Ultrahot Electron Formation under Excess Electron Drift through Solid Xe

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The formation of "hot" (8 eV) electrons under excess electron drift in a moderate electrostatic field through solid xenon has been experimentally proved by observation of secondary electrons emitted from the photocathode. At $T = 77$ K and $U = 1000$ V one drifting electron produces about 20 (172 nm) photons, the efficiency of electric field–to–vacuum ultraviolet emission conversion is 15% tending to grow with temperature. A self-sustained electric discharge has been generated in solid Xe using a three-electrode cell with a zinc cathode.

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In 1994 one of the authors (E. B. G.) proposed a new model which explained the peculiarities of excess electron drift through heavy condensed rare gases (RG) — Xe, Kr, and Ar — by the excitation of electron states of the matrix (excitons) [1,2]. Though heavy RG are known as an ideal medium for electron motion with small energy losses and very high electron mobility, the assumption of an electron being accelerated by the electric field in a solid or liquid up to energies of 8–12 eV needed to be experimentally proved. It was, at that time, accepted that the limiting energy of drifting electrons could not be significantly higher than that corresponding to the Ramsauer minimum in the cross section of electron elastic scattering in the corresponding gas, i.e., less than 0.3–0.7 eV [3]. It is worthy to mention the effect under consideration is to be peculiar only to condensed state. The substitution of the correspondent densities to the gas model formulas gives the VUV luminescence threshold in a far MV/cm range of electric field, and nobody has observed the luminescence under electron drift through enough dense RG. The gas condensation dramatically changes the drift nature — the electron mobility in Xe gas jumps up 4 orders of magnitude just in triple point [3]. That strong diminishing the elastic losses of electron allowing its overheating can be qualitatively interpreted as the compensation of the momentum change under electron scattering on many RG atoms coherently. Such compensation is impossible for "chemical" processes — electronic excitation, reactive collisions — when an electron interacts only with one center, their cross sections should be as large as in a gas (the transformation in condensed matter of such a size effect as the Ramsauer one is of special interest). In particular, the electron scattering at the metastable negative ion state $(Xe^-)^*$, lying 0.4 eV below the lowest energy of atomic excitation, can retard that excitation and consequently diminish the quantum yield of VUV luminescence [4].

In 2000, VUV emission from molecular excitons Xe_2^* ($\lambda \approx 172$ nm) has been directly observed with electrons emitted by a cold cathode drifting through liquid xenon in moderate electric fields [5]. Unfortunately from the data of [5] one cannot estimate, even approximately, the efficiency of such an emission. Meanwhile, since according to [1,2] the electronic excitation should be the *main* channel of energy loss of electrons, every electron can produce many excitons step-by-step, and correspondingly many VUV photons. So, to demonstrate the validity of the hot electrons model and its application in practice it is necessary to confirm in an experiment the high yield value of VUV electroluminescence.

Its reliable measurement is rather complicated since we need to know both the number of electrons entering the sample and the total number of photons emitted. We have chosen the experimental approach demonstrated briefly by Fig. 1. We used a three-electrode scheme. The cathode was made of zinc possessing relatively high photoelectron yield in the UV region. The Xe crystal was grown in the bottom part of the cell between anode and grid. Its upper interface was 0.1–0.2 mm beneath the mesh grid. The upper space was filled by a few mbar of Xe (at its saturated vapor pressure when the experiments were carried out at $T = 125$ K) or Ar (if the temperature was 77 K). The photocathode was exposed to short pulses of a Nd:YAG laser 4th harmonics [$\lambda = 266$ nm, $\tau = 1$ ns, $f = 10^4$ pulses per second] through an orifice in the center of the stainless steel anode, by using a quartz fiber. The number of seed photoelectrons was 10^4–10^5 per pulse. The VUV photons arisen under electron drift through the sample striking the photocathode surface formed the secondary photoelectrons. There were several reasons for leaving a gas gap between crystal and cathode: (i) it allowed suppression of the so-called back-diffusion effect drastically diminishing the probability of photoelectron input to the bulk crystal under its direct contact with the cathode [6]; (ii) in the electric field applied between the cathode and the mesh grid the seed photoelectrons ionize gas atoms forming an electron avalanche; (iii) this peculiar photoelectron multiplier works as well

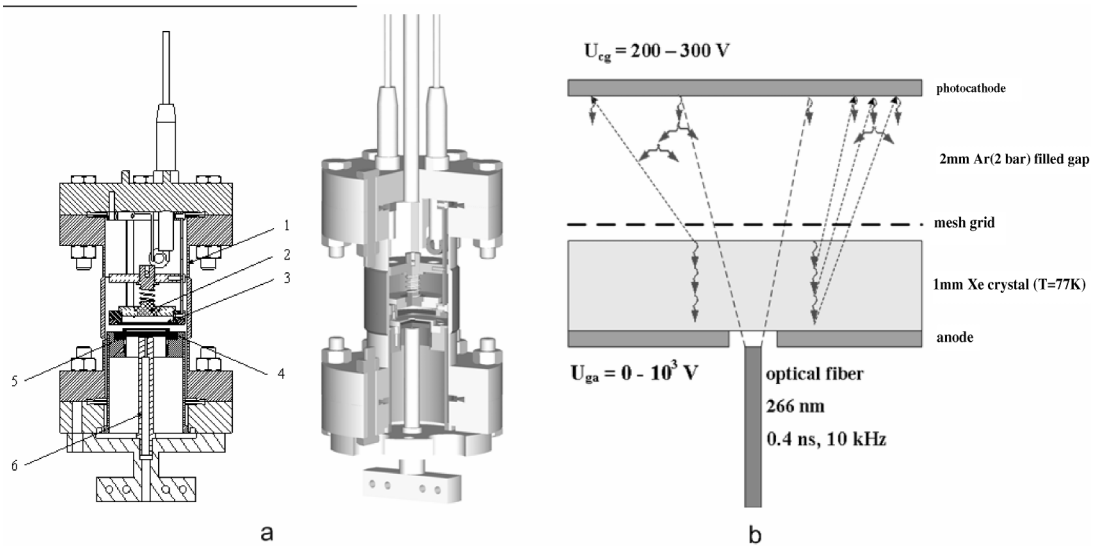

FIG. 1. The experimental cell design (a) and its schematic view (b). 1: cell body; 2: zinc photocathode; 3: mesh grid; 4: anode with central orifice; 5: sapphire viewport; 6: fiber holder.

for VUV photons emitted by xenon excitons, promoting a powerful positive feedback, up to the development of a self-sustained electric discharge.

Experimental setup.—Only the parts designed for application in high vacuum systems were used in the experimental setup, and they were either welded together or connected with copper gaskets. All tubes were made of stainless steel and could be heated up to 200 °C for outgassing. We carefully purified the xenon sample (probably to better than 1 ppb) by using the spark-discharge method first proposed in [7]. It is based on a long-term exposure of liquid xenon to a high-voltage spark between a titanium blade and the metallic anode submerged in the liquid. The xenon storage tanks were equipped with a nonevaporative getter for further xenon purification. Such precautions were intended mainly to allow working during several hours without noticeable suppression of the electric field applied to the sample by the space charge of motionless negative ions formed by electrons captured by the oxygen traces. Because in condensed Xe of our purity the free-path of excess electron is to be more than 2 m [8], the probability of electron capture by impurities during its drift through the sample of 2 mm thickness is less than 10^{-3} and such an effect cannot affect the current signals. The body of the cell was made of a double-flanged glass high vacuum connector [9] capable of working at liquid nitrogen temperature. A 14 mm diameter copper rod, connected to the bottom flange, formed a heat link to the liquid nitrogen bath.

The cell was placed inside a transparent glass Dewar filled with liquid nitrogen. The nitrogen level was well below the cell body but the copper rod was deeply immersed into the liquid. By using the heater attached to the bottom flange the temperature of cell could be increased up to 165 K, corresponding to equilibrium between liquid xenon and its saturated vapor. Then the cell was connected with the storage xenon tank and the gas was left to condense. The heater was switched off and the sample slowly converted into a transparent solid. Two kinds of experiment were carried out. One where the cell temperature was kept near 125 K when the xenon saturated vapor pressure was 3 mbar, and the other where the whole cell was submerged into liquid nitrogen at $T = 77$ K, and was filled with a few mbar of pure argon. The distance between cathode and grid was 2 mm, and that between grid and anode was either one or 2 mm. The grid was grounded. Negative and positive voltages were supplied to cathode and anode, namely U_{cg} and U_{ga}, from two independent power supplies. The laser induced electron currents in the upper and lower spaces of the cell were measured as function of U_{cg} and U_{ga} by using a 500 MHz oscilloscope. The signals of gas current between cathode and grid were more interpretable (between grid and anode, for instance, the current of secondary electrons should be distinguished from the drift current of primary electrons) and only those will be reported in this Letter.

Results and discussion.—First of all it was necessary to determine the "gas photomultiplier" dynamic range and time resolution. The current signal from seed photoelectrons in vacuum has a duration of 2 ns being close to that of the laser pulse and it was already saturated at $U_{cg} = 100$ V. With gas in the cell the amplitude of the signal grew exponentially with U_{cg}. Typical sets of signals for different voltages in xenon at room temperature and Argon at 77 K are shown in Fig. 2. The maximum signals in both cases are close to these corresponding to self-sustained discharge development. It was found that the pulse characteristics for a given gas density are independent of temperature and of the U_{ga} value (in the absence of Xe crystal). The gas pressure mainly affects

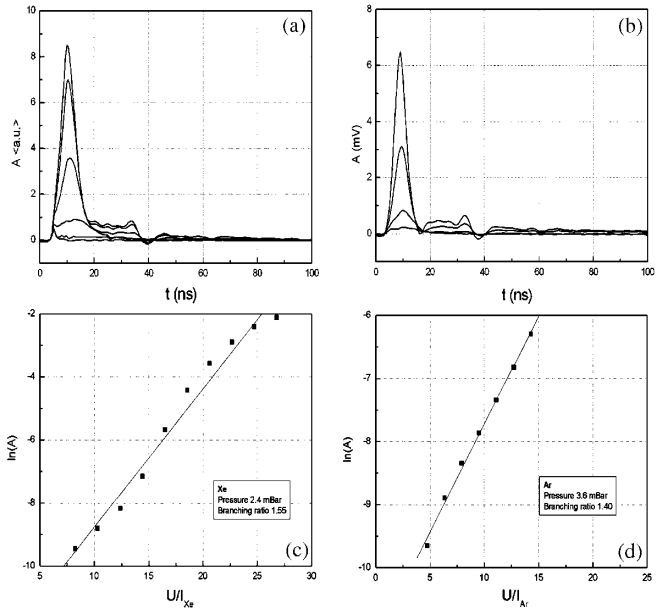

FIG. 2. Electron current pulses at different U_{cg} voltage in the cathode-grid gap filled with Xe (1.2 mbar, 300 K) (a); and Ar (1.2 mbar, 77 K) (b); and logarithms of their peak intensity vs dimensionless voltage, U_{cg}/I, (I: the ionization potential) —(c) and (d), correspondingly. The highest voltages are in the vicinity of the discharge threshold.

the pulse width. The voltage dependence of the pulse amplitude for Xe and Ar shown in Fig. 2 were well fitted by:

$$J = J_0(\alpha)^{U/I} = J_0 \exp\left(\frac{U}{I}\ln\alpha\right), \tag{1}$$

where I is the ionization potential and $1 < \alpha < 2$ is the so-called branching ratio. The most important for us were the following: (i) the multiplication factor J/J_0 was as high as 500–1000 and was rather reproducible and high enough to compensate the low (about 20%) probability of VUV photon quanta transport to the photocathode (determined by geometry and grid transparency) and low (about 10^{-3}), photoemission efficiency of the Zn photocathode at $\lambda = 172$ nm. (ii) The primary electrons pulse duration (< 10 ns) was shorter than any other characteristic time in the system.

In the cell with solid Xe the secondary electrons should appear first of all as a result of cathode photoelectron emission induced by VUV (172 nm) quanta, emitted under crystal surface bombardment by primary electrons from the gas, whose energy is sufficient even for effective ionization of the Xe atoms. It should be seen as a tail of a short pulse of primary electrons exponentially decaying with characteristic time equal (due to the high speed of light and very fast electron transport through the gas multiplier) to the radiative time of molecular excitons in solid Xe, $\tau_R = 30$ ns [10]. If the primary electrons that entered the solid and are accelerated by the electric field generate excitons during their whole trajectory to the anode, a long tail should follow the signal. At a voltage U_{ga} well below the threshold of self-sustained electrical discharge, that contribution to the secondary electron current should be observed as a plateau extending to the time the primary electrons arrive to anode, $\tau_d = d/v_d$. Here d is the crystal thickness and v_d is a electron drift velocity, which at our applied voltages is independent of field strength [11].

The experimental results are in a good agreement with above considerations (see Fig. 3). The tail of the electron current signal at low voltages (the lowest curves) indeed consists of an exponentially decaying signal with a characteristic time of 30 ns followed by a prolonged plateau, whose duration is proportional to the crystal thickness and whose intensity grows with U_{ga}. The plateau duration corresponds to an electron velocity $v_d = 1.3 \times 10^5$ cm/s at $E = 5$ kV/cm, close to limiting drift velocity of excess electrons in solid xenon of high purity [7]. We should stress that the plateau observed belongs to secondary electrons moving through the gas, not to the drift of primary electrons through the sample being out of our electrical circuit.

The correctness of the interpretation is clearly demonstrated by peculiarities of the transition to a self-sustained discharge. Because of the use of a photo sensitive cathode, a positive feedback providing a chain-branched growth of the charge-carriers number was realized by secondary electron photoemission, described by the so-called third Townsend coefficient. This is true even without Xe in the cell. However if the UV light emission without solid Xe occurs very fast in the allowed ($\tau_R \cong$ 10 ns) optical transitions in the excited gas, the positive feedback created by VUV emission from excitons formed by electrons drifting through the solid, should be strongly delayed. It should manifest itself as the so-called regenerative phenomenon, arising while approaching a discharge threshold. The threshold corresponds to the case where every primary electron results in a secondary one. It is easy to realize that the position of the regenerative peak should always correspond to the moment of positive feedback termination. Comparing Figs. 2 and 3 we clearly

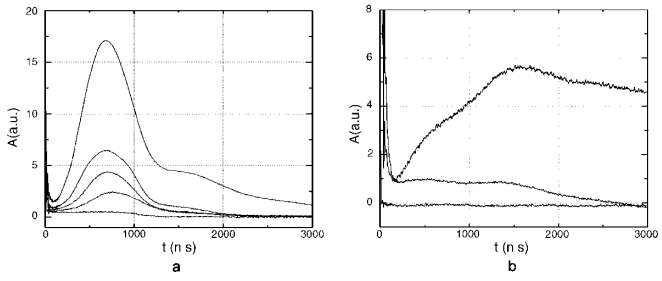

FIG. 3. Electron current in a gas (cathode-grid) gap at different voltages applied to the Xe crystal. (a) 1 mm thick crystal, $T = 125$ K, gas Xe; $U_{cg} = 380$ V; $U_{ga} = 270$ (plateau), 310, 330, 350, and 370 V; (b) 2 mm thick crystal, $T = 77$ K, gas Ar; two lower curves at $U_{cg} = 280$ V; $U_{ga} = 0$ (baseline), 1000 V (plateau); upper curve at $U_{cg} = 400$ V and $U_{ga} = 700$ V.

see that contrary to the gas cell where regenerative phenomena are apparent only by a signal broadening, the position of the regenerative peak in the cell with solid Xe exactly corresponds to the moment when the primary electrons disappear reaching the anode. It unambiguously proves that only *VUV luminescence following the electron drifts inside the solid Xe* creates the positive feedback, causes regeneration and then the appearance of a self-sustained discharge.

Of course, far below the threshold, the ratio of the areas of the peaks belonging to secondary electrons originated from bulk and surface exciton emission is equal to the ratio of the corresponding quantum yields per drifting electron (naturally this ratio has to be a function of U_{ga}). Moreover, such an estimate looks reasonable because most of the processes governed the measured signal reproducibility, such as (i) variation of photoelectron emission efficiency due to cathode surface poisoning; (ii) mesh partial blocking by solid xenon particle sedimentation; (iii) presence of an uncontrolled gap between grid and crystal surface, leading to additional electron multiplication in the gas, etc., do not affect the ratio, because their influence is the same for both contributions. The ratio of the slow and fast components of electron current tail areas for the data of Fig. 3(b) ($T = 77$ K, $d = 2$ mm, $U_{ga} = 1000$ V) is equal to $\eta = 20 \pm 5$. Since the quantum yield of electroluminescence from surface excitons hardly differs from unit, one may consider this value as an estimate of the VUV quanta yield per one drifting electron. Of course that value should be higher for higher voltage, but the value of the efficiency of direct conversion of the electrostatic field energy to VUV radiation, $\kappa \equiv \eta h\nu/U = 15^{+15}_{-5}\%$, has a more universal sense. For $T = 125$ K [Fig. 3(a)] due to the weakness of the surface exciton signal the estimation is less reliable but both the VUV photons yield and the transformation efficiency seem to be even higher.

Naturally, no seed electrons and no laser are necessary anymore above the self-sustained discharge threshold since the cw discharge ignites simply by switching on the power supply. The discharge is accompanied by a very bright visible emission characterized by a broadband spectrum (the intensity is many orders of magnitude higher than that of the glow of a gas discharge initiated in the absence of solid Xe). To estimate the attainable discharge current the experiments have been carried out when the "cathode-grid" power supply was replaced by a 10 mF capacitor, charged to a voltage exceeding the threshold voltage necessary for the cw discharge. Since the duration of the visible light pulse is equal to $\tau = 70$ ms at $U = 300$ V, the maximum discharge current is $J = CU/2\tau = 20$ A. The origin of that emission is obviously not from xenon but from impurities. In spite of careful purification the density of impurities remaining in Xe, $\approx 10^{13}$ cm^{-3}, is sufficient to allow for emission under excitation by either an electron impact (the current is rather high) or VUV photons absorption (their flux is even higher). An indirect evidence for such a mechanism is the fact that the current degradation due to voltage compensation by the space charge, formed by electron capture by the trace oxygen, does not exist in a regime of self-sustained discharge—possibly F centers are steadily bleaching by VUV emission and drifting electrons. Both these agents would cause as well the photo- and plasmochemical reactions of an impurity intentionally embedded in the xenon matrix. Our cell is ideal for such a study.

Conclusion.—The phenomenon of multiple VUV quanta emission proves that the excess electrons drifting through solid Xe indeed can be accelerated in moderate electrostatic field up to the energies of 8 eV. Such a behavior, no doubt, takes place as well in liquid Xe and, at higher energies in condensed Kr and Ar. It means the electronic excitation of a matrix should be the main factor determining the characteristics of electron motion in heavy RG and it should be taken into account under the examination of electron transport in any nonpolar dielectric. The technique of bulky electric discharge organization inside a solidified RG developed in this work can serve as a prototype of both effective VUV light source (as exciton lasers and lamps) and the reactor for studying the interaction of impurities intentionally embedded to a low temperature inert matrix with high energy electrons.

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[1] E. B. Gordon, V.V. Khmelenko, and O. S. Rzhevsky, Chem. Phys. Lett. **217**, 605 (1994).
[2] E. B. Gordon, O. S. Rzhevsky, and V.V. Khmelenko, Kvantovaya Elektron. **21**, 227 (1994).
[3] S. S.-S. Huang and G. R. Freeman, Phys. Rev. A **24**, 714 (1981).
[4] E. B. Gordon and A. F. Shestakov, Low Temp. Phys. **27**, 883 (2001).
[5] A. S. Schussler *et al.*, Appl. Phys. Lett. **77**, 2786 (2000).
[6] E. Aprile *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **343**, 129 (1994).
[7] E. M. Gushchin, A. A. Kruglov, and I. M. Obodovskii, Sov. Phys. JETP **55**, 650 (1982).
[8] M. Ichige *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **333**, 355 (1993).
[9] Produced by Caburn MDC Ltd., The Old Dairy, The street Glynde, East Sussex BN86SJ U.K.
[10] E. V. Savchenko and I. Ya. Fugol's, in *Cryocrystals* edited by B. I.Verkin and A. F. Prikhod'ko (Naukova Dumka, Kiev, 1983), Part 4 (in Russian).
[11] G. Ascarelli, J. Phys. Chem. **84**, 1193 (1980).