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DIMENSIONS AND SHAPE OF THE CROSS SECTION OF FORMATIONS RESPONSIBLE FOR ANOMALOUS FIELD-ELECTRON EMISSION OF ORGANIC SEMICONDUCTORS

In papers (^{1}), attention was drawn to unusual effects of field-electron emission from tungsten tips on whose surface copper phthalocyanine had been adsorbed. On the screen of an electron projector, in addition to the usual picture of the surface of a single crystal of tungsten, relatively bright spots were observed in the form of circles and of two- and four-petal figures (abbreviated as "twos" and "fours"). It was subsequently shown that various bright spots, sometimes of a very complex but symmetrical appearance, are formed upon adsorption or condensation on metallic tips of various low-molecular compounds (see the reviews (^{2}) and (^{3})). Various hypotheses concerning the mechanism by which the indicated spots arise did not agree with the experimental data. In one of the recent books on field-electron emission, the mechanism of appearance of the indicated spots is declared to be enigmatic (^{4}).

It should be noted that, although more than enough considerations have been published concerning the structure of the molecular complexes responsible for the unusual patterns, there are no reliable experimental and quantitative data on these complexes in the literature. Many authors confined themselves to estimates and conjectures (^{5}).

The aim of our work is to obtain quantitative information on the cross section of the complexes. Determining the shape and dimensions of the cross section of a complex of molecules that give rise to the enigmatic patterns of field-electron emission is especially important because these patterns have often been attributed to individual molecules (^{3,4,6}).

Obtaining these data is also important for testing the recently proposed "waveguide" theory of the appearance of spots (^{7}).

In order to determine the transverse dimensions of the formations under discussion from their images on the projector screen, it is necessary to know the local magnification. In our opinion, the answer to this question is contained in the work of Rose (8).

The formula for the local magnification proposed by Rose, as far as we know, has not been experimentally verified by anyone. This is not surprising, since the "placing" on the tip of a metallic point with radius $\rho \leqslant 1\ \mu$ of some calibration object of known dimensions $\ll 1\ \mu$ is not an easy task. We have circumvented these difficulties.

According to Rose, the local magnification M_l, in the case of a metallic hemisphere of radius ρ located on a metallic tip of paraboloidal shape with radius of curvature at the vertex R, is determined from the relation

$$M_l = M_0 \cdot 1.1 \left(\frac{R}{\rho}\right)^{1/2}, \tag{1}$$

where M_0 is the magnification in the case of a "macrotip"

$$M_0 = D/\beta R, \tag{2}$$

D is the distance from the tip of the point to the screen, and β is the coefficient of compression of the image caused by the presence of the cylindrical part of the point.

The numerical value of β is easily determined experimentally and ranges from 1.3 to 1.8. Substituting the value of M_0 into (1), we obtain

$$M_l = \frac{1.1D}{\beta(R\rho)^{1/2}}. \tag{3}$$

If the diameter of the bright spots of anomalous field emission on the projector screen is denoted by $2W$, and the transverse size of the complex forming the spots by $2a$, and if the complex is regarded as being close in shape to a hemisphere and, in electrical conductivity, similar to a metal, then

$$M_l = \frac{W}{a} = \frac{1.1D}{\beta(Ra)^{1/2}}. \tag{4}$$

Assuming that approximately the same values of a correspond to certain types of spots, and that $\beta = \text{const}$ and is the same for all points of the tip, we obtain

$$\frac{W^2}{D^2} R \cong \text{const}. \tag{5}$$

By determining W in one and the same projector, i.e., at $D = \text{const}$, but for different radii of the point, one can experimentally check the validity of relation (5) and ultimately determine the dimensions a:

$$a = \frac{W^2}{D^2}\frac{\beta^2}{1.21}R. \tag{6}$$

In experimentally checking relation (5), it is necessary to bear in mind both a certain scatter of the values of a and β, and the low accuracy of the measurements of W (the measurements were carried out with an ocular micrometer). Therefore it is necessary to have a large statistical sample of values of $\frac{W^2}{D^2}R$.

In all, 600 spots were measured: pairs and quadruplets. Copper phthalocyanine and anthraquinone, repeatedly purified in vacuum of 10^{-8} mm Hg by fractional distillation, were used as the objects giving pairs and quadruplets. These substances were condensed from the vapor onto a tungsten point cooled with liquid nitrogen. The radius of the point was determined in each experiment by the Drechsler and Henkel method (^{9}). From experiment to experiment it was varied by heating at 2500° for 5–60 sec in a reverse electric field. After the completion of an individual experiment, the substance deposited on the point was desorbed in a positive electric field, the strength of this field being approximately 3 times greater than the strength of the imaging field. The sequence of operations was: desorption, heating, determination of the radius, condensation of the substance, observation. After a series of experiments, R changed by approximately a factor of 3. Further experiments were stopped, since the pairs and quadruplets became small and inconvenient to measure. In each experiment a series of photographs was obtained with a Konvas motion-picture camera. The magnitude W was measured for a large number of pairs and quadruplets, and the mean value $\overline{W}$ was determined from 20–50 spots.

In Fig. 1, points show the values of the quantity $\frac{\overline{W}^2}{D^2}R$ for different values of $\frac{R}{D^2}$. It is seen that the values of $\frac{\overline{W}^2}{D^2}R$ group near two straight lines parallel to the abscissa axis. The scatter of W relative to the straight lines amounts to 10%. Taking the true value of the constant $\frac{\overline{W}^2}{D^2}R$ to be the distance from the abscissa axis to the straight line, we determined the mean value $\overline{a}$, using the formula

$$\left(\frac{\overline{W}^2 R}{D^2}\right)_{\text{av}} \frac{\overline{B}^2}{1.21} = \overline{a}.$$

For the case of phthalocyanine $\overline{a}_{\text{dw}} = 8.2$ Å, $a_{\text{quad}} = 10.6$ Å; for anthraquinone $\overline{a}_{\text{dw}} = 13.7$ Å (quadruplets were not observed). The values of $\overline{a}$ for phthalocyanine are in good agreement with the estimate of the emitting area of the complex, 100 Å^2, made in work $^{(11)}$. One may also compare our value of $\overline{a}_{\text{dw}}$

Figure 1

Figure 1: Figure 1

with that calculated on the basis of the data of work (11). If the numerical values of the quantities entering formula (6) are used: $\overline{W} = 0.25$ cm, $R = 3 \cdot 10^{-5}$ cm, $D = 3.5$ cm, $\beta = 1.54$, then the value $\overline{a}_{\mathrm{dw}} = 7.5$ Å, which is very close to the value we obtained, 8.2 Å. The value of $\frac{\overline{W}^2}{D^2}R$ based on the data of (11) is shown in Fig. 1 by a cross. If the X-ray structural-analysis data given in (10) are used, it turns out that the "dimensions" of copper phthalocyanine are $8.20 \times 8.20\ \text{Å}^2$, and those of anthraquinone $7.40 \times 5.20\ \text{Å}^2$, i.e., along the radius a, in the case of phthalocyanine at least one molecule is accommodated, and in the case of anthraquinone two molecules. Most likely, these estimates have no physicochemical meaning, since in the electric field polymer chains are formed, the structure of which in detail may differ from the structure of free molecules.

Fig. 1. Experimental values of W^2R/D^2 as a function of R/D^2; the cross denotes the value of W^2R/D^2 calculated from the data of work (11)

Nevertheless, one may assert that the doublets and quadruplets on the screen are not due to single molecules adsorbed on the surface of the point, but to polymeric "whiskers" of the condensate growing on the point.

It is of interest to compare the ratio $a_{\mathrm{dw}}/a_{\mathrm{quad}}$ with that predicted by the "waveguide" theory (7). According to this theory, the wave number of the electron wave k for the case of a waveguide of circular cross section with radius a is related to a by

$$k = \frac{v_{ni}}{a}, \tag{7}$$

where v_{ni} is the i-th root of the Bessel function of order n. Doublets and quadruplets, according to the theory, correspond to the first roots of the Bessel functions of the first and second order.

For $k = \mathrm{const}$

$$\frac{a_{\mathrm{dw}}}{a_{\mathrm{quad}}} = \frac{v_{11}}{v_{21}}. \tag{8}$$

Theoretically, expression (7) is valid for the minimum dimensions a_{dw} and a_{quad}, but since the scatter of the values of a is small, $\overline{a}$ may be taken instead of a_{min}.

The experimental value of the ratio $a_{\mathrm{dw}}/a_{\mathrm{quad}}$ proved to be 0.773, the theoretical value 0.746. The experimental results obtained for the determination of a show that the assumptions underlying the derivation of Rose' s formula are also valid for complexes giving anomalous field electron emission; i.e., our experimental results are yet another proof of the validity of the model of metal-like molecules [12,13] for the substances studied in a strong electric field. Since the "waveguide" theory was based on the assumption of the presence of delocalized electrons, the results of our work are also, to some extent, a confirmation of the correctness of the foundations of this theory.

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