f, \quad (1)$$

where  $E_i$  is the initial and  $E_f$  the final energy of the electron trapped by the impurity. Let the electronegative center be in a fixed Wigner–Seitz cell at the point  $r_f$ . The probability of this event is  $p(r_f)d^3r_f$ . It is clear that  $p(r_f) = N$ , where  $N$  is the number density of electronegative molecules. Since we agreed to neglect the effects of the

redistribution of the charges in the RM associated with the presence of the electronegative molecules, and if we take into account the small size of the negative ion, we can take the electron energy in the final state to be approximately

$$E_f = E_e + \langle W(r_f) \rangle, \quad (2)$$

where  $E_e$  is the energy of an electron in an isolated negative ion and  $\langle W(r_f) \rangle$  the average value of the effective single-electron intracell potential<sup>12</sup> in the region where the electron is localized on the impurity. The probability of a radiative transition is given by the well known formula from time-dependent perturbation theory,

$$dW_{fi} = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_i - E_f - \hbar\omega) \frac{d\kappa}{(2\pi)^3}, \quad (3)$$

where the transition matrix element for spontaneous decay has the form

$$V_{fi} = -\frac{e}{mc} \left( \frac{2\pi c^2 \hbar}{\omega} \right)^{1/2} \mathbf{e}_p \langle f | \hat{\mathbf{P}} \exp(i\mathbf{k}\mathbf{r}) | i \rangle. \quad (4)$$

Here  $\mathbf{e}_p$  and  $\mathbf{k}$  are the polarization vector and the wave vector of the emitted photon,  $\hat{\mathbf{P}}$  is the momentum operator,  $|i\rangle$  is the electron wave function in the RM conduction band, and  $|f\rangle$  is the wave function of the electron trapped by an electronegative impurity. For the latter we can use various approximations of the wave function in a negative ion,<sup>11</sup> although in our case, where the electron trapped by the impurity is strongly localized (compared to its RM state), the actual form of this function is unimportant.

In the dipole approximation, using the identity

$$\langle f | \hat{\mathbf{P}} | i \rangle = -im\omega \langle f | \mathbf{r} | i \rangle,$$

we can rewrite the transition matrix element in the form

$$V_{fi} = \frac{ie\omega}{c} \left( \frac{2\pi c^2 \hbar}{\omega} \right)^{1/2} \langle f | \mathbf{e}_p \mathbf{r} | i \rangle. \quad (5)$$

After summing over all possible states of the photon field, we find for the transition probability from the RM state  $|i\rangle$  to the impurity state  $|f\rangle$

$$W_{fi} = \frac{4e^2 (E_i - E_f)^3}{3\hbar^4 c^3} |\langle f | \mathbf{r} | i \rangle|^2. \quad (6)$$

We now consider the integral

$$\langle f | \mathbf{r} | i \rangle = \int \psi_f^*(\mathbf{r}) \mathbf{r} \psi_k(\mathbf{r}) d\mathbf{r}.$$

Since the electronegative impurity is at the point  $r_f$ , the electron wave function  $\psi_f^*(\mathbf{r})$  at the impurity is localized close to that point. To high accuracy, we can thus write

$$\langle f | \mathbf{r} | i \rangle = \mathbf{r}_f \psi_k(\mathbf{r}_f) \int \psi_f^*(\mathbf{r}) d\mathbf{r}.$$

We can now simplify Eq. (6), assuming that the volume of the impurity equals  $V$ :

$$W_{fi} = \frac{4e^2 (E_i - E_f)^3 r_f^2 V}{3\hbar^4 c^3} |\psi_k(\mathbf{r}_f)|^2. \quad (7)$$

We thus see that the capture probability for an electron of energy  $E_i$  from the RM conduction band is directly proportional to the square of the modulus of the wave function, i.e., to the charge density of the electron at the point where the impurity is localized. This is just the reason why the capture is practically impossible if the impurity is far from the region where electron motion is classically allowed.

For the number of transitions per unit volume and unit time,

$$W = \sum W_{fi},$$

where the summation is over all RM states (we assume the  $|f\rangle$  state to be nondegenerate). We find

$$W = \frac{4e_f^2 V}{3\hbar^4 c^3} \int dE_i N(E_i) f(E_i) (E_i - E_f)^3 |\psi_k(\mathbf{r}_f)|^2, \quad (8)$$

where  $N(E_i)$  is the density of states in the RM conduction band and  $f(E_i)$  is the Fermi distribution function.

The electron wave functions  $|i\rangle$  in the RM conduction band can be written in the form of Bloch functions. However, such a representation is not altogether convenient for the calculations. The fact is that RM is made up of highly excited atoms, in which the electrons are predominantly at a distance of the Bohr radius from the ion. In RM there occurs an additional collapse of the electrons to the regions farthest from the ions—to the boundaries of the elementary cells of the condensate which was formed. For the calculations it is thus advisable to use Wannier functions localized at the sites.

We expand the wave function  $|i\rangle$  of an electron with wavevector  $\mathbf{k}$  in the conduction band in the lattice vectors  $\mathbf{a}_j$  of the RM,

$$|i\rangle = (\Omega)^{1/2} \sum_j \varphi(\mathbf{r} - \mathbf{a}_j) \exp(i\mathbf{k}\mathbf{a}_j), \quad (9)$$

where  $\Omega$  is the volume of an elementary cell of the RM. We assume the volume of the RM to be equal to unity, so that the total number of elementary cells is equal to  $1/\Omega$ . The Wannier functions  $\varphi(\mathbf{r} - \mathbf{a}_j)$  pertaining to different sites are orthogonal, and they are, moreover, normalized to unity. For the square of the modulus of the RM electron wave function, we find

$$|\psi_k(\mathbf{r})|^2 = \Omega \sum_j |\varphi(\mathbf{r} - \mathbf{a}_j)|^2 + \Omega \sum_{j \neq l} \varphi^*(\mathbf{r} - \mathbf{a}_j) \times \varphi(\mathbf{r} - \mathbf{a}_l) \exp(i\mathbf{k}(\mathbf{a}_j - \mathbf{a}_l)). \quad (10)$$

The density of the RM electron liquid  $n(\mathbf{r})$  can also be written in the site representation:

$$\begin{aligned} n(\mathbf{r}) &= \sum_k |\psi_k(\mathbf{r})|^2 \\ &= \sum_j |\varphi(\mathbf{r} - \mathbf{a}_j)|^2 + \Omega \sum_k \sum_{j \neq l} \varphi^*(\mathbf{r} - \mathbf{a}_j) \\ &\quad \times \varphi(\mathbf{r} - \mathbf{a}_l) \exp(i\mathbf{k}(\mathbf{a}_j - \mathbf{a}_l)). \end{aligned} \quad (11)$$

The second term in Eq. (11) is equal to zero, since

$$\Omega \sum_k \exp(ik(\mathbf{a}_j - \mathbf{a}_l)) = \delta_{jl}.$$

On the other hand, the RM electron liquid density can be written as a sum of nonintersecting cell densities:

$$n(\mathbf{r}) = \sum_j \rho(\mathbf{r} - \mathbf{a}_j).$$

The electron liquid density at each site (in each elementary cell) can, in the approximation of spherical Wigner-Seitz cells of radius  $R_{WS}$  be defined by the functions

$$\rho(r) = \begin{cases} \rho_0 \exp(-(r - R_{WS})^2/D^2) & \text{for } r < R_{WS} \\ 0 & \text{for } r > R_{WS} \end{cases}. \quad (12)$$

The variational parameter  $D$  mimimizes the energy of the system for  $D \approx 1.8R_n^{0.4}$  where  $R_n$  is the radius of the Ashcroft pseudopotential of the excited atom in atomic units. The coefficient  $\rho_0$  must be determined from the condition that the cell is electrically neutral,

$$\int_{\Omega} d\mathbf{r} \rho(\mathbf{r}) = 1.$$

If we now compare (11) and (12), we get as the zeroth approximation for the Wannier functions, apart from the phase,

$$\varphi^{(0)}(\mathbf{r} - \mathbf{a}_j) = \rho^{1/2}(\mathbf{r} - \mathbf{a}_j), \quad (13)$$

and for the square of the modulus of the wavefunction, which occurs in (8), we find

$$|\psi_k(\mathbf{r}_f)|^2 \approx \Omega \sum_j |\varphi^{(0)}(\mathbf{r}_f - \mathbf{a}_j)|^2 = \Omega \rho(\mathbf{r}_f), \quad (14)$$

where out of the whole sum, only the density of the electrons in the cell containing the impurity remains. Notwithstanding the rather artificial form of our approximation of the Wannier functions, they are orthonormal, and give the correct form for the expression for the electron density. It is possible in this approximation to estimate the characteristic time for the intrinsic RM recombination due to transitions to low-lying unoccupied orbitals of the RM ions.<sup>5,9</sup> It is useful to bear in mind that Wannier functions are used precisely for computational purposes, although they are not always suitable for a direct interpretation of physical phenomena.<sup>13</sup>

Substituting (14) into (8) and summing over all possible positions of the impurity inside the elementary cell, taking into account that the total number of cells is equal to  $1/\Omega$ , we find for the probability  $W_r = \Omega W$  of radiative electron capture

$$W_r = \frac{16\pi e^2 V \Omega N}{3\hbar^4 c^3} \int_{\Omega} d\mathbf{r}_f r_f^4 \rho(r_f) \int dE_i N(E_i) f(E_i) \times (E_i - E_f)^3. \quad (15)$$

We can further simplify the problem using the fact that the RM electrons are localized near the boundaries of the cells, i.e., the steep behavior of  $\rho(r)$ . Indeed, the first integral in

(15) is concentrated practically completely on  $r_f \approx R_{WS}$ . However, in that region the effective cell potential changes slowly,  $\langle W(r_f) \rangle \approx W(R_{WS})$ . Moreover, the electron energy  $E_i$  runs through values from the bottom of the conduction band to the limiting value of the Fermi energy  $E_f$ . Since the RM conduction band is relatively narrow, we can reasonably accurately replace the frequency (1) of the emitted photons by an average quantity

$$\hbar \langle \omega \rangle \cong E_f - E_e - W(R_{WS}). \quad (16)$$

We assume here that  $|E_e|$  is much larger than the RM conduction band width.

Using the sum rule

$$\int dE_i N(E_i) f(E_i) = \frac{1}{\Omega},$$

we finally obtain for the decay probability

$$W_r = \frac{4e^2 V N \langle \omega \rangle^3 R_{WS}^2}{3\hbar c^3}. \quad (17)$$

For numerical estimates it is convenient to make this formula dimensionless, using atomic units (the Bohr radius  $a_0$  and the atomic frequency  $\omega_a = me^4/\hbar^3$ ),

$$W_r = \frac{4VN}{3} \left( \frac{e^2}{\hbar c} \right)^3 \left( \frac{\langle \omega \rangle}{\omega_a} \right)^3 \left( \frac{R_{WS}}{a_0} \right)^2 \omega_a. \quad (18)$$

For  $n=12$  we have for the cell radius  $R_{WS} = 113.4$ .<sup>12</sup> If the impurity parameters are such that  $\hbar \langle \omega \rangle = 1$  eV,  $V = 3 \cdot 10^{-23}$  cm<sup>-3</sup>,  $N = 10^{17}$  cm<sup>-3</sup> (roughly a 10% content of impurities in relation to the skeleton density), the probability for the trapping of a RM electron is

$$W_r = 4 \cdot 10^4 \text{ s}^{-1}.$$

This means that after a time of the order of  $2.5 \cdot 10^{-5}$  s<sup>-1</sup>, electronegative molecules with an electron affinity energy of 1 eV are changed to negative ions, absorbing electrons from the RM conduction band in the process. This is several orders of magnitude shorter than the time for intrinsic recombination (see Table I) due to transitions to low-lying unoccupied orbitals of the RM ions.<sup>9</sup>

The trapping of RM electrons by electronegative impurities is thus, indeed, an extremely efficient channel for the transition of electrons from the RM to an energetically more favorable state, with the formation of negative ions.

#### 4. IMPACT IMPURITY RECOMBINATION OF RM

We turn to a consideration of impurity recombination of RM due to Auger processes. In impact recombination, one of the RM electrons (1) collides with another electron (2) and makes a transition to an impurity orbital  $|f\rangle$ , transferring the excess energy to the second electron. We shall assume that the second electron does not flip into another band as a result of this transition. The transition probability is

$$W = \frac{2\pi}{\hbar} |M_{f,3,2,1}|^2 \delta(E_1 + E_2 - E_3 - E_f). \quad (19)$$

It is convenient to write the matrix element of the perturbed screened Coulomb potential using the Bloch components of the wave functions  $U_k(r)$ . To simplify the calculations, we assume that the electronegative molecules form an unfilled impurity band. The behavior of an electron in this band can be described using a linear combination of impurity orbitals. The matrix element takes the form

$$M_{f,3,2,1} = V_{k_3-k_1} I_1 I_2 \delta_{k_1+k_2, k_3+k'_1}, \quad (20)$$

where the Fourier component of the screened Coulomb potential with a screening constant  $\lambda \approx 1/D$  is

$$V_{k_3-k_1} = \frac{4\pi e^2}{\lambda^2 + |k_3-k_1|^2}, \quad (21)$$

while the overlap integrals of the Bloch factors of the wave functions are evaluated inside a single elementary cell

$$I_1 = \frac{1}{\Omega} \int_{\Omega} dr_1 U_3^*(\mathbf{r}_1) U_1(\mathbf{r}_1), \quad (22)$$

$$I_2 = \frac{1}{\Omega} \int_{\Omega} dr_2 U_f^*(\mathbf{r}_2) U_2(\mathbf{r}_2).$$

The number of transitions per unit time and unit volume is determined by summing (19) over all possible states of the system,

$$W' = \frac{2\pi}{\hbar} \sum_{3,2,1} |M_{f,3,2,1}|^2 N(E_1 + E_2 - E_3) f(E_1) f(E_2) \times [1 - f(E_3)]. \quad (23)$$

We give an upper estimate of the probability  $W_0 = \Omega W'$  for nonradiative trapping. To do this, we replace the form factor (21) by its maximum value,

$$(V_{k_3-k_1})_{\max} = 4\pi/\lambda^2,$$

and we simplify the square of the moduli of the overlap integrals (22), using the fact that the modulus of the integral of any function is no greater than the integral of the modulus of that function,

$$|I_1|^2 \leq 1, \quad |I_2|^2 \leq V\rho(r_f).$$

We then put the electron energies close to the Fermi energy,  $E_1 \approx E_2 \approx E_3 \approx E_F$ , thereby obtaining an estimate for the probability of impact trapping of a RM electron:

$$W_0 = \frac{32\pi^3 e^4 V\rho(r_f) N(E_F)}{\hbar \lambda^4 \Omega}. \quad (24)$$

The density of states near the Fermi level can be estimated to be

$$N(E_F) \approx 2mD^2/\hbar^2\Omega.$$

Hence, the probability of trapping an RM electron through the nonradiative mechanism is estimated by the expression

$$W \approx 36\pi V\rho(r_f) (D/R_{WS})^6 \omega_a. \quad (25)$$

As in the case of radiative transitions, the trapping of electrons from the RM conduction band through the nonradiative mechanism is thus possible only in spatial regions where the electron liquid is localized.

Finally we have for the probability of nonradiative impurity decay after averaging over the volume of an elementary cell

$$W_0 \approx 36\pi V N (D/R_{WS})^6 \omega_a. \quad (26)$$

We emphasize that this formula can be used only for a crude estimate of the rate of impurity impact recombination. For the impurity and RM parameters given earlier, we find with  $n=12$

$$W_0 \approx 2.5 \cdot 10^6 \text{ s}^{-1},$$

which means that possibly nonradiative processes may dominate.

Comparing (26) with Eq. (18) for the probability of radiative recombination, we see that as the level  $n$  of excitation increases, the rate of radiative processes increases rapidly (proportional to  $R_{WS}^2$ ), while the rate of impact recombination, in contrast, decreases rapidly (proportional to  $R_{WS}^{-6}$ ). This means that even if Auger processes dominate for low-excitation CES, ultimately radiative recombination will become the main mechanism for RM when the level of excitation increases.

## 5. STRUCTURE OF RM IN THE PRESENCE OF ELECTRONEGATIVE IMPURITIES

We have everywhere assumed implicitly that the electronegative molecule abundance was negligible in comparison with the RM electron density:

$$N/\rho \ll 1. \quad (27)$$

In the opposite case, the structure of RM is fundamentally changed, since due to the trapping of electrons the coupling between excited atoms in the lattice is lost. Therefore, if there are many electronegative impurities, ultimately they must inevitably lead to a restructuring and a decay of the RM.

Of course, if there are very few electronegative molecules inside the RM, we can altogether neglect the electron trapping processes. We give in Table I the calculated lifetimes  $\tau$  due to intrinsic recombination processes. Since in our case nonradiative transitions dominate, the condition for neglecting impurities is given by

$$W_0 < 1/\tau,$$

whence follows the requirement for the density of the molecules:

$$N < N_0 = \frac{1}{36\pi V \omega_a \tau} \left( \frac{R_{WS}}{D} \right)^6. \quad (28)$$

For RM of cesium with an excitation level  $n=12$ , we find from this for the impurity density  $N_0 = 7 \cdot 10^9 \text{ cm}^{-3}$ .

Now let only the weaker condition (27) be satisfied. Apparently in this case one can easily describe a catalytic process for destroying RM when there are electronegative gases present: an electronegative atom absorbs an electron,

it becomes a mobile negative ion which collides with a positive ion in the RM lattice, and neutralizes the latter through recombination. The original electronegative atom is formed, as well as a new neutral atom which may or may not be electronegative. This means that a catalytic process is realized or, on the other hand, a process with multiplication of electronegative centers which may be explosive in nature.

Does this happen? Is a catalytic process realized? Of course, electronegative impurities in RM absorb electrons and, as one can see from the earlier consideration [see Eqs. (7) and (25)], the absorption of electrons occurs predominantly at the boundaries of the Wigner–Seitz cells.

We turn now to Eq. (2) for the energy of an electron trapped by an electronegative impurity. The dashed curve in Fig. 1 shows the position of the energy level of an electron trapped by an impurity at different points of the elementary cell of RM formed from atoms with  $n=12$ . We see that the energy of the electron in the final state, i.e., in fact, the energy of the negative ion, has a local minimum near the boundary of the Wigner–Seitz cell, exactly like the RM electrons. The nature of this minimum is the same as for the RM electrons; an effective attraction occurs due to exchange–correlation interactions with the RM electrons, the density of which is small here.<sup>3)</sup> Thus, for the resulting newly-formed negative ions as well, there is a potential barrier which prevents them from penetrating the inner regions of the ions of the RM lattice, and which suppresses the recombination of ions with the corresponding development of a catalytic process.

We thus conclude that as long as the abundance of electronegative molecules is negligible, effective trapping of electrons from RM will occur, but the negative ions formed

will not recombine with the positive ions in the lattice, being incorporated instead into the RM structure.

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<sup>1)</sup>At room temperature we have  $n_0=2.5 \cdot 10^{19} \text{ cm}^{-3}$ .

<sup>2)</sup>As an example, we give the electron affinity energies for a few molecules (eV): O<sub>2</sub>: 0.44, H<sub>2</sub>O: 0.9, O<sub>3</sub>: 2.0, NO: 0.03, NO<sub>2</sub>: 2.4, SO<sub>2</sub>: 1.06.

<sup>3)</sup>The polarization interaction of a charge with its image is a classical analog of this interaction.

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