LASER BREAKDOWN OF MIXTURES OF NEON WITH ARGON AND THE THE ROLE OF PHOTOIONIZATION OF EXCITED ATOMS

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We measured the threshold fields for the breakdown of mixtures of argon and neon by giant pulses from ruby and neodymium lasers. The existence of the previously observed effect[1] of a sharp drop in the threshold in argon with a small neon additive at the frequency of the neodymium laser was confirmed. It is shown that no such effect exists in the case of the ruby laser. A lowering of the threshold in neon with a small admixture of argon was observed in the case of a neodymium laser; there was likewise no lowering of the threshold at the frequency of the ruby laser. It is concluded on the basis of the obtained data that the photoionization of the excited atoms has a high probability in the case of the ruby and a low probability in the case of the neodymium laser, when a larger number of quanta is necessary. The effects in argon with an admixture of neon remain unexplained; the explanation given in [1] is subjected to criticism.

1. INTRODUCTION

In an investigation of the breakdown of mixtures of inert gases by neodymium-laser radiation, Smith and Haught[1] have observed a curious phenomenon. When 1% neon was added to argon at sufficiently high pressure, the threshold for the breakdown of argon was considerably lowered, although the threshold for the breakdown in pure neon is higher at any pressure than the threshold in pure argon. When the content of the neon in the mixture with the argon was varied from 1 to 20%, the threshold remained constant, and at a pressure 5×10^4 mm Hg it was one-third as large, with respect to the light intensity, as the threshold in pure argon (lower by a factor 1.7 with respect to the field intensity).

It might be assumed that the addition of neon, which has no Ramsauer minimum of the elastic cross section for electrons, fills this minimum for argon, thereby increasing the rate at which the electrons acquire energy in the field when they collide with the atoms. However, when helium or nitrogen, which likewise have no Ramsauer minima, is added to the argon, the threshold does not decrease. In mixtures of argon with helium, the threshold changes monotonically from a lower value for pure argon to a higher one for pure helium.

It is important that addition of neon lowered the threshold in argon only at a pressure above 5×10^3 mm Hg, and the larger the pressure the stronger the lowering. The indicated pressure corresponds precisely to approximate equality of the time between collisions of the atoms and the time constant of the development of the avalanche, i.e., the atom-atom collisions can affect the development of the avalanche only at higher pressures. This circumstance has led the authors of [1] to assume that the lowering of the threshold is connected precisely with collisions of the atoms of neon and argon.

Smith and Haught interpreted the observed lowering of the threshold by assuming that addition of neon to the argon decreases the "diffusion-like losses" accompanying the process of avalanche ionization in the region of the focus (that such losses exist is seen from experiment, namely, the threshold in both the pure gas and in mixtures is lowered if the diameter of the focal spot is increased).

The decrease in the loss is connected by Smith and Haught directly with the effect occurring in the case of electric breakdown in the Penning mixture (neon with argon admixture), Usually the excitation of the atoms by electrons that acquire energy in the field slows down the development of the electron avalanche, since the electron loses its energy without reaching the energy needed for ionization of the atoms. Addition of argon to the neon changes the action of the exciting collisions, transforming them from "harmful" to "useful" for the avalanche. The reason is that the neon excitation potential, 16.6 eV, is barely larger than the ionization potential of the argon, 15.8 eV, and the excited atom of the neon, in collisions with the argon atom, transfers its energy resonantly to the latter, ionizing it. Thus, the act of excitation of the main gas in the Penning mixture is accompanied by rapid ionization of the admixture, i.e., by multiplication of the electrons; the development of the avalanche accelerates, and the breakdown threshold consequently is lowered.

In our opinion, the considerations advanced by Smith and Haught and pertaining to a true Penning mixture, cannot explain the effect they observed in the "inverse" mixture (argon with neon admixture).[1)] In fact, the effective cross section for the ionization of argon by electron impact is much larger than the cross section for the excitation of neon,[3] and in addition, in the case of a 1% admixture, the concentration of the argon is 100 times larger than the concentration of the neon. Therefore an electron that acquires an energy higher than 16.6 eV under the influence of the field has a much larger probability of ionizing the argon than of exciting the neon. Consequently, the two-step process—excitation of the neon followed by transfer of excitation to the ionization of the argon—will not affect in any way the rate of ionization and the development of the avalanche. The statements made by Smith and Haught concerning the

[1)]This circumstance was noted by one of the present authors while editing the collection of translations [2] in which [1] was included.

"decrease of the diffusion-like losses" in the system following addition of neon to the argon are not explained sufficiently well and we must say that we do not understand the concrete physical meaning imparted to them by the authors.

The failure of attempts to find an adequate explanation for the results of Smith and Haught has induced us to repeat their experiments and, in addition, to expand the program of the experiments. It would be of interest to investigate the entire range of compositions of the mixture of argon with neon, from pure argon to pure neon, i.e., to study also the true Penning mixture, as well as to consider breakdown at other wavelengths, using a ruby laser. The results of the measurements with a small neon admixture turned out to be striking. The conclusions by Smith and Haught that the breakdown threshold of argon is lowered by addition of a small amount of neon was fully confirmed in the case of a neodymium laser (we confess that we were ready for the opposite), but in the case of the ruby laser no such effect was observed! We point out immediately that we cannot think of a satisfactory explanation for these effects.

On the other hand, the results of measurements of thresholds in the Penning mixture with a small admixture of argon are quite remarkable and make it possible to draw certain essential conclusions concerning the role of ionization of excited atoms under the influence of the laser radiation itself, a question which has long been discussed in the literature of laser breakdown and which has not yet been fully resolved. Our experiments have shown that a small admixture of argon to neon strongly lowers the threshold at the frequency of the neodymium laser and has no effect in the case of the ruby laser. This can be interpreted as a result of the larger probability of ionization of excited neon atoms by ruby-laser radiation (apparently via two-photon absorption) and the low probability of photoionization at the neodymium-laser frequency, when a larger number of quanta is necessary. In the former case the Penning effect does not accelerate the ionization process, which is fast as it is, and in the latter it greatly accelerates it. (This will be discussed in detail in Sec. 3.)

2. EXPERIMENT AND RESULTS

A cell with volume 80 cm^3 was filled with the investigated gas at high pressure. The laser radiation was focused at the center of the volume by a lens with $f = 2.54$ cm. The diameter of the focal spot was 0.14 mm in the case of the ruby laser and 0.1 mm in the case of the neodymium laser. We used Q-switched lasers. For a more exact determination of the breakdown threshold, we used a specially developed continuous radiation attenuator.[4] The breakdown event was registered with the aid of a photomultiplier which detected the appearance of the flash. The scattered laser light was cut off in this case by suitable filters. An oscillogram of the laser pulse was taken during each shot. The average power was determined by dividing the total pulse energy, measured in each experiment, by the duration at the half-width. We then calculated the mean-squared electric field of the light wave at the focus.

Much attention was paid to the accuracy with which the desired composition of the mixture was established and to ensuring its homogeneity, particularly at low contents of one of the gases. Argon and neon of high purity were used: the nitrogen and oxygen impurities amounted to thousandths of a percent; there was no neon in the argon at all, nor was there any argon in the neon.

The mixture with a small content of one of the gases, say 99.5% neon plus 0.5% argon, was prepared in the following manner. First the cell was scrubbed several times with argon by filling it to a pressure ≈ 100 atm followed by complete emptying of the gas. This served to eliminate leftover mixture from the preceding experiment, and a pure atmosphere of the gas constituting the admixture (argon) was produced in the cell. The cell was then filled with argon, say to 1 atm, after which neon was admitted to a total pressure of 100 atm. The pressure in the chamber filled with such a 1% mixture was then dropped to 50 atm, after which neon was again admitted to a pressure of 100 atm, producing a mixture containing 0.5% of argon.

This procedure was used to prepare mixtures containing one of the gases up to several tenths of 1%, the accuracy with which the composition was determined being 0.1%. Altogether we investigated the entire range of argon and neon mixtures, starting from the absolutely pure gases; the range of total pressures was from 1 to 100 atm. The main series of the measurements was performed at a pressure of approximately 80 atm.

At the employed pressures, cell dimensions, and temperature, total diffusion mixing of the gases occurred after several hours, but to guarantee full homogeneity of the mixture, especially at low contents of one of the gases, the mixture was kept in the cell for several days before the experiment in some of the control experiments. Inhomogeneity of the gas, naturally, could lead to ambiguity of the results (in cases when the threshold depended strongly on the composition), for even if the mixture had the same integral composition, it was possible to have a mass of one composition in the focal region in one experiment, and one of a different composition in the next experiment. A guarantee that this did not occur was the complete reproducibility of the results over many experiments, which were repeated hundreds of times with different prior storage times of the mixture, different procedures for its preparation, gradual changes of the composition in either direction, etc.

The results of the measurements of the threshold fields in the mixtures of neon and argon at the frequencies of the neodymium and ruby lasers are shown in Figs. 1 and 2. The experimental conditions in this series of measurements were close to those of the experiments of Smith and Haught: the pressure in our experiments was 6×10^4 mm Hg ≈ 80 atm, while in [1] it was 5.2×10^4 mm Hg. The characteristic diffusion length of the focal region, determined by the diameter of the focus and by the length of the caustic in accordance with a formula given in [1], was $\Lambda = 1.75 \times 10^{-3}$ cm in our case (neodymium laser) and $\Lambda = 1.6 \times 10^{-3}$ cm in [1]. In the case of the ruby laser we obtained $\Lambda = 2.6 \times 10^{-3}$ cm.

The results of our measurements are in good agreement with the results of Smith and Haught for the neon contents investigated by them, from 1 to 20%, and for a neodymium laser. As follows from our measurements

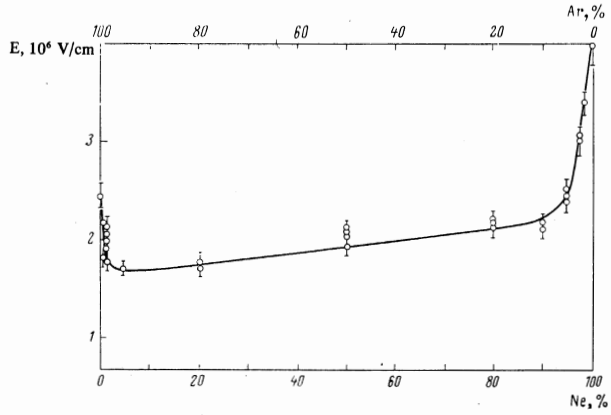

FIG. 1. Threshold field for the breakdown of mixtures of neon with argon as a function of the composition. Neodymium laser, gas pressure 80 atm, focal-spot diameter 1×10^{-2} cm, $\Lambda = 1.75 \times 10^{-3}$ cm.

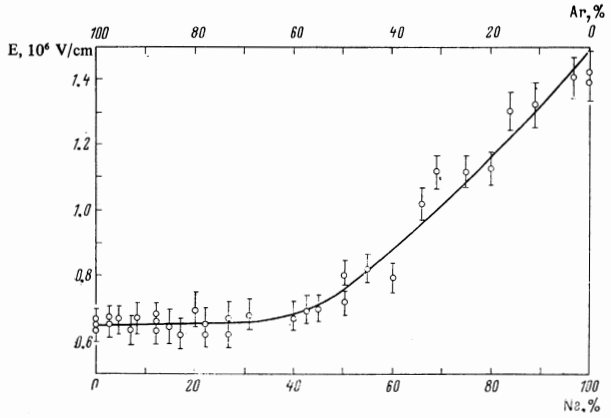

FIG. 2. Threshold field for the breakdown of mixtures of neon with argon as a function of the composition. Ruby laser, gas pressure 80 atm, diameter of focal spot 1.4×10^{-2} cm, $\Lambda = 2.6 \times 10^{-3}$ cm.

(see Fig. 1), even an admixture of neon smaller than in [1] (0.5%) greatly lowers the breakdown threshold in argon. Measurements were made with even smaller admixtures of neon, 0.2–0.3%, but the scatter of the results was too large to permit the definite conclusion that the threshold had been lowered. When the neon concentration was increased from 1 to 20%, the threshold remained constant (Fig. 1), being below the threshold of the argon, as in [1], after which it increased gradually and in the region of small argon concentration a sharp jump was again observed.

It is more natural to state it differently: addition of a small amount of argon to the neon lowers the breakdown threshold greatly, and the lowering is the stronger the larger the amount of the admixture; the threshold drops to a value which is even somewhat lower than the threshold in pure argon.

Nothing of this type was observed at the ruby-laser frequency, namely the threshold varied monotonically from the threshold of pure argon to the threshold of pure neon with monotonic variation of the mixture composition. Very careful checks with numerous repetitions of the experiments did not reveal, in the case of the ruby laser, any jumps connected with addition of one gas to the other. This was the case at all pressures in the investigated range from 1 to 100 atm. In the case of the neodymium laser, on the other hand, the amount of lowering of the threshold following the addition of neon to argon increased with increasing pressure, as was observed in [1].

3. THE QUESTION OF THE IONIZATION OF EXCITED ATOMS BY LASER RADIATION

When an electron absorbs light quanta in elastic collisions with atoms and acquires an energy slightly exceeding the excitation potential, it loses this energy, with high probability, to excitation of the atoms without reaching the ionization potential. During the initial stage of the development of the avalanche, which is what principally determines the threshold for the laser breakdown,[5] the number of excited atoms is small and their ionization by electron impact is very abrupt. Therefore the electron must acquire energy many times and lose it again to excitation before it succeeds in "jumping through" the excitation band without experiencing inelastic collision, reaching the ionization potential and ionizing an ordinary atom. Thus, if by virtue of some mechanism the excitation of the atom is not accompanied by fast production of a new electron, the loss to excitation slows down the development of the avalanche and raises the threshold for the breakdown.

The mechanism of "utilization" of the excited atoms may be detachment of the electrons from them under the influence of the laser radiation itself. This is possible only if several quanta are simultaneously absorbed. For example, the energy required to ionize an excited neon atom is 21.6–16.6 = 5 eV, corresponding to 2.8 times the ruby-laser quantum energy and 4.7 times the neodymium energy.

In order for a sufficient number of electrons to be produced during the time of the giant laser pulse, $\approx 3 \times 10^{-8}$ sec, the time necessary for the production of the new population (the time constant of the avalanche) should be approximately $\theta \approx 10^{-9}$ sec. This means that the photoionization of the excited atoms can influence the development of the avalanche only if the latter occurs with a probability not lower than $w \sim 10^9$ sec^{-1}. A simple estimate by means of the Keldysh formula[6] shows that, say for three-quantum ionization with such a probability, the fields required are $\approx 10^7$ V/cm, which is larger by one order of magnitude than the actual threshold field in the breakdown of neon under a pressure of 80 atm at the ruby-laser frequency, $E = 1.5 \times 10^6$ V/cm (see Fig. 2). Incidentally, the experiments of Voronov and Delone[7] on multiphoton ionization of atoms from the ground state have shown that the number of quanta required is actually always smaller than follows from the value of the ionization potential. The mechanism operating here is apparently the broadening of the upper levels of the atom in the light field, leading to a lowering of the boundary of the continuous spectrum.[8] If this is indeed the case, and the lowering in neon exceeds 1.4 eV, then two ruby quanta suffice for the ionization of the excited atom.

The two-quantum effect apparently proceeds at a sufficient rate. Thus, according to the Zernic formula[9] for the 2s state of hydrogen at a quantum flux 2.1×10^{28} cm^{-2} sec^{-1}, corresponding to $E = 1.5 \times 10^6$ V/cm. we have $w = 6.7 \times 10^9$ sec^{-1}. It is possible that owing to

the broadening of the levels there appear new possibilities for the resonant transitions via the intermediate state and this increases the probability of the three-proton processes to the required level.

Unfortunately, all these considerations are purely speculative, since there is no corresponding theory for excited atoms. Nor does a comparison of the measured threshold fields with the calculated ones under different assumptions lead to any reliable conclusions concerning the role of photoionization of the excited atoms—the uncertainties or the inaccuracies in both types of data are too large. Thus, for example, in experiment one always measures values averaged over the field focal volume, whereas in fact the cascade develops predominantly in those places where there is an increased local field.

The results presented here for the Penning mixture give, in our opinion, some experimental grounds for concluding that photoionization of the excited atoms does play a role, at least under our concrete conditions. When a small amount of argon is added to neon, a new mechanism for utilization of the excited atoms arises. Obviously, it can greatly influence the rate of development of the avalanche, when the lifetime of the excited neon relative to ionization of the argon is $\tau_p \approx \theta \approx 10^{-9}$ sec. Bearing in mind that the cross section of the indicated process is $\sigma_p \approx 2.6 \times 10^{-16}$ cm^2,[10] we find that at 80 atm this is obtained if the argon concentration is 2–3%.

It is seen from Figs. 1 and 2 that in the case of a ruby laser the indicated admixture has practically no influence on the breakdown threshold, while in the case of a neodymium laser it is precisely this admixture which greatly lowers the threshold. This immediately suggests that in the former case there exists, even without the admixture, a sufficiently rapid mechanism for the ionization of the excited atoms, whereas in the latter case there is no such mechanism. This assumption is in full agreement with the considerations advanced above, namely that in the case of the ruby laser there can occur two-photon or at most three-photon ionization of the excited atoms (the latter does not seem probable to us), and at the frequency of the neodymium laser the process requiring a larger number of photons is not effective in practice. It agrees with estimates that show the location of the "bottleneck" in the chain of processes leading to multiplication of the electrons in either case.

Let us consider pure neon at a pressure of 80 atm. The rate of growth of the energy of the electron ϵ in the light field can be estimated from the well-known formula

$$\frac{d\varepsilon}{dt} = \left(\frac{e^2E^2}{m}\frac{1}{\omega^2+\nu^2} - \frac{2m}{M}\varepsilon\right)\nu, \qquad (1)$$

where ω is the frequency of the light, ν the frequency of elastic collisions of the electron with the atoms, m the electron mass, and M the atom mass; the second term characterizes the elastic losses.

Data on $\nu(\epsilon)$ are contained in [3]; in our case $\nu \sim 10^{13}$–10^{14} sec^{-1}. At the neodymium-laser frequency $\omega = 1.9 \times 10^{15}$ sec^{-1} and a threshold field $E = 4 \times 10^6$ V/cm, the time necessary to acquire an energy equal to the ionization or excitation potential (the difference between the latter is small) turns out to be approximately $\tau \approx 3.6 \times 10^{-11}$ sec, and the elastic losses are small.

We see that the electron acquires energy in the field very rapidly, compared with the multiplication time, $\tau \ll \theta$, meaning that the multiplication rate is limited by another process, namely the energy loss to excitation: the electron must acquire and lose energy many times before it succeeds in jumping over the excitation band. Since the electron loss due to diffusion drift out of the region of the focus is low under our high pressures, the electron executes, roughly speaking, $\theta/\tau \approx 30$ acts of excitation before it performs ionization. This figure agrees in general with the estimate of the probability of "breaking through" the excitation band, obtained by the method used in [5]. It is clear that no rapid photoionization of the excited atoms occurs in this case, the "bottleneck" being precisely the inelastic losses.

The situation is entirely different in the case of the ruby laser. It follows from (1) that at $\omega = 2.7 \times 10^{15}$ sec^{-1} and at a threshold field $E = 1.5 \times 10^6$ V/cm the elastic losses play a larger role and in general do not allow the electron to acquire an energy higher than $\epsilon_{max} \approx 10$ eV. In view of the approximate character of the estimate, this figure, of course, should not be taken literally; ϵ_{max} naturally, is larger or else there would be no multiplication whatever, but it is clear that in this case the "bottleneck" is precisely the acquisition of the energy and the elastic energy losses limit the rate of multiplication. The ionization of the excited atoms must inevitably occur rapidly, since it is even more difficult for the electron to jump through the excitation band in this case than in the preceding one (the probability of "breaking through" decreases with decreasing field and with increasing frequency[5]).

Thus, this estimate, too, favors the assumption that the photoionization of the excited atoms is produced rapidly by ruby-laser light and slowly by neodymium-laser light.

4. CONCLUDING REMARKS

A few words concerning effects occurring in argon with a small admixture of neon. As already noted in the Introduction, we cannot propose at present a satisfactory explanation for these effects, but we do not agree with the ideas of Smith and Haught[1] which pertain more readily to a Penning mixture. Incidentally, their conclusions are independent of the frequency of the light, whereas our experiments have shown clearly that the effect of the lowering of the threshold exists only in the case of a neodymium laser but not a ruby laser.

In addition, it is known[10] that the Penning effect is possible also when excited helium collides with argon, the cross section here being even larger than in the collision between neon and argon. Yet addition of helium to argon, as evidenced by the authors of [1], produces no effect. We note that to answer the question of the influence of a small admixture of neon to argon, it would be of interest to verify the influence of the admixture at the frequency of the infrared CO_2 laser.[11] We should stop and discuss briefly the question of "diffusion-like" losses. The existence of such losses follows from the experiments of [1] and from the measurements of [12], which have shown convincingly that the breakdown thresholds increase with decreasing diameter of the fo-

cus, as if diffusion drift of electrons from the region of the focus were in operation.

Direct estimates show (this is noted by Smith and Haught,[1] see also [5]) that at high pressures the electrons do not have time to diffuse from the focal region within the time $\theta \approx 10^{-9}$ sec, this being the condition for the reality of the losses. Smith and Haught connect the losses with diffusion of the resonant radiation but, first, this process is too slow, since even the act of reradiation requires a time on the order of 10^{-8}–10^{-9} sec, and the mean free path of the resonant quanta is small; second, it could influence only the number of excited atoms, which, as already noted above, has little influence on the threshold.

We assume that the "diffusion-like" losses constitute a true diffusion of electrons, not from the "large" focal region, but from much smaller inhomogeneities, where there is an increased local field and where the avalanche develops predominantly (the existence of such inhomogeneities of the laser field is universally known). When the focal spot is decreased by using another lens, as was done in the experiments, the dimensions of the inhomogeneities are accordingly reduced.

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