

## Reflection of Slow Electrons from the Surface of Pure Tungsten and from Tungsten Covered by Thin Films

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(Submitted to JETP editor June 30, 1955)

J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 667-674 (April, 1956)

The reflection of slow electrons from the surface of both pure tungsten and tungsten covered with adsorbed films of barium and various thicknesses, and of oxygen, is investigated. Particular attention is given to achieving a very high vacuum in the experimental tubes so that the components of residual gases ( $p_{\text{eff}} \approx 10^{-10} - 10^{-11}$  mm) condensed on the surface could not have a measurable effect. The results of the experiments show an unusual dependence on the primary electron energy  $V$  of the coefficient of secondary emission  $R$  for pure W and O-W, and a large effect  $P$  on  $R$  of the films of Ba adsorbed on W with a thickness smaller than, and of the order of a monatomic layer. The correct correlation is also obtained between the threshold of emission of the secondary electrons and the work function of the target.

THE contemporary period of development of the physical cathode electronics is characterized in part by a renewed increased interest in the problem of a solid body covered by thin and active films. This interest is connected with the fact that such systems-cathodes are again beginning to assume a serious importance as practical sources of electrons<sup>1</sup>, and also that at the present time these investigations can be carried out on a high experimental level previously entirely unattainable. Among these systems belong first of all tungsten covered by thin adsorbed layers of electro-positive barium, which appears to be a model of the contemporary porous metal-coated ( $L$ ) cathodes. In this project, together with recently completed accurate investigations of the work function of similar systems<sup>2</sup> a great interest also encourages the study of reflection of slow electrons from such surfaces and also from tungsten covered by a film of electro-negative oxygen. This method has not been used thus far to study directly the surface potential barrier of similar film systems. These circumstances have stimulated us to undertake the present work.

As is well known, a study of elastic reflection of slow electrons is a very difficult problem from the experimental point of view. First, it is very difficult to achieve in the experimental tube such vacuum conditions that would fully guarantee a complete cleanliness and also reliability of the obtained results. We particularly emphasize here the role of this factor since the coefficient of elastic reflection of slow electrons  $R$  is very sensitive to changes of the surface composition entirely undetectable by other methods. From this point of view the majority of the work completed to date may not be sufficiently reliable.

Since we had appropriate ionization techniques to obtain, maintain and measure very high vacuum in experimental tubes, i.e., pressures  $p \lesssim 10^{-9}$  mm<sup>3</sup>, we have decided to carry out the present investigation.

Two designs of the experimental tubes were used in the present work; the first is shown schematically in Fig. 1. The experimental target was a disk of rolled tungsten ribbon, which could be moved into two positions: 1) outside of the measuring system where it could undergo thorough cleaning by electron bombardment, and where films of Ba and Ag of the desired thickness could be evaporated on it; 2) inside of the collector (position 2) where the measurements were made. The only disadvantage of this system was that its collector did not have a spherical form which could reflect itself on the accuracy of the interpretation (even though to only a very small degree) of the trapping curves of the reflected electrons (see below). The layer of Ag used as an additional control was always thick; the films of Ba deposited on W were both monatomic with various degrees of coverage  $\Theta$ , and thick. The density of Ba atoms in this film could be accurately determined by a measurement of the contact potential  $V_k$  of the target relative to the tungsten cathode of the gun<sup>2</sup>. The contact potentials were measured in position 2 by a precisely parallel displacement of the voltampere characteristics  $I$ -5 of the current in the target  $I_M$ , which on a semilogarithmic graph has a linear character. This led to a correct order of magnitude of temperature of the electrons  $T \approx 2300^\circ$ , as is evident from Fig. 2. The accuracy of the focusing of the beam of slow electrons, very important in this case, was tested first by means of a collection of the beam on a

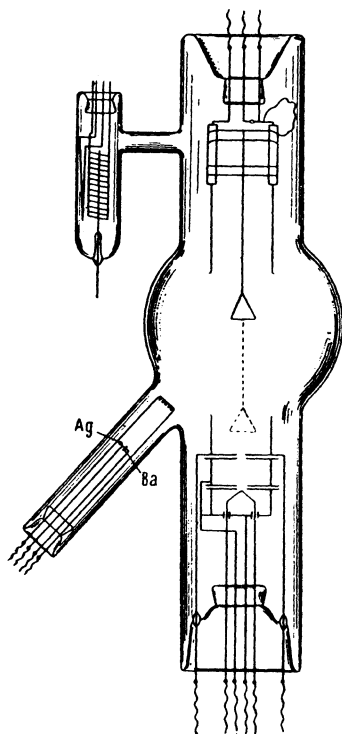


FIG. 1. Diagram of the experimental tube.

model of our system of electrodes, whose collecting disk was divided into a set of isolated rings with individual leads. The system was pumped constantly at a pressure  $p \approx 10^{-6} - 10^{-7}$  mm. This test has shown that our primary beam of electrons up to energy  $V_p = 2V$  is well focused on the surface of the target and consequently, no substantial errors should originate from this surface.

Together with the tubes of the first design we have made a considerable use of tubes of a second design, which differed only in the shape of the target. In the second design the target was made in  $\Pi$  shape of the same tungsten ribbon, 0.06 mm thick, 4 mm wide and 6 mm long in the front end. This target was placed in a fixed position inside the collector and could be directly heated by flowing through it current of an appropriate magnitude. In this case, even without mentioning two new possibilities discussed below, we could carry out the measurements of the coefficient of reflection of electrons from W both immediately, as the target has cooled after its high temperature degassing (similarly to the bulb of the first design), and also after the degassing but still directly from a glowing target, for example, at  $T \approx 1700^\circ K$  where the films adsorbed on tungsten are basically absent. In the latter case the tungsten target was

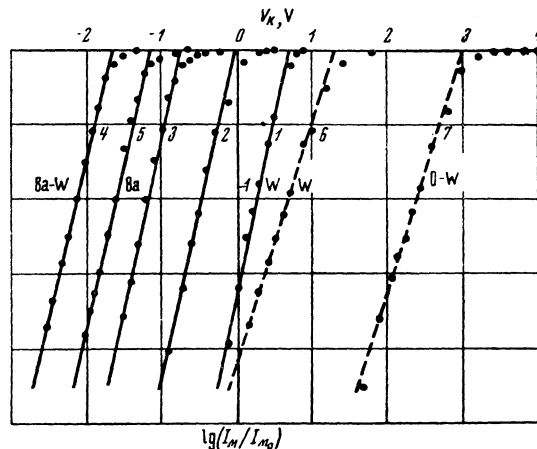


FIG. 2. Volt-ampere characteristic curves: 1- $\Delta\varphi = 0$ ; 2- $\Delta\varphi = 0.7$ ; 3- $\Delta\varphi = 1.5$ ; 4- $\Delta\varphi = 2.4$ ; 5- $\Delta\varphi = 1.9$ ; 6- $\Delta\varphi = 0$ ; 7- $\Delta\varphi = 1.7$  ev.

heated by an alternating current passed through a half wave rectifier to remove the magnetic field due to the large heating current through the tungsten ribbon and the potential drop caused by it across the target, and the measurements were carried out in the half period when the current was shut off. This scheme has been successfully used by us several times previously<sup>4</sup>. Furthermore, to separate out the electrons reflected from the target due to its spontaneous thermal emission as a result of the heating, the primary beam was modulated by 50 periodic square wave pulses synchronized with the shutting off of the heating current, on which was superimposed a sinusoidal signal of frequency 7.8 kc. The current of reflected electrons was amplified and was measured on an oscilloscope.

A great deal of attention was paid to achieving the proper vacuum conditions in the tubes<sup>5</sup>. After lengthy and very careful pumping and outgassing, spraying of Ba gas getter and finally sealing off the bulb, the initial pressure of the residual gases inside the tube was about  $p_0 \approx 10^{-7}$  mm; This pressure was measured by a modified ionization gauge<sup>6</sup> soldered to the experimental tube (see Fig. 1). After the sealing off of the tube this ionization gauge was working constantly as an activator of ionizing gas absorption<sup>3,6</sup>. By these means, the pressure of the residual gases in the bulb was reduced to  $p \approx 3 \times 10^{-9}$  mm and was maintained at that level. However, it can be shown that  $p_{\text{eff}}$  of that part of the residual gases which in fact can be adsorbed on the studied surface and cause deterioration of the obtained results, is still at a much lower level. This can be seen from the

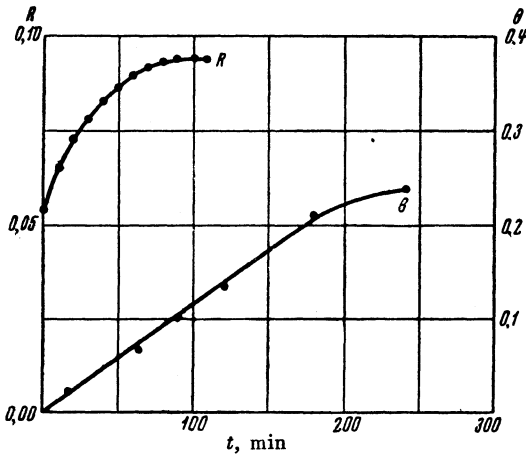


FIG. 3. The change of the quantities  $R$  and  $\theta$  for a tungsten ribbon which is left cold in the tube.

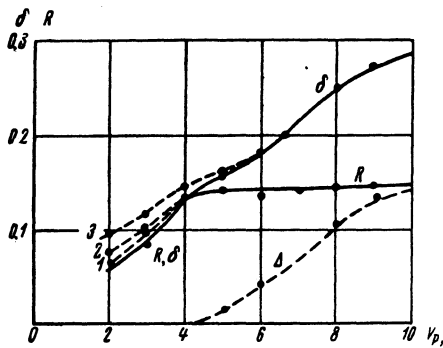


FIG. 4. The variation of the quantities  $\delta$  and  $R$  for clean tungsten as a function of the energy of primary electrons.

analysis of the mass-spectrograms of the gas in similar glass tubes used for a long period of time<sup>6,7</sup>, and also by a direct application to these experimental tubes of the method of "flashing"<sup>3,8</sup> and also from the measurement of the coefficient of elastic reflection  $R$  (see below). As an illustration of this very important circumstance we shall show that in one case where the tungsten target of the second design was flashed we obtained a result shown in Fig. 3. Here the ordinate on the right hand side is the drop in pressure in the bulb at the moment of flash, recalculated to the corresponding fraction  $\theta$  of covering the target by the adsorbed gas on an assumption that a monomolecular layer has  $1.25 \times 10^{14}$  mol/cm<sup>2</sup><sup>8</sup>; the abscissa is the time of the preceding adsorption. From the slope of the initial linear portion of the curve  $(d\theta/dt)_{t=0}$  one can obtain  $p_{eff} \approx 10^{-11}$  mm at a time that the ionization gauge shows  $p = 3.5 \times 10^{-9}$  mm. The second curve in the same

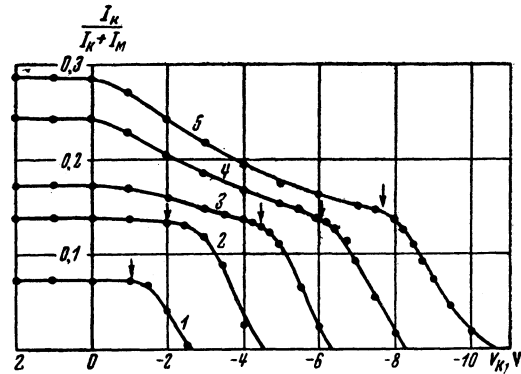


FIG. 5. The family of trapping curves for clean tungsten: 1 -  $V_p = 2$ ; 2 -  $V_p = 4$ ; 3 -  $V_p = 6$ ; 4 -  $V_p = 8$ ; 5 -  $V_p = 10$  v.

figure gives the typical time dependence of the coefficient  $R$  for tungsten at a constant  $V_p = 2V$  (the scale is on the left-hand ordinate); here, from the quantity  $(dR/dt)_{t=0}$  one obtains a value  $p_{eff} = 10^{-10}$  mm. Thus, the value of the quantity  $p_{eff} < p$  lies within these very low limits  $10^{-10} - 10^{-11}$  mm. It allows us to assume that we work under sufficiently pure conditions if the measurements are made immediately after the outgassing of the target. Furthermore, one sees immediately the error in the measured quantity  $R$  that can be introduced under actual conditions. It should be noted that even for such low pressures of the residual gases in the tube there exists a slow but still noticeable increase of the reflection coefficient  $R$  with time (see Fig. 4). This may increase by a factor of two or more over its initial value. This limiting value of the quantity  $R$  at a fixed  $V$  may vary in different cases because of its dependence on the pressure and the composition of the residual gases in the tube. By the way, under the same conditions one observes only a small increase ( $\lesssim 0.1$  ev) in the work function of the investigated surface. The work function is determined from the changes in the contact potential. In this manner the coefficient  $R$  of elastic reflection of electrons appears to be very sensitive to the smallest changes in the composition of the surface under investigation. Therefore, all of our subsequent data refer to the initial uncontaminated values of the quantity  $R$ . The fact that the deviation from the linear dependence of  $R$  and  $\theta$  on  $t$  in Fig. 3 begins at different times  $t_R$  and  $t_\theta$ , where  $t_R < t_\theta$ , is evidently a manifestation of the entirely different physical character of the two



FIG. 6. The variation of the quantity  $R$  as a function of the energy of primary electrons for W and Ba-W with coverage corresponding to: 1- $\Delta\varphi=0$  (W); 2- $\Delta\varphi=0.7$ ; 3- $\Delta\varphi=1.5$ ; 4- $\Delta\varphi=2.4$ ; 5- $\Delta\varphi=1.9$  eV (Ba).

measures of the number of adsorbed molecules. Indeed, if the effective interaction separation between the gas molecules falling on the surface and those already adsorbed is simply their gas kinetic diameter  $d_k \approx 3 \text{ \AA}$ , and for impinging slow electrons is of the order of magnitude of a phase wavelength  $\lambda_e$  which is of the order  $8 \text{ \AA}$  for  $V_p = 2V$ ; then  $\lambda_e > d_k$  to which corresponds  $t_R < t_\theta$ .

The determination of the coefficient of elastic reflection  $R$  of electrons from the investigated surface was carried out by the usual method based on a preliminary determination of the curve of the trapped current in the collector circuit  $I_k$  for all values of  $V_p$ . An example of such a family of curves for the case of pure tungsten is given in Fig. 5; the arrows point to those values that characterize elastic reflection and whose appropriate ordinates give us the value of the quantity  $R$ . Even though our system was not spherical, the points of inflection of the curves of Fig. 5 are sufficiently clearly apparent to enable us to separate out reliably from all electrons leaving the target the group that was elastically reflected. Control experiments with a spherical system led to the same results.

An example of a similar determination of the coefficient of elastic reflection  $R$  of electrons as a function of the energy  $V_p$  of the primary electrons impinging on the target, taking into account contact potential difference, is shown in Fig. 4. Here, one of the two solid curves gives  $R = f(V_p)$  for thoroughly cleaned tungsten surface. This curve was reproduced many times with tubes of both designs, and also using the modulation of the primary beam. The second solid curve gives the dependence on  $V_p$  of the relative number  $\delta$  of all electrons leaving the target, measured in the

saturated states for  $V_k = +2V$  (Fig. 5). Both inelastically reflected and also secondary electrons will be included in the number  $\delta$ . As is apparent from Fig. 4, both of these curves merge, in the region of small values of  $V_p$ , beginning at  $V_p \approx 4-5$  V, which may be regarded as a threshold of secondary emission from W (see below). The group of dotted curves 1, 2 and 3 give the same quantity  $\delta$  measured at various times  $t_1 < t_2 < t_3$ , which are the periods for which the target remained cold after its high temperature cleaning. We notice that as a result of adsorption of a part of the residual gases on the target, the increase in  $\delta$  is principally on the left-hand side of the curves where almost all emitted electrons are elastically reflected. This increase becomes more pronounced as  $V_p$  decreases. Thus, Fig. 4 immediately shows the effect of the adsorption of films from residual gases on the target in the regions of various values of  $V_p$ .

On a closer inspection of Fig. 4 attention is drawn to the unusual form of the curve  $R = f(V_p)$  for pure W. Regardless of the detailed description of this phenomenon one should expect a decrease in  $R$  with an increase in  $V_p$ , while the experiments repeated many times show here an opposite relation, particularly in the region of small  $V_p$ . On the other hand, a thick layer of silver deposited on the same W had a somewhat more normal dependence. In comparing the data for W and Ag with the data obtained by Myers<sup>9</sup> we have concluded that the curve  $R = f(V_p)$  obtained by him for W corresponds to our W covered by an adsorbed film. For Ag, the disagreement of some degree is only in the initial part of the curve.

An attempt to explain the above facts encounters immediately great obstacles, particularly since one of the least clear facets of the problem is the role played here by the polycrystalline character of the investigated tungsten surface. This is so even though there are indications that rolled tungsten ribbon should have its surface composed of microcrystals with predominant orientation of the (100) axis<sup>10</sup>. We have attempted to clarify this problem for W which may be subjected to high temperature cleaning by crystallizing the tungsten ribbon through an appropriate temperature treatment. This treatment consisted of repeated turning on and off of the heating current which heated the central part to about  $1800^\circ \text{ K}$ . Simultaneously, a very steep temperature gradient was established along the ribbon by conducting away heat through thick leads, and consequently, an elastic strain was established as well<sup>11</sup>. It turns out that by

this means one partly succeeds in crystallizing the ribbon, obtaining crystals as large as  $\approx 0.1$  mm in the regions where  $dT/dx$  was maximum. We have unfortunately not succeeded in obtaining larger crystals. Of course, this amount of crystallization is still far from necessary, but nevertheless we obtained both the contact potential curves and the curve  $R = f(V_p)$  in one of our tubes of the second design for very carefully cleaned tungsten both before crystallization and after crystallization. However, we could not find any noticeable difference between the two sets of curves.

With a gradual adsorption of thin films on an ordinarily (uncrystallized) clean tungsten surface ( $\varphi_0 = 4.5$  ev) with various degrees of coverage  $\theta$ , we obtain the results shown in Fig. 6 with curves 1-5 consecutive in time (similarly to Fig. 2). The films are characterized by the average value of the work function  $\Delta V_k = \Delta \varphi$  determined from changes of the contact potential  $\varphi = \varphi_0 - \Delta \varphi$ . The greatest density of a monolayer of Ba corresponds to  $\Delta \varphi = 2.4$  ev (curve 4), i.e., it is somewhat smaller than the one corresponding to the optimum covering where  $(\Delta \varphi)_m = 2.9$  ev<sup>2</sup>, i.e.,  $\varphi_m = 1.6$  ev. The last curve 5 refers to a thick layer of Ba for which it is well known that  $\varphi = 2.6$  ev. In Fig. 6 one notices that the character of the curve  $R = f(V_p)$  changes sharply with a gradual adsorption of a film of Ba on tungsten even within the limits of a monatomic layer. We see that with a growth of the quantity  $\theta$  the behavior of the curves deforms gradually within the limits  $\theta < 1$ , finally assuming the normal character of decreasing  $R$  with an increase in  $V_p$ . Finally, the curve 5 for a thick layer of Ba has a normal appearance and agrees well with the measurements of Bruining<sup>12</sup>,

Together with an investigation of electropositive films Ba-W, we have undertaken an investigation of electronegative films O-W. We used tubes of the second design, which, after all the above-described operations and measurements with clean tungsten, were soldered to a second vacuum system by means of a special side connection. The additional vacuum system was designed to introduce various pure gases at low pressures into the tube. Pure oxygen was let into the tube at a pressure  $\approx 10^{-5}$  mm and the ribbon was carefully heated in its atmosphere at  $T \approx 1300^\circ$  K. Oxygen was meanwhile periodically pumped out and the change in the work function was determined by the previously described method. In this manner, as

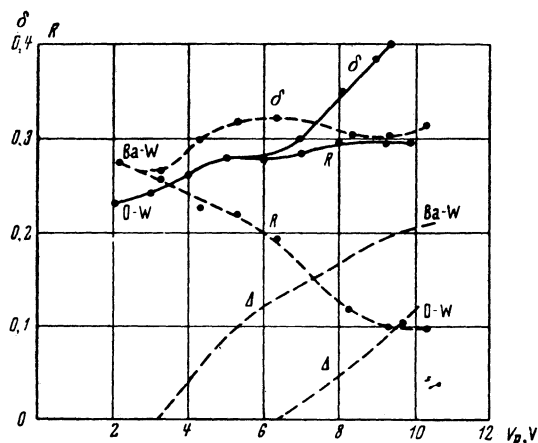


FIG. 7. The dependence of  $\delta$  and  $R$  of the energy of primary electrons for Ba-W and O-W.

is evident from the two dotted curves 6 and 7 of Fig. 2, the change in the contact potential in the reverse direction was  $\Delta V_k = \Delta \varphi = -1.7$  ev, i.e.,  $\varphi = 6.2$  ev, which is quite close to the limiting value of  $\varphi_m = 6.3$  ev<sup>13</sup> quoted in the literature. As this level was reached, the residual gases were pumped out very carefully and all the above described measurements were carried out. The results for the O-W system are given in Fig. 7; for comparison the data for our Ba-W system with  $\Delta \varphi = 2.4$  ev are included in dotted lines which (together with Fig. 4 for pure W) give a complete picture of the problem of interest to us. We see that the data for O-W are very similar in character to the data for pure W, differing only by greater value of  $R$  and  $\delta$ , but at the same time entirely different from the data for Ba-W.

As has already been shown above, one of the tasks of our investigation was the study of the structure of the surface potential barrier for monolayer systems by the method of reflection of slow electrons. In a direct utilization of our experimental data for this purpose one must be careful to a certain extent. First of all, the tungsten surface may have a polycrystalline character and then the work function may vary over its surface and thus both the height of the potential barrier  $\Delta \varphi \gtrsim 0.3$  ev and also the nature of the local contact fields will vary from place to place. Secondly, a film on W with  $\theta < 1$  may have a somewhat spotty character with the linear dimensions of non-uniformities  $a$  probably much greater than wavelength  $\lambda_e$  of the primary electrons probing the surface ( $a \gg \lambda_e$ ). The reflection from the entire surface is then a sum of the reflection effects from the separate elements of the surface—both

System	$V_p'$ in v	$\varphi$ in ev
W . . . . .	4—5	4.5
Ag . . . . .	3—4	4.3
Ba . . . . .	3—4	2.6
Ba—W . . . . .	~3	2.1
O—W . . . . .	~6	6.2

clean and covered by a film<sup>14</sup>. Therefore, it makes sense to compare with theory only the curves 4 and 7 for Ba-W and O-W (see Fig. 2) with a coverage close to optimum, where one can consider the tungsten base to be covered more or less continuously and uniformly. With that goal one should make a theoretical computation of the dependence  $R = f(V_p)$  on the basis of well-known methods<sup>15</sup>, selecting the appropriate form of the total potential barrier. However, in view of the reasons given above, such work would be somewhat premature at the present time, before our experiments are extended to the reflection from uniform single crystals, which will be our problem in the near future. Still, it should be noted that, for example, the increase of the quantity  $R$  with the degree of coverage  $\theta$  in the region of small  $V_p$  observed in Fig. 6 is theoretically quite real since we gradually pass from a potential barrier of continuous hyperbolic shape for clean W to a barrier with more sharply defined wall formed by a superposition on the preceding barrier of a rapid potential change due to the film of Ba atoms adsorbed on W. We ascribe similar reasons to the growth of the quantity  $R$  in passage from W to O-W.

The main object of our study was the elastic reflection of electrons which takes place without noticeable losses of energy. Together with this effect one observes on the trapping curves the effect of a second group of emitted electrons with noticeably smaller energies<sup>16</sup> when the energy  $V_p$  of the primary electrons exceeds a particular value  $V_p'$ . This means that for  $V_p > V_p'$  the number of all emitted electrons  $\delta$  and the number  $R$  of elastically reflected ones will increasingly differ, as is shown in Figs. 4 and 7 by the dotted curves for the quantity  $\Delta = \delta - R$ . The threshold values obtained for the latter curve, i.e., the quantity  $V_p'$ , and also the work function  $\varphi = \varphi_0 - \Delta V_k$  of the various systems considered by us are given in the accompanying Table. It is evident

from the Table (thus far only qualitatively, since we did not specifically concern ourselves with this question) that the values of  $V_p'$  correlate with the corresponding values of  $\varphi$  which agree with the condition  $V_p' + \varphi \approx 2\varphi$ . The last fact may be used to a certain extent as an argument that we deal with a threshold of the secondary emission<sup>17</sup> and not with the appearance of inelastic losses, and that therefore the curve  $\Delta = f(V_p)$  characterizes a purely secondary emission. However, we cannot prove this fact, since our work is only of a qualitative nature.

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