

# Decay kinetics of triplet He( $2^3S$ ) excitations in liquid and solid helium

A. V. Konovalov and G. V. Shlyapnikov

*I. V. Kurchatov Atomic Energy Institute*

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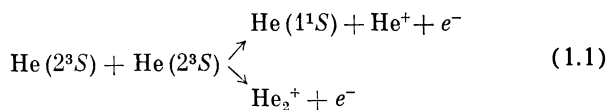
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A theory describing the decay kinetics of the metastable triplet state of helium He( $2^3S$ ) in liquid and solid helium has been constructed. Of fundamental importance in liquid helium is the presence of a strong magnetic field which polarizes the electron spins and imposes a prohibition on the process of ordinary Penning ionization during the paired interaction of triplet excitations. Penning ionization continues to be possible only when the weak spin dipole interaction of triplet particles is taken into account. The corresponding exchange-dipole mechanism of Penning ionization leads to a characteristic decay time  $\tau_{\text{exd}} \approx (10^{17}/n)$  sec and becomes dominant when the density of triplet helium is  $n > 10^{16} \text{ cm}^{-3}$ . At lower densities, the decay mainly involves spontaneous de-excitation of the triplet molecules He $_2$  ( $^3\Sigma_u^+$ ), which are formed efficiently when triplet helium atoms interact with helium atoms in the ground state. A quantum-mechanical calculation of the characteristic time of this process gives  $\tau_s \approx 10$  sec. A fundamentally different situation independent of the magnetic field takes place in solid helium at  $T \lesssim 1$  K, when the diffusion of triplet excitations is frozen. The latter fact itself suppresses ordinary Penning ionization (as well as exchange-dipole ionization), the probability of which decreases exponentially as the distance between the triplet particles increases, and up to  $n \sim 10^{19} \text{ cm}^{-3}$ , the radiative decay of triplet molecules with a characteristic time  $\tau_s \approx 10$  sec becomes predominant. Only at higher  $n$  does the direct dipole mechanism of Penning ionization with a characteristic time  $\tau_{\text{dd}} \propto 1/n^2$  predominate, this being a process caused by the electric dipole interaction of triplet molecules at the average distance between them. This process turns out to be possible because of the presence of a nonzero, albeit very small, dipole moment for the transition of the triplet molecule He $_2$  ( $^3\Sigma_u^+$ ) to the ground electronic state.

## 1. INTRODUCTION

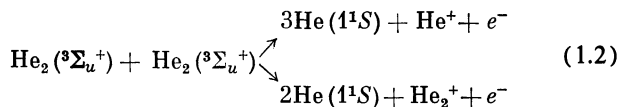
The unique long-lived metastable triplet state of the helium atom He( $2^3S$ ), which has a radiative lifetime  $\tau_0 \approx 8 \times 10^3$  sec,<sup>1,2</sup> elicits great interest in view of the prospects of developing new macroscopic quantum systems and the possibility of storing high-energy excitations (the excitation energy of this state is 19.8 eV). However, the development of systems with a high concentration of triplet helium involves serious difficulties.

In the gaseous phase under ordinary conditions, such difficulties involve decay due to the nonthreshold process of Penning ionization (see, for example, Ref. 3):



The characteristic decay time satisfies  $\tau \propto 1/n$ , where  $n$  is the density of triplet helium, and is of order seconds starting at densities as low as  $n \sim 10^9 \text{ cm}^{-3}$ .

The decay of triplet excitations of He( $2^3S$ ) in liquid helium also involves the process of Penning ionization (see Ref. 4). The situation in this case is unusual because the ionization process involves the participation of excited triplet molecules He $_2$  ( $^3\Sigma_u^+$ ), which have a binding energy  $\approx 1.5$  eV and are formed in times  $\sim 10^{-5}$  sec when He( $2^3S$ ) atoms recombine with the surrounding unexcited helium atoms. In this case the decay process



turns out to be diffusion-controlled, i.e., the decay event takes place with a probability of order unity when molecules approach by diffusion to a certain distance  $r_0$ . This distance is determined by equating the characteristic ionization time and characteristic diffusion time  $\tau_D \sim r_0^2/D$  ( $D$  being the diffusion coefficient of triplet molecules in liquid helium) and turns out to be somewhat greater than the interatomic distance in liquid helium  $R_0 \approx 3.5$  Å. In that case decay time is  $\tau \propto 1/4\pi r_0 D n$ , and at the experimentally achieved densities of triple helium  $n \sim 10^{12} - 10^{13} \text{ cm}^{-3}$ , it amounted to  $\sim 10^{-2} - 10^{-3}$  sec.<sup>3</sup>

Experiments in solid helium<sup>5</sup> indicate a marked retardation of the diffusion of the triplet molecules He $_2$  ( $^3\Sigma_u^+$ ) even at temperatures close to the melting point. At the triplet helium density reached,  $n \sim 10^{14} - 10^{15} \text{ cm}^{-3}$ , spontaneous radiative decay of the excited molecules He $_2$  ( $^3\Sigma_u^+$ ) is dominant, for the characteristic time of which the value  $\tau \approx 15$  sec was obtained.<sup>5</sup> These results, however, contradict the conclusion reached in an earlier experiment<sup>6</sup> that the nature of the decay in liquid and solid helium for  $T > 1$  K is identical.

The present paper discusses the conditions leading to the maximum retardation of the decay kinetics of triplet helium. In liquid helium, this is associated with a strong magnetic field corresponding to the condition

$$2\mu_B H/T > 1 \quad (1.3)$$

and polarizing the electron spins of the particles. In this case, the reaction (1.2) [as well as (1.1)], which takes place along with the exchange interaction of the particles and is

characterized by the law of conservation of total electron spin, turns out to be forbidden. In the presence of total spin polarization in the initial state of the transition, the spin is 2, whereas in the final state it does not exceed 1. The nonzero probability of Penning ionization arises here only when one takes into account the weak spin dipole interaction of the triplet molecules, which leads to a virtual change of spin when they come close together, and which makes possible the subsequent ionization transitions owing to the exchange interaction.

The probability of ionization by such an exchange-dipole mechanism at distances between particles of the order of the average interatomic distance  $R_0$  is found to be  $\sim 7$  orders of magnitude smaller than the probability of ordinary Penning ionization. The process of ionization decay of the triplet molecules changes to the so-called weak collision mode (the ionization probability for one collision is much smaller than unity) with a characteristic time  $\tau_{\text{exd}} \propto 1/n$  on the order of seconds for  $n \sim 10^{17} \text{ cm}^{-3}$ . The characteristic time of ordinary Penning ionization, which remains finite in a real system by virtue of the presence of  $\text{He}_2({}^3\Sigma_u^+)$  molecules with a zero projection of the spin onto the magnetic field axis, increases as the factor  $\exp(2\mu_B H/T) \gg 1$ , and for  $2\mu_B H/T > 15$  ( $T = 1 \text{ K}$ ,  $H > 10 \text{ T}$ ), this decay channel may be neglected.

Our systematic quantum-mechanical analysis of the  $\text{He}_2$  quasimolecule showed that by virtue of the electrostatic and spin-orbit interactions for the molecular transition  $\text{He}_2({}^3\Sigma_u^+) \rightarrow \text{He}(1^1S) + \text{He}(1^1S)$  there exists a nonzero, albeit very small, dipole moment. In addition, this radiative transition also has a nonzero amplitude when the spin-dependent relativistic terms  $\sim 1/c^2$  are taken into account in the Hamiltonian of the interaction between the helium quasimolecule and the electromagnetic field. The time, found by allowing for both of these factors, of spontaneous radiative decay of the  $\text{He}_2({}^3\Sigma_u^+)$  molecule via dipole radiation is  $\tau_r \sim 10 \text{ sec}$ , which agrees with the experimental data of Ref. 5. Thus, this is the time that will determine the decay of triplet excitations in liquid helium in a strong magnetic field for  $n \leq 10^{16} \text{ cm}^{-3}$ . At high densities, however, the dominant process of decay becomes the exchange-dipole Penning ionization, and the decay time begins to decrease in proportion to  $1/n$ .

In solid helium, the Penning ionization process can be depressed even more by freezing the diffusion of the  $\text{He}_2({}^3\Sigma_u^+)$  triplet molecules (in particular, by lowering the temperature). In this case, the ionization decay takes place because the triplet molecules interact at the average distance between them, and the contribution of the exchange mechanisms, which decreases exponentially as the intermolecular distance increases, to the ionization probability becomes insignificant. Now the leading mechanism is the direct dipole mechanism—by virtue of the existence of a dipole moment (albeit very small) for the molecular transition  $\text{He}_2({}^3\Sigma_u^+) \rightarrow \text{He}(1^1S) + \text{He}(1^1S)$ , the reaction (1.2) takes place as a result of the electric dipole interaction of two molecules  $\text{He}_2({}^3\Sigma_u^+)$ . By virtue of this mechanism (which is weak compared to the exchange channels of ionization when the molecules approach each other to distances  $\sim r_0$ ), the ionization probability is practically independent of the polarization of the electron spins and correspondingly, of the

external magnetic field. When the triplet molecules are located at the average distance from each other, the characteristic time of ionization decay is  $\tau_{\text{dd}} \propto 1/n^2$ . Comparing it with the time for spontaneous radiation of a triplet molecule,  $\tau_r \sim 10 \text{ sec}$ , shows that in the presence of frozen diffusion, radiative decay remains dominant up to triplet helium densities  $n \sim 10^{19} \text{ cm}^{-3}$ .

## 2. EXCHANGE-DIPOLE MECHANISM OF PENNING IONIZATION

As was noted in the Introduction, when the electron spins in the system are polarized, the reactions (1.1) and (1.2) can take place only by virtue of the presence of the spin dipole interaction. The latter stimulates the virtual change of the spin and of its projection during the paired interaction of triplet particles, thereby opening up the possibility of ionization transitions owing to the exchange interaction. On the whole, at internuclear distances  $R$  much greater than the atomic size  $\langle r \rangle$ , the physical picture of such an exchange-dipole mechanism of the ionization process can be visualized as the excited electron of one atom being forced out into the continuous spectrum by the excited electron of another atom. The “remaining” electron itself, by changing the direction of spin because of the spin dipole interaction, occupies the space left vacant, not in the excited state, but in the ground state. We shall examine this process as it applies to the paired interaction of atoms, keeping in mind that in the case of molecules, the ionization probability will have a similar value.

The scale of change in the energy of motion of the nuclei during ionization is small compared to the energy of the ejected electron ( $\approx 15 \text{ eV}$ ). This makes it possible to neglect the motion of the nuclei in the law of conservation of energy, and to sum the transition probability over the final states of this motion. As a result, in the condensed phase, the problem actually reduces to finding the probability of Penning ionization at a fixed internuclear distance  $R$ . Here the inequality  $R \gg \langle r \rangle$  can obviously be used, since it holds even when  $R$  is of the order of the interatomic distance  $R_0$ .

The initial state of the reaction (1.1) in the presence of polarization of the electron spins corresponds to the excited electron term  ${}^5\Sigma_g^+$ . The corresponding electron wave function can be written in the form

$$\Psi_i = \hat{A} \{ \psi_{10}(\mathbf{r}_{a1}) \psi_{20}(\mathbf{r}_{a2}) \psi_{10}(\mathbf{r}_{b3}) \psi_{20}(\mathbf{r}_{b4}) \times \chi(\mathbf{r}_2, \mathbf{r}_4) \beta_{-1}(1) \beta_{-1}(2) \beta_{-1}(3) \beta_{-1}(4) \}. \quad (2.1)$$

Here  $\hat{A}$  antisymmetrizes with respect to the permutations of the electrons;  $\psi_{nl}(\mathbf{r}_{ai})$  is the coordinate wave function of the  $i$ th electron in atom  $a$ , corresponding to the principal quantum number  $n$  and to the orbital angular momentum  $l$ , and  $\beta_\sigma(i)$  is its spin function, corresponding to the projection  $\sigma$  onto the direction of the magnetic field. The correlation function  $\chi$  allows for the distortion of the wave functions of electrons of different atoms when they are distant from their nuclei owing to their interaction with one another and with a foreign nucleus. This distortion will be taken into account only for excited electrons, on the assumption that by virtue of the high binding energy of the electron in the ground state ( $\approx 24 \text{ eV}$ ), this electron is localized on its nucleus.

In the final state, we have the quasimolecule  $\text{He} + \text{He}^+$  with the electron configuration  ${}^2\Sigma_g^+$ , and an electron of high

energy ( $\approx 16$  eV), whose motion may be considered free. The final-state wave function is

$$\begin{aligned} \psi_i = & 2^{-1/2} \hat{A} \{ \psi_{10}(\mathbf{r}_{a1}) \psi_{10}(\mathbf{r}_{a2}) \tilde{\chi}(\mathbf{r}_{a1}, \mathbf{r}_{a2}) \\ & \times \varphi_{10}(\mathbf{r}_{b3}) \exp(i \mathbf{k} \mathbf{r}_{b4}) + \psi_{10}(\mathbf{r}_{b1}) \psi_{10}(\mathbf{r}_{b2}) \\ & \times \tilde{\chi}(\mathbf{r}_{b1}, \mathbf{r}_{b2}) \varphi_{10}(\mathbf{r}_{a3}) \exp(i \mathbf{k} \mathbf{r}_{a4}) \} \\ & \times \beta_{-1}(1) \beta_{-1}(2) \beta_0(3) \beta_{\sigma'}(4), \end{aligned} \quad (2.2)$$

where  $\varphi_{10}$  is the coordinate wave function of the electron in the ground state of the atomic ion  $\text{He}^+$ ;  $k$  is the momentum of the ejected electron;  $\sigma$  and  $\sigma'$  are, respectively, the projections of the spins of these electrons onto the direction of the magnetic field;  $\tilde{\chi}$  is a correlation function that takes into account the distortion of the wave functions of the electrons in the helium atom as they move away from the nucleus because of the interaction with the ion (the distortion of the wave function of the electron in the  $\text{He}^+$  ion may be neglected).

We find the probability of exchange-dipole Penning ionization by using first-order perturbation theory in the spin dipole interaction:

$$\begin{aligned} \mathcal{V}_d = & \frac{1}{2} \sum'_{ik} \mathcal{V}_{ik}, \\ \mathcal{V}_{ik} = & \frac{4\mu_B^2}{r_{ik}^5} [ (\hat{S}_i \hat{S}_k) r_{ik}^2 - 3 (\hat{S}_i \mathbf{r}_{ik}) (\hat{S}_k \mathbf{r}_{ik}) ] \end{aligned} \quad (2.3)$$

( $r_{ik}$  is the vector of the distance between electrons centered on different atoms, and  $\hat{S}_i$  and  $\hat{S}_k$  are the operators of their spins). The main contribution to the amplitude of the transition over the exchange-dipole channel

$$V^{\sigma\sigma'}(k) = \langle i | \mathcal{V}_d | f \rangle,$$

is due to the region of electron coordinates which is located far from the nuclei and is localized near the internuclear axis. This is the region of coordinates with which the exchange interaction of atoms under the indicated condition  $R \gg \langle r \rangle$  is connected. In this case, the functions  $\chi$  and  $\tilde{\chi}$  can be calculated by use of the Herring-Gor'kov-Pitaevskii method (see Ref. 7).

The matrix element of the transition for any term  $\hat{V}_{ik}$  in the interaction operator  $\hat{V}_d$  arises mainly between the components of the initial wave function (2.2), which corresponds to centering one of the interacting electrons (in the initial state it is excited, and in the final state it is in the ground state) on different nuclei. The second interaction electron, being excited in the initial state, emerges in the final state into the continuous spectrum. The most effective distances  $r_{ik}$  between these electrons are on the order of the Bohr radius  $a_0$ . Thus, the physical picture of the process of exchange-dipole Penning ionization is as follows. An excited electron of one of the atoms moves far from its nucleus; approaches an excited electron of another atom (which has also moved away from its nucleus) and forces it out into the continuous spectrum. By changing the direction of spin because of the spin dipole interaction with this electron, it takes the latter's place, but in the ground state, not an excited state. Direct calculation of the transition amplitude by use of the wave functions  $\psi_i$  (2.1) and  $\psi_f$  (2.2) and of the interaction Hamiltonian (2.3) gives

$$V^{\sigma\sigma'}(k) = 0,42 \frac{\mu_B^2}{a_0^3} \frac{Y_{1\sigma}(\vartheta, \varphi) Y_{1\sigma'}(\vartheta, \varphi)}{k^{1/2}} \left[ \frac{R}{a_0} \right]^{c_1} \exp\left(-c_2 \frac{R}{a_0}\right), \quad (2.4)$$

where  $c_1 = 2.1$ ,  $c_2 = 0.46$ , and  $\vartheta$  and  $\varphi$  are the polar and azimuthal angles, characterizing the position of the internuclear axis relative to the direction of the magnetic field. For the probability of Penning ionization we obtain

$$\begin{aligned} W_{\text{exd}}(R) = & \frac{2\pi}{\hbar} \sum_{\sigma\sigma'} \int \frac{d^3k}{(2\pi)^3} |V^{\sigma\sigma'}(k)|^2 \delta\left(\frac{\hbar^2 k^2}{2m} - \Delta E\right) \\ = & 0,067 \left(\frac{\mu_B^2}{a_0^3}\right)^2 \frac{1}{\hbar \Delta E} \left[\frac{R}{a_0}\right]^{2c_1} \exp\left(-2c_2 \frac{R}{a_0}\right). \end{aligned} \quad (2.5)$$

Here  $\Delta E \approx 15$  eV is the energy of the ejected electron (the difference between twice the excitation energy of the  $\text{He}(2^3S)$  atom and the ionization potential of the helium atom in the ground state). Averaging over the directions of the internuclear axis relative to the magnetic field was also performed.

It is of interest to compare the result obtained with the probability  $W_{\text{ex}}$  of ordinary Penning ionization due to the exchange interaction (there is no polarization of the electron spins in the system). The probability  $W_{\text{ex}}(R)$  was found in Ref. 8 by numerical calculation. A direct estimate of  $W_{\text{ex}}(R)$  in the presence of a small parameter  $\langle r \rangle/R$  shows that in comparison with  $W_{\text{ex}}$ , the probability of exchange-dipole ionization  $W_{\text{exd}}$  (2.5) contains a small parameter  $\alpha^4 = (e^2/\hbar c)^2$ . This is easy to understand physically, i.e., the parameter  $\alpha^4$  is the square of the ratio of the energy of the spin dipole interaction of electrons to the energy of their Coulomb interaction at a distance of order  $a_0$ .

### 3. RADIATIVE LIFETIMES OF THE TRIPLET MOLECULES $\text{He}_2(^3\Sigma_g^+)$ : DECAY KINETICS OF TRIPLET EXCITATIONS IN LIQUID HELIUM

The abnormally long radiative lifetime of the triplet state of the helium atom  $\text{He}(2^3S)$ , which is the closest excited state, is due to the strict parity prohibition and total angular momentum prohibition of any type of one-quantum radiative transitions to the ground state  $1^1S$ , except the magnetic-dipole transition. As for magnetic dipole transitions whose probability in the atoms has the scale  $\sim \omega \alpha^5$  ( $\omega$  being the characteristic atomic frequency), they turn out to be forbidden here because of the necessity of a change in total spin. This prohibition is lifted when the Hamiltonian of the interaction of the atomic system with the photon field allows for the spin-orbit terms and relativistic corrections to the Zeeman interaction and for the finiteness of the wavelength. These terms contain the small parameter  $\alpha^2$  as compared to the Zeeman interaction itself. Correspondingly, the time for spontaneous radiation is on the scale  $\sim \omega \alpha^9$  ( $\sim 10^3$  sec).

Spontaneous radiative decay should have a fundamentally different character for the triplet molecules  $\text{He}_2(^3\Sigma_u^+)$ , formed in liquid and solid helium in times of  $\sim 10^{-5}$  sec as a result of recombination of  $\text{He}(2^3S)$  atoms with helium atoms in the ground state. First of all, the parity prohibition of the dipole radiative transition to the ground electronic state  $\text{He}_2(^1\Sigma_g^+)$  is lifted. The total-spin prohibition of this transition is lifted, while at the same time, the interatomic electrostatic interaction and spin-orbit interaction in the

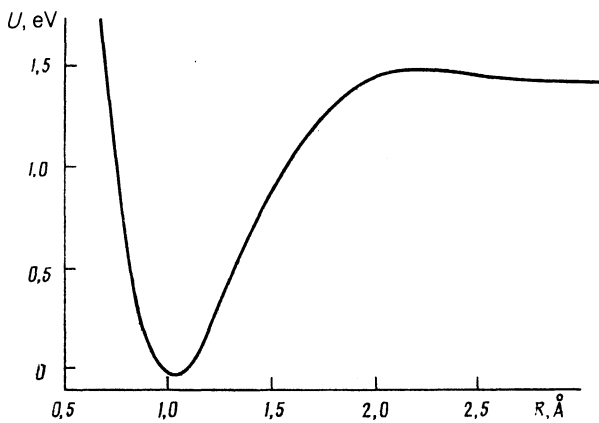


FIG. 1. Potential curve of the  ${}^3\Sigma_u^+$  term of the  $\text{He}_2$  molecule, composed of He atoms in the triplet state,  $2^3S$  and ground state  $1^1S$ ;  $U(R) = 0$  corresponds to the ground vibrational state.

atoms are taken into account. Because the atoms approach each other to small distances  $\sim 1 \text{ \AA}$  in the  $\text{He}_2$  ( ${}^3\Sigma_u^+$ ) molecule (see Fig. 1), the interatomic electrostatic interaction effectively adds states with the same spin, but with a nonzero orbital angular momentum, to the atomic  $s$  states. At the same time, as the spin-orbit interaction takes place in the atoms, such states include a small contribution (of order  $\alpha^2$ ) of states with a different spin, and this ultimately lifts the total-spin prohibition. The dipole moment  $d(R)$  of the electronic transition  ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$  amounts to  $\sim \beta^2 e a_0$ . Keeping in mind that the characteristic probability of spontaneous radiation for the allowed dipole transitions in the atomic systems amounts to  $\sim \omega \alpha^3$ , in the case under consideration we obtain the de-excitation probability  $\sim \omega \alpha^7$ , and this corresponds to a time scale of seconds for the spontaneous radiative decay time  $\tau$ . The same scale of probability of spontaneous (electric-dipole) radiation  $\sim \omega \alpha^7$  for the  ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$  transition arises when the Hamiltonian of interaction of the helium quasimolecule with the electromagnetic field allows for spin-dependent relativistic corrections containing the parameter  $\alpha^2$ , which is small in comparison to the dominant term (naturally, the spin-orbit interaction in the atoms can be omitted here).

To determine the dipole moment  $d(R)$  of the electronic transition  ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ , we used the LCAO approximation for the electron wave functions of the initial and final states. Direct analysis shows that the quantity  $d(R)$  is primarily determined by the following combinations of atomic orbitals:

$\text{He}_2$ ( ${}^3\Sigma_u^+$ )	$\text{He}$ ( ${}^1\Sigma_g^+$ )
$1^1S + 2^3S$	$1^1S + 1^1S$
$1^1S + 2^3P$	$2S^1 + 1^1S$
$1^1S + 3^3D$	$3^1S + 1^1S$
$2^1S + 2^3S$	$2^1P + 2^1P$
$3^1S + 2^3S$	$2^1S + 2^1S$
$2^3P + 2^1S$	$2s2s + 1^1S$

The  $R$ -dependent expansion coefficients, which determine the "weight" of each of the combinations in the LCAO expressions for the wave functions, were taken from the quantum-mechanical calculations of Ref. 9. The spin-orbit interaction in the atoms

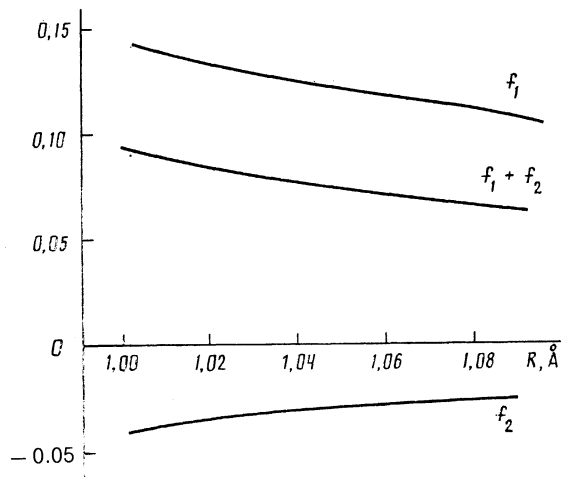


FIG. 2. The functions  $f_1(R)$  and  $f_2(R)$ .

$$\hat{V}_{so} = 2\mu_B^2 \left\{ \sum_i \frac{\hat{S}_i [\mathbf{r}_i \hat{p}_i]}{r_i^3} - \sum_{ik} \frac{(\hat{S}_i + 2\hat{S}_k) [\mathbf{r}_{ik} \hat{p}_i]}{r_{ik}^3} \right\} \quad (3.1)$$

( $p$  is the momentum operator of the electron,  $\hat{r}_i$  is its distance from the nucleus,  $r_{ik} = r_i - r_k$ ), determines the addition of the  $\alpha^2$  scale of the  ${}^1P$  atomic states to the  ${}^3P$  and  ${}^3D$  states, and conversely, of the  ${}^3P$  and  ${}^3D$  states to the  ${}^1P$  state. It is these additions that result in a nonzero value of the transition dipole moment, which is conveniently represented in the form

$$d(R) = \alpha^2 e a_0 f_1(R).$$

The result of a direct calculation of the function  $f_1(R)$  is shown in Fig. 2.

The spin-dependent additions  $\sim \alpha^2$  to the Hamiltonian of the interaction between a helium quasimolecule and an electromagnetic field,

$$\begin{aligned} \hat{H}_{int} = & - \sum_j \frac{\hbar e^3}{2m^2 c^3} \left\{ \hat{S}_j \left[ \nabla_j \left( \frac{1}{r_{aj}} + \frac{1}{r_{bj}} \right), \hat{A}_j \right] \right. \\ & \left. + \frac{e\omega_0 \hbar}{2m^2 c^3} i \hat{S}_j [\hat{A}_j, \hat{p}_j] \right\} \\ & - \sum_{kj} \frac{2\mu_B e^2}{m c^2 r_{kj}^3} (\hat{S}_k [\mathbf{r}_{kj} \hat{A}_j]) \end{aligned} \quad (3.2)$$

( $\hat{A}_j$  being the operator of the vector field potential at the point where the electron is located  $r_j$ , and  $\omega_0$  being the transition frequency), lead to the electric dipole transition  ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$  even without inclusion of the spin-orbit interaction (the terms which do not contribute to this transition have been omitted). Direct calculation of the transition amplitude (with the same LCAO functions of the initial and final states) showed that this amplitude is equivalent to the presence of a transition dipole moment equal to  $\alpha^2 e a_0 f_2(R)$ , the function  $f_2$  being somewhat smaller than  $f_1$  and of opposite sign. This function is shown in Fig. 2.

Thus it may be assumed that there exists an effective dipole moment of the electronic transition  ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$  of the  $\text{He}_2$  quasimolecule, equal to

$$d_{eff}(R) = \alpha^2 e a_0 [f_1(R) + f_2(R)]. \quad (3.3)$$

It is evident from the form of the potential curve of Fig. 1 that the  $\text{He}_2({}^3\Sigma_u^+)$  molecule radiates in a narrow spectral range whose width is significantly smaller than the characteristic energy of the emitted photon  $\Delta E \approx 14$  eV. This makes it possible to perform the summation over the final states of nuclear motion in the expression for the reciprocal decay time, and to write it in the form (the indices  $i$  and  $f$  correspond to the initial and final states of nuclear motion)

$$\frac{1}{\tau_*} = \frac{4}{3} \frac{(\Delta E)^3}{\hbar^4 c^4} \sum_f |\langle i | d_{eff}(R) | f \rangle|^2 = \alpha^7 \left( \frac{\Delta E}{e^2/a_0} \right)^2 \frac{\Delta E}{\hbar} J_0, \quad (3.4)$$

$$J_0 = 4/3 \int \chi_0^2(R) [f_1(R) + f_2(R)]^2 R^2 dR, \quad (3.5)$$

where  $\chi_0(R)$  is the wave function of the vibrational motion of the  $\text{He}_2({}^3\Sigma_u^+)$  molecule. For a molecule in the ground vibrational state, direct calculation gives  $J_0 \approx 9 \times 10^{-3}$ , and we have

$$\tau_* \approx 10 \text{ sec}. \quad (3.6)$$

Actually,  $\tau_*$  (3.6) determines the upper bound of the lifetime of triplet excitations in condensed helium. Radiative decay dominates when the density  $n$  of the triplet molecules is low. At sufficiently large  $n$ , decay due to Penning ionization becomes predominant, and the characteristic decay time decreases.

In liquid helium in a zero magnetic field, ordinary Penning ionization takes place efficiently at intermolecular distances  $r_0$ , where the ionization time  $W_{ex}^{-1}(r_0)$  becomes equal to the characteristic time of diffusion separation  $\tau_D \sim r_0^2/D$ . According to existing experimental data,<sup>4</sup> the diffusion coefficient of the  $\text{He}_2({}^3\Sigma_u^+)$  triplet molecule in liquid helium at  $T \approx 1.5$ – $2$  K is  $D \sim 10^{-4}$  cm<sup>2</sup>/sec. Direct calculation gives  $r_0 \approx 10a_0$ , whence for the ionization rate constant corresponding to such a diffusion-controlled regime, we have (cf. Ref. 3)

$$\alpha_{ex} \approx 4\pi r_0 D \approx 6 \cdot 10^{-11} \text{ cm}^3/\text{sec}. \quad (3.7)$$

The characteristic time of ionization decay  $\tau_{ex} \approx 1/\alpha_{ex} n$  then becomes smaller than  $\tau_*$  (3.5), and correspondingly, ionization decay predominates over spontaneous radiative decay starting at a concentration of triplet molecules as low as  $n > 2 \times 10^9$  cm<sup>-3</sup>.

In a strong magnetic field corresponding to the condition (1.3), ordinary Penning ionization may also take place. Now, however, the fraction of molecules with a spin projection onto the field direction different from 1 is  $\exp(-2\mu_B H/T) \ll 1$  [the total magnetic moment of the  $\text{He}_2({}^3\Sigma_u^+)$  triplet molecule in the state with a zero rotational moment is identical to the spin magnetic moment  $2\mu_B$  of this molecule (see Ref. 10), since the projection of the orbital angular momentum of the electrons onto the axis of the molecule is zero]. Thus, the ionization rate constant acquires this small factor (ordinary Penning ionization can take place only when triplet particles interact with different projections of the electron spin), decreasing exponentially as the temperature is lowered.

The characteristic time  $W_{exd}^{-1}$  of the Penning ionization according to the exchange-dipole mechanism, ionization

which takes place even when the polarization of the spins is total and which is independent of temperature, considerably exceeds the diffusion time  $\tau_D$  at  $T \approx 1$ – $1.5$  K even at the interatomic distance  $R_0$ . We thus have a weak-collision regime, i.e., the molecules must encounter each other in order to enter into the ionization process. The rate constant of the process in this case is

$$\alpha_{exd} = \int_{R_0}^{\infty} W_{exd}(R) d^3R. \quad (3.8)$$

Using the expression (2.5) for  $W_{exd}(R)$  and considering that the integral is set up with  $R$  close to  $R_0$ , we obtain

$$\alpha_{exd} \approx 10^{-17} \text{ cm}^3/\text{sec}. \quad (3.9)$$

Comparing this result with the quantity  $\alpha_{ex} \exp(-2\mu_B H/T)$ , which corresponds to ordinary ionization, one can readily ascertain that exchange-dipole ionization becomes stronger for  $2\mu_B H/T > 12$  ( $T = 1$  K,  $H > 10$  T).

As the temperature decreases, the diffusion coefficient of triplet molecules in liquid helium increases, which only intensifies the weak-collision regime. Consequently, the result (3.9) can be used not only at temperatures  $\approx 1$ – $2$  K, for which the estimate of  $\tau_D$  was made, but also at lower  $T$ .

The rate constant of exchange-dipole ionization  $\alpha_{exd}$  (3.9) is  $\sim 7$  orders of magnitude smaller than  $\alpha_{ex}$  (3.7). Thus the polarization of electron spins by a strong magnetic field makes it possible to increase appreciably the actually attainable concentration of triplet particles in liquid helium. The characteristic time of exchange-dipole ionization  $\tau_{exd} = 1/\alpha_{exd} n$  remains greater than  $\tau_* \approx 10$  sec (3.6) and correspondingly, ionization decay is weaker than spontaneous radiative decay up to triplet helium densities  $n \sim 10^{16}$  cm<sup>-3</sup>.

#### 4. DIRECT DIPOLE MECHANISM OF PENNING IONIZATION. DECAY KINETICS OF TRIPLET EXCITATIONS IN SOLID HELIUM

Formation of triplet excitations of  $\text{He}(2^3S)$  in solid helium is associated with efficient formation in the latter of  $\text{He}_2({}^3\Sigma_u^+)$  triplet molecules, as in liquid helium. However, in contrast to the liquid, where the diffusion coefficient increases as the temperature decreases, the coefficient of vacancy diffusion in solid helium decreases with temperature in accordance with the law

$$D \propto \exp(-E_0/T), \quad (4.1)$$

where  $E_0 \approx 9.5$  K is the energy of vacancy formation. This should cause a difference of the temperature dependence of the kinetics of ionization decay in solid helium from the case of the liquid phase.

The entire picture changes fundamentally at low temperature ( $T < 1$  K), when vacancy diffusion is "frozen." The abnormally small width of the band for quantum diffusion (according to our estimates,<sup>11</sup>  $\sim 10^{-6}$  K) and the large deformation potential of interaction of triplet molecules cause static destruction of the band even at very low concentrations of triplet molecules ( $n \sim 10^{13}$  cm<sup>-3</sup>). Therefore, quantum diffusion is apparently ineffective at high concentration of triplet helium even in the case of a perfect crystal. This

means that at low temperature, we have to deal with impurity triplet molecules frozen in the crystal.

In such a situation, it is clear that in analyzing the kinetics of Penning ionization, it is necessary to consider the interaction of triplet molecules at the average distance  $\bar{R} \propto n^{-1/3}$  from each other. In this case, for  $n \ll n_0$  ( $n_0$  being the crystal density) the exchange mechanisms of Penning ionization (exchange-dipole mechanism in a strong magnetic field and ordinary exchange mechanism in a zero field), the probability of which decreases exponentially as the distance between the triplet particles increases, are insignificant. The leading role is, assumed by the direct dipole mechanism of ionization, consisting in the fact that as a result of the interaction of the dipole moments of two triplet molecules, one of them is de-excited and forms two helium atoms in the ground state (as a result of the electronic transition  $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ , whose dipole moment, as was shown in the preceding section, is not zero), and the other is ionized.

Consider the Penning ionization of an isolated triplet molecule due to the electric dipole-dipole interaction

$$\mathcal{V}_{dd} = \frac{(\hat{\mathbf{d}}_1 \hat{\mathbf{d}}_2) R^2 - 3(\hat{\mathbf{d}}_1 \mathbf{R})(\hat{\mathbf{d}}_2 \mathbf{R})}{R^5}, \quad (4.2)$$

with a similar molecule separated from it by a distance  $R$ . As the dipole moment of the  $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$  transition we use the quantity (3.3). The dipole moment  $\mathbf{d}_i(k, \mathbf{R})$  ( $k$  being the momentum of the emitted electron) corresponding to the ionization was found by using a plane wave for the emitted electron, and quasimolecular electron wave functions obtained by the LCAO method in Refs. 9 and 11. Owing to the fact that the energy scale of the emitted electron is large in comparison with the change in the energy of nuclear motion, this energy may be neglected in the law of conservation of energy, and the square of the matrix element in the transition probability can be summed over the final states of nuclear motion. As a result, for the ionization probability we have

$$\begin{aligned} W_{dd}(R) &= \frac{2\pi}{\hbar} \int \frac{d^3k}{(2\pi)^3} \delta\left(\Delta E - \frac{\hbar^2 k^2}{2m}\right) \\ &\times \sum_f |\langle i | V_{dd}(\mathbf{R}, \mathbf{R}_1, \mathbf{R}_2) | f \rangle|^2 \\ &\approx 24\pi\alpha^4 J_0 J_1 \left(\frac{a_0}{R}\right)^6 \left(\frac{e^4}{a_0^2 \Delta E \hbar}\right). \end{aligned} \quad (4.3)$$

Here use is made of the transition matrix element

$$\begin{aligned} \mathcal{V}_{dd}(\mathbf{R}, \mathbf{R}_1, \mathbf{R}_2) &= [(\hat{\mathbf{d}}_{eff}(\mathbf{R}_2) \hat{\mathbf{d}}_i(k, \mathbf{R}_1)) \\ &\times R^2 - 3(\hat{\mathbf{d}}_{eff}(\mathbf{R}_2) \mathbf{R})(\hat{\mathbf{d}}_i(k, \mathbf{R}_1) \mathbf{R})] / R^5, \end{aligned} \quad (4.4)$$

where  $\mathbf{R}_1$  and  $\mathbf{R}_2$  are, respectively, the vector of internuclear distance in the molecule undergoing ionization and the molecule undergoing de-excitation. The direction of the vector  $\mathbf{d}_{eff}(\mathbf{R}_2)$  [see Eq. (3.3)] is perpendicular to the axis of the quasimolecule  $\mathbf{R}_2$ . The dipole moment  $\mathbf{d}_i(k, \mathbf{R}_1)$  is directed along the vector  $k$ , and its magnitude is conveniently represented in the form

$$d_i(k, R_1) = e a_0 k^{-\hbar} f_0(k, R_1). \quad (4.5)$$

The quantity  $J_0$  appearing in the expression (4.3) is determined by Eq. (3.5) and amounts to  $9 \times 10^{-3}$ , and  $J_1$  is

$$J_1 = \int \chi_0^2(R_1) |f_i|^2(R_1) R_1^2 dR_1 \approx 6. \quad (4.6)$$

Assuming that the triplet molecules are uniformly distributed throughout the crystal, we can approximately determine the characteristic time of ionization decay on the basis of the relation

$$\frac{1}{\tau_{dd}} \approx \int_R^\infty W_{dd}(R) n d^3R.$$

Substituting here the expression (4.3) for the probability of ionization decay, we obtain

$$\tau_{dd} \approx 10(10^{19}/n[\text{cm}^{-3}])^2. \quad (4.7)$$

This time becomes equal to the time of spontaneous radiative decay  $\tau \approx 10$  sec only for  $n \approx 10^{19} \text{ cm}^{-3}$ . At lower densities, however, radiative decay predominates. Thus, in solid helium during frozen diffusion, the attainable concentration of triplet excitations is substantially increased with respect to the liquid phase.

It should be noted that the probability of Penning ionization according to the direct dipole mechanism and correspondingly, the decay time  $\tau_{dd}$  (4.7), are independent of the polarization of the electron spins. This is entirely natural, since the process in question involves the electric dipole interaction of triplet molecules. Thus, in contrast to the situation in liquid helium, an external magnetic field does not affect the kinetics of ionization decay of triplet molecules in solid helium when they undergo frozen diffusion.

<sup>1)</sup> This estimate is based on the mechanism of transfer of excitation and chemical bonding into the adjacent cell.

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