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Effect of an Adsorbed Film of Dipole Molecules on the Electronic Work Function

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An experimental investigation was performed, under high-vacuum conditions, of the variation of the work function of tungsten when an accurately measured film (of varying thickness) of cesium chloride molecules was deposited on it; these molecules contained an admixture of radioactive isotope Cs^{134} and, as a result, the density of the molecules in the film could be determined fairly accurately by the magnitude of its activity. It was shown that a film of CsCl molecules, having their own dipole moment, causes a decrease in the value of the work function of the tungsten; however, this decrease is considerably less than that produced by a film of cesium atoms. A comparison was made between these systems and data extracted from the literature for BaO--W and Ba--W systems. A discussion of several ways in which the results obtained here may be interpreted theoretically closes the paper.

THE investigation of the electronic properties of the surfaces of metals covered by adsorbed films of various, usually electropositive atoms has been the object of numerous works that have been carried out over a fairly long period of years.[1] Interest in this question lies, first, in the possibility of a broad and convenient study of the given physical problem and the application of electronic methods to the study of adsorption phenomena and, second, in the fact that systems such as these are invariably the base for many modern, efficient electron emitters. In the past the object of these investigations has usually been films of cesium, barium and thorium atoms and of the products of evaporation from an oxide cathode; the method of investigation was the following: variation in the magnitude of the photo- and thermoemissions; variation of contact potential as determined from the displacement of the current-voltage curves; and variation of the work function as determined from the shift of the red end of photoemission and from the change in the slope of the temperature dependency of thermoemission as expressed in the form: $\ln(I/T^2)=f(1/T)$.

As a result of these investigations, which were performed almost entirely with metals under conditions of high vacuum, the limits of the variation of the work function φ were determined; however, the density of the atoms adsorbed in the film N, on which this variation was based, was determined indirectly and this fact would usually introduce a certain element of arbitrariness, hampering a subsequent reliable interpretation of the results obtained. Moreover, there were absolutely no data on the effect of films of atoms deposited on the surface of nonmetals or on the effect of films of molecules, including polar molecules, i. e., those having a permanent dipole moment, deposited on the surface of solids of unlike nature, under high-vacuum conditions. Here we can mention only investigations of the effect of the adsorption of molecules of different vapors (water, alcohol, etc.) on the work function of various semiconductors under ordinary--not high-vacuum--conditions in connection with the problem of surface conditions;[2] these investigations are somewhat removed from the problem in which we are presently interested. Nevertheless, it is understandable that all these problems are of prime importance in the electronics of the surfaces of solids and of modern, efficient electron emitters--the cathodes.

It was not until 1950 that a work[3] appeared in which was posed the problem of studying the separate effect of films of BaO, SrO, and CaO dipole molecules on the variation of the work function of metals by means of a comparatively accurate measurement of the density of the molecules composing the adsorbed film. In this work a number of interesting results were reported; however, the conditions under which the experiments were performed do not give complete assurance of a sufficiently accurate determination of the value of N; furthermore,

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[1] Zh. De-Bur, *Electron emission and adsorption phenomena*, ONTI, 1936. A. Reiman, *Thermionic emission*, GITTL, 1940. C. Hering and M. Nichols, *Thermoelectronic emission*. L. Dobretsov, *Electron and ion emission* GITTL, 1952.

[2] N. Morgulis, J. Exper. Theoret. Phys USSR 16, 959 (1946). V. Lashkarev and V. Liashenko, *Memorial volume of the 70th anniversary of the academician A. F. Ioffe*, Publishing House of Academy of Sciences, USSR, p. 535 (1950). V. Liashenko and I. Stepko, Izv. Akad. Nauk SSSR Ser. Fiz. 16, 211 (1952). B. Il'in, *Nature of adsorption forces*, GITTL, 1952.

[3] G. Moore and H. Allison, Phys. Rev. 77, 246 (1950).

an unsatisfactory circumstance here was the heating of the substrate together with the adsorbed layer in the determination of the thermoelectric constants; consequently, there was the possibility of an uncontrolled alteration in the layer.* Therefore, with a far-reaching and more reliable study of this entire problem in mind, a series of similar investigations was performed in our laboratory; the first and second parts of these investigations, devoted to the Ba--W and BaO--antimony-cesium photocathode systems, have been completed.[4] Determination of the value of φ was made by means of contact potential and the shift of the red end of the photoeffect; this did not require heating the layer. Conductometric titration was used for determining the value of N; the part played by the reflection coefficient in the condensation of atoms and molecules on the surface could then be considered additionally. It is important to mention that here, too, we used the taper method successfully, providing the layer with a constantly and widely varying thickness; this procedure was worked out by us and has been extensively used in the past in the investigation of photo-and secondary-electron emission.[5] Finally, a paper was published quite recently which treated the ThO_2--Mo system;[6] here, a method of thermoemission with heating of the film was likewise used for determining the variation of the value of φ; a radiographic method of counting the α-particles of the natural radioactivity of thorium in the thick part of the layer with extrapolation toward the thin portion was used for measuring the value of N. However, the necessity of considerable heating of the Mo substrate led to the reduction of the ThO_2 film at its thin part and to results that were typical for the well-known Th--Mo system, etc. Thus, we see that the problem in which we are interested may be considered as barely begun and that it will require extensive and profound study. In this paper we shall present the results of our latest investigations of the problem; and, what is more important in this problem, these investigations have been conducted using the most perfect procedure.

The objects of investigation in the present work were the polar molecules of cesium chloride, having in the free or gaseous state a permanent dipole moment $p=10 \times 10^{-18}$ cgs units;[7] these molecules were deposited on the surface of tungsten. CsCl, tagged by a radioactive isotope Cs^{134}, having a specific activity of ≈ 350 mCu/g and a half-life of 1.7 years, and providing, in the main, β-radiation with an energy of 0.65 mev and γ-radiation with an energy of 0.09 mev, was used in the work. The tube used for the investigation was somewhat similar to that used previously;[4] it is shown schematically in Fig. 1. Its basic components

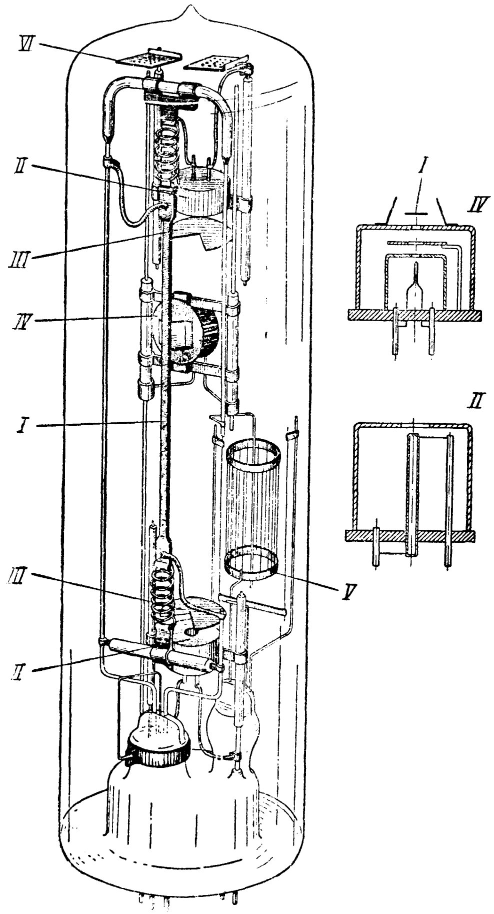

FIG. 1. *1*-Tungsten ribbon; *2*-evaporator; *3*-receiver; *4*-electron gun; *5*-manometer; *6*-getter.

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* *Correction.* After this work had been sent to prees, there appeared the paper of P. Russell and A. Eisenstein, J. Appl. Phys., 25, 954 (1954), inwhich were given the results of an investigation of thermoelectric emission and electronic diffraction of thin films of barium oxide deposited on nickel. Remarks made by us with respect to work[3] apply fully to this work.

[4] V. M. Gavriliuk, Trudy Inst. Fiz. Akad. Nauk Ukrainian SSR 5, 87 (1954); Zh. Tekhn. Fiz. 25, 14 (1955)

[5] N. D. Morgulis, Trans. Jan. 1942 session, Ukrainian SSR, partII, p. 215. N. Morgulis, P. Borziak, and B. Diatlovitskaia, Izv. Akad. Nauk SSSR Ser. Fiz. 12, 126 (1948). P. Borziak and N. D. Morgulis, Dokl. Akad. Nauk SSSR 61, 625 (1948). B. Diatlovitskaia, Dokl. Akad. Nauk. SSSR 63, 641 (1948). N. Morgulis and N. Nakhodkin, Dokl. Akad. Nauk. SSSR 94, 1029 (1954).

[6] A. Shul'man and A. Rumiantsev, Dokl. Akad. Nauk SSSR 93, 455 (1953).

[7] E. Rittner, J. Chem. Phys. **19**, 1030 (1951).

were: 1) a long (≈200 mm), flattened tungsten ribbon *I*, which was coated with a tapering film of CsCl molecules of varying density N; this ribbon was carefully degassed in advance by heating to high-temperature incandescence; 2) a platinum evaporator *II* in the shape of a small tube filled with CsCl and enclosed by a thermal screen of tantalum; an orifice 0.5 mm in diameter was made at the base of the tube; by heating the evaporator to a suitable temperature it was possible to deposit a clump of CsCl molecules on the tungsten surface; 3) a regulating receiver *III*, carefully located, on which a part of the evaporated CsCl molecules were condensed; 4) an electron gun with suitable electrodes *IV*; it was moved along the tungsten ribbon, permitting a determination of the variation of contact potential V_k from the displacement of the current-voltage curves; this gave us the distribution of the average value of the work function φ for a given section of the surface, at various locations along the ribbon; and 5) placed inside the tube envelope, a modified ionization manometer system *V*, having a central ion collector--a thin filament--and an external cathode with deflector;[8] this permitted continuous regulation of the degree of vacuum in the tube down to very low values of the order of $\lesssim 10^{-9}$ mm.

It is quite understandable that particular attention was given to obtaining and maintaining the highest possible vacuum in the experimental tube. With this in mind, the following was done:

1) The process of evacuating and degassing the glass envelope and the entire metal armature of the tube was performed most diligently and lasted for some 25-30 hours; most important, the process was repeated regularly several times. The vacuum plan made it possible to heat the glass enevelope, the last trap, and the ionization manometer and to bake the metal parts of the tube during evacuation. The excessively large barium getter *VI* was degassed and partially dusted before unsoldering the tube and, partially after unsoldering; the getter coating was distributed for maximum gas-absorption capacity; in case of necessity, the tube could still be cooled by immersing the envelope in a Dewar flask filled with liquid nitrogen. In this manner it was possible to obtain and hold a vacuum of $\lesssim 10^{-7}$ mm for a long time in the unsoldered tube.

2) Since this level of pressure of residual gases in the tube is considered absolutely unsatisfactory from the standpoint of the high requirements which must be exhibited at the present time in the methods of investigation for our problem, we resorted to the following procedure. It has long been known that absorption may be increased considerably by ionizing the residual gases in the tube; in this the ionization manometer system was of particular use;[9] in the given case it acted as activator for the absorption of the ionized gas by the carefully degassed surface of the glass envelope and by the getter speculum. Actually, by starting our manometer periodically about every half-hour we were able to obtain and hold a vacuum of the order of $p \approx 1\text{-}3 \times 10^{-9}$ mm; for measuring the value of full pressure p, our manometer was graduated in advance. Moreover, there are at present serious reasons for supposing that the effective partial pressure of that part of the residual gases that can actually be adsorbed on the surface of the tungsten, that is, to distort the results obtained here, is much lower still and may even reach a value of $p_{\mathrm{eff}} \lesssim 10^{-10}$ mm.**

The method of approach for the measurements themselves was as follows. By heating the evaporator filled with CsCl to a temperature of approximately 450°C, where the vapor pressure reaches a value of $\gtrsim 10^{-4}$mm, evaporation and deposition on the cold tungsten ribbon in the form of a layer having a constantly changing density takes place. At this time neither surface migration nor reevaporation of the CsCl molecules can take place. It is an easy matter to show that, since the evaporator is made of passive material--platinum--and the heat of dissociation of these molecules is fairly high, $Q = 106$ kcal/g mol, they do not dissociate into atoms during the evaporation process, and the layer deposited on the cold tungsten ribbon will consist practically of CsCl dipole molecules alone; incidentally, this is seen from a comparison of the CsCl--W and the Cs--W systems (see Fig.7). Similarly, we assume that there will be no partial reduction of the film of these molecules on the tungsten ribbon during its later temporary heating to a temperature of approximately 600°C[10] (see below), since, for example, the heat of formation of one of the typical chlorides, WCl_6, is equal to

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[8] R. Bayard and D. Alpert, Rev. Sci. Instr. 21, 571 (1950).

*******Correction.* After this paper had been sent to press, experiments were completed for an evaluation of the value of p_{eff}; a description and the results of these experiments were presented in a brief report by one of the authors (N. Morgulis, Zh.Tekhn.Fiz. 25,1667 (1955).

[9] H. Schwarz, Z. Physik 122,437 (1944). D. Alpert, J. Appl. Phys. 24, 860 (1953). D. Alpert and R. Buritz, J. Appl. Phys. 25, 202 (1954). H. Hagstram, Rev. Sci. Instr. 24, 1135 (1953).

[10] N. Ionov, J. Exper. Theoret. Phys USSR 12, 58, (1942).

97 kcal/g mol. For other tungsten chlorides there are no data even for this quantity, and the simultaneous absence of other essential parameters prevents us from making a quantitative thermochemical calculation of the degree of reduction of the CsCl by metallic tungsten as was done, for example, for BaO in the problem of the oxide thermocathode.[11] For purposes of comparison, however, let us point out that the film of adsorbed BaO molecules, having Q=126 kcal/g mol, displays no reduction during heating of the tungsten substrate before approximately 600 °C, as is seen from the value of the work function.[3] For this reason, the transformation of BaO--W into Ba--O--W, is likewise very improbable.

Having completed all necessary measurements (see below), during which the temporary heating of the tungsten ribbon under investigation to a temperature of approximately 600 °C took place, the tube was opened, and the tungsten ribbon *I*, with the CsCl film deposited on it, and the receiver *III* were removed. The use of a cesium compound tagged by the radioactive isotope Cs^{134} had the following very important advantage: it made it possible for us to determine directly, and with great accuracy, the actual final (after heating) density distribution of the molecules along the ribbon at various places $N=f(x)$, as well as the total quantity deposited on the receiver. Knowledge of the latter quantity made it possible for us, analogously to the previous case,[4] to determine also the distribution of the original (before heating) concentration of molecules $N_0 = f(x)$ along the ribbon. This was done by taking into account the shape and location of the evaporator with respect to the tungsten ribbon and the law of density distribution in a molecular clump along the ribbon. Use was also made of the well-known expression for the condensation of vapors leaving an orifice in a tube,[12]

$$N_0 = \frac{n}{\pi h^2} \frac{x/h}{[1+(x/h)^2]^2}(1-R), \qquad (1)$$

where h is the perpendicular distance between the molecules, x is the coordinate of the receiver along the ribbon, n is the total quantity of evaporated molecules, and R is the reflection coefficient of the molecules during incidence on the hard surface. We shall not stop here to discuss the very interesting question of the reflection coefficient;[13] it will be examined in another paper appearing shortly. However, we shall introduce here in Fig. 2 the results of our determinations of the value of R, using a somewhat simplified procedure, for CsCl molecules at various densities of coated film $R=f(N_0)$ for cold substrates of Ni, Mo, and W; these measurements were also made using a procedure of

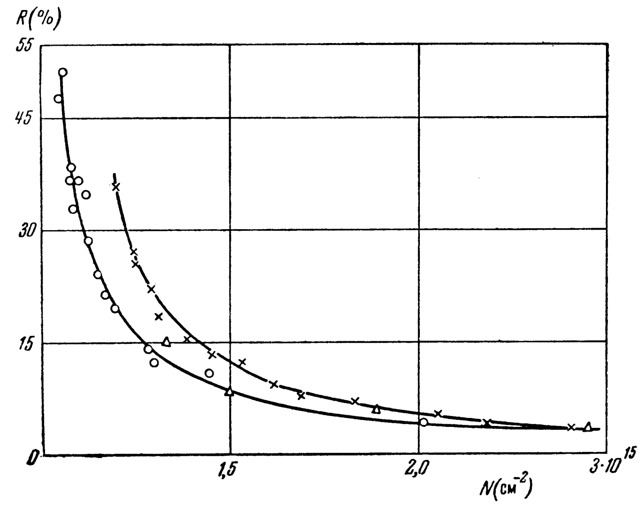

FIG. 2. × — Ni; ○ — Mo, △ — W

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[11] A. White, J. Appl. Phys. 20, 856 (1949). E. Rittner, Philips Res. Rep. 8, 184 (1953).

[12] S. Vekshinskii, *New method of metallography investigation of alloys*, p. 28, GTTI,, 1944.

[13] Iu. Khariton and Shal'nikov, *Mechanism of condensation and formation of colloids*, GITTI, 1934. M. Devienne, J. phys. radium 13, 53 (1952); 14, 257 (1953). N. Morgulis, V. Gavriliuk, and A. Kulik, Dokl. Akad. Nauk SSSR 101, 479 (1955).

tagged atoms.[13] We observe here a marked decrease in the value of R, from more than 50% at N=10 ^{14} cm^{-2} (degree of coverage $\theta>1$) to less than 10% at N=10 ^{15} cm^{-2}, where a second and other layers of molecules begin to form. Therefore, it is clear that a consideration of this factor will be necessary in future studies of adsorption processes.

On the other hand, a direct determination of the final density distribution of the CsCl film on the tungsten ribbon $N=f(x)$ was of particular interest, because it provided the most direct and reliable value of this function with a high degree of accuracy and sensitivity, reaching $\approx 4 \times 10^{13}$ cm^{-2} as a result of the comparitively high specific activity of the original radiocative preparation. In other measurements of the deposition of CsCl molecules at various places on the tungsten ribbon, we either placed a thick lead screen with a narrow slit between computer and ribbon, or divided the ribbon into small parts of the order of three millimeters in length and then determined the activity of the deposit of each division individually, by the usual method. The counting time for obtaining the necessary accuracy[14] varied depending on the background; our accuracy was fairly high. The absolute value of N at various places on the ribbon was determined on the basis of the specific activity of the cesium chloride being used and the efficiency of numeration during a fixed, steady arrangement of the ribbon with respect to the computer; activity was determined on the basis of β-radiation.

Determination of the variation of contact potential V_k, i.e., of the average value of the work function φ at each individual position of the ribbon, resulted from the variation of the displacement of the current-voltage curves from the given position of the tungsten ribbon, which played the role of collector of electrons in the system, and was placed opposite the given position of the electron gun; it was possible to move the latter along the entire ribbon. In order to avoid distortions in the measurements of the current-voltage characteristics (Fig. 3) owing to a varying drop of potential in the leads, the sliding contacts and the tungsten filament of the electron gun, the latter was heated by alternating current obtained from a mercury-vapor rectifier tube having a fixed resistance across the plate circuit. For this reason, the data for the current-voltage curves, that is, the measurement of the electron current, were recorded only during the half-cycle when the heating current circuit was closed by the action of the rectifier tube, i.e., when there was no voltage drop in the cathode circuit of the gun. The example of a similar family of mutually displaced curves is represented in Fig. 3. Their values were recorded, naturally, in the region of initial velocities of very low-density electron emission. This displacement is of an absolutely normal (parallel) character, and the temperature of the electrons of the tungsten filament--cathode of the electron gun, determined from the slope of these curves, has the plausible value of about 1800 °K; all this tends to confirm the reliability of our method of approach.

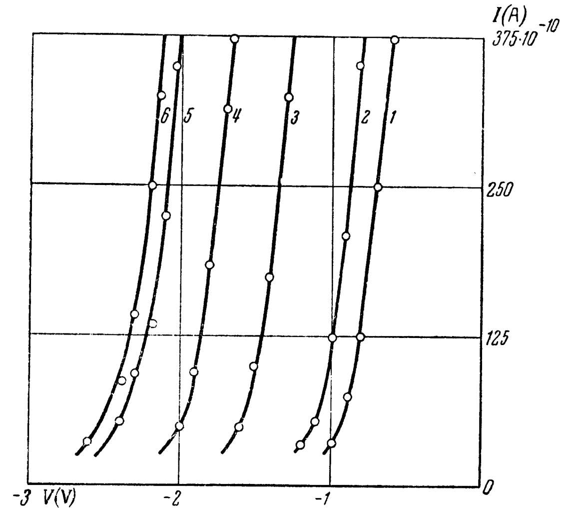

FIG. 3.

The results of measurements performed in this manner are represented in three figures in which the following are given: 1) the distribution of the surface concentration of the CsCl molecules along the tungsten ribbon immediately after dusting $N_0=f(x)$ (Curve I) and, then, after heating at T=600°C for one minute, $N=f(x)$ (Curve II, Fig. 4); 2) the distribution of the variation of the work function along the ribbon $\Delta\varphi=f(x)$ for these two extreme cases (solid lines) and for one intermediate case (broken line, Fig. 5); and 3) the same distribution $\Delta\varphi=f(x)$ for the same three cases but for a different tube (Fig. 6), where, naturally, the distribution $N=f(x)$ along the ribbon was somewhat different. For example, we see in Fig. 4 the variation in the linear distribution of the surface concentration which exists as a result of equal heating; this variation is obviously connected with the evaporation of an excess of CsCl molecules, corresponding somewhat to a nonuniform distribution of the temperature of the ribbon; Fig. 4 also shows the variation of the linear distribution of the work function caused by the above variation.

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[14] D. Taylor, J. Sci. Instr. 27, 206 (1950).

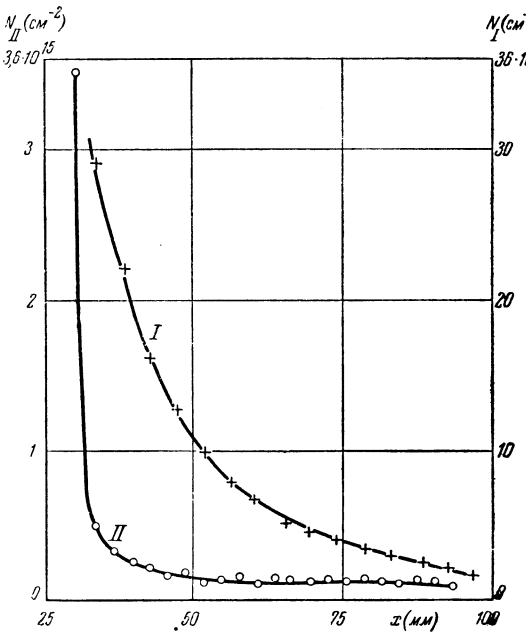

FIG. 4.

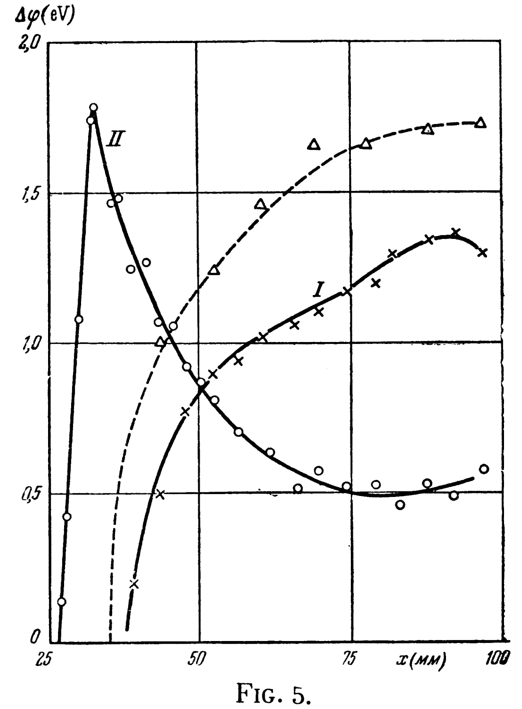

FIG. 5.

The results of the recorded measurements are represented (on two different scales) in Fig. 7, where the fundamental function $\varphi=f(N)$ is plotted for the following cases: a) the film of CsCl molecules on the tungsten immediately after dusting (before heating), represented by triangles; b) two different films (Figs. 5 and 6) after heating as described above, represented by circles and crosses. As seen from Fig. 7, all experimental points, with the exception of the two to the right, are found well within the single function $\varphi=f(N)$, which obviously implies the unchangeableness of the state of the CsCl molecules adsorbed on the surface of the tungsten substrate before and after heating. The error in the statistical determination of the value of N in one cycle of measurements is represented by the horizontal lines ; in other measurement cycles the error was many times smaller, and was too small to show on the graph. For greater clarity, we have plotted in Fig. 7 the function of the variation of the work function of tungsten $\varphi=(\varphi_0-\Delta\varphi) = f(N)$, taking $\varphi=4.5$ ev for pure tungsten.[1] Here, too, we have represented the similar function for a film of cesium atoms on tungsten substrate as derived from the literature (broken line).[15]

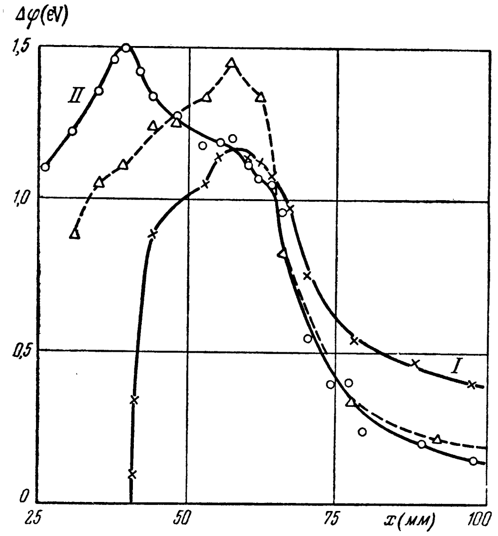

FIG. 6.

Inspection of the composite Fig. 7 shows that the adsorbed film of CsCl dipole molecules, having in the free gaseous state their own dipole moment $p=10 \times 10^{-18}$ cgs units, does reduce the work function of the tungsten substrate, but to a much lesser degree than does a film of cesium atoms. This is demonstrated by the fact that the maximum value of $\Delta\varphi$ is considerably less here, while the surface concentration N needed to obtain this effect is noticeably greater. It is interesting to note that

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[15] J. Taylor and I. Langmuir, Phys. Rev. **44**, 423, (1933). I. Langmuir, cited in Usp. Khim. 10, 570(1941).

this result, for some reason, is exactly contrary to that derived from a parallel comparison of the similar BaO--W and Ba--W systems. Thus, the film of BaO dipole molecules influences the work function of tungsten to a greater degree--a reducing effect--than does a film of Ba atoms, although the Cs--W and Ba--W systems are fairly similar to each other. All this can be seen from the composite table, where the dipole moment of BaO molecules in the free state, which is still undetermined, can be evaluated as

$$p = ne(R_1 + R_2) - ne(\alpha_1 + \alpha_2)(R_1 + R_2)^{-2}. \quad (2)$$

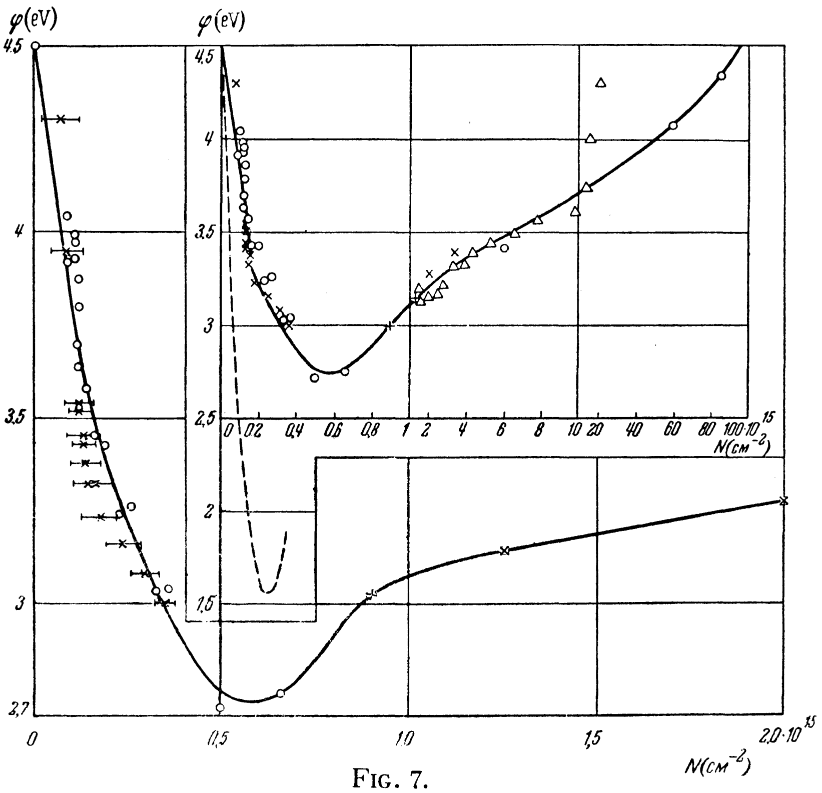

FIG. 7.

Herein R_1 and R_2 are the radii of the cation and the anion, α_1 and α_2 are their polarizabilities,[16] and n is the multiplicity of charges of the ions; for a free BaO molecule the latter must also be equal to unity, since only thus is the criterion satisfied[16] that the difference between the ionization energy of the cation and the affinity energy of the anion must be fairly small. The quantity p_0 in the table given below is the effective dipole moment of the unknown molecules in the adsorbed state in a film of infinitesimal (degree of coverage $\theta \approx 0$) surface concentration, where their interaction can be disregarded; p_0 is defined as $p_0 = (1/4\pi)(d\varphi/dN)_{N=0}$. As regards the interesting (in particluar for CsCl, as well) optimum degree of coverage $\theta_{opt} = N_m/N_1$, there is always some element of arbitrariness in its determination, owing to ignorance of the density of the total number of vacant sites N_1. Here, one should bear in mind[17] that in our case of flattened tungsten ribbon, the exterior surfaces of the microcrystalline particles should display a tendency toward advantageous grain formation with indices (100), for which $N_1 = 1.0 \times 10^{15}\,\mathrm{cm}^{-2}$.

The results given in the table include our own for CsCl--W, and those derived and worked out for comparison from other investigations for Cs--W[15], BaO--W[4], and Ba--W[4]; they can be summarized

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[16] O. Rice, *Electronic structure and chemical binding*, 1940, pp.178 and 220. F. Seitz, *Modern theory of solids*, 1949. G. Herzberg, *Molecular spectra and molecular structure*, 1939.

[17] I. Langmuir, Phys. Rev. 22, 374 (1923). L. Tonks, Phys. Rev. 38, 1030 (1931). L. Apker, E. Taft and J. Dickey, Phys. Rev. 73, 46 (1948).

as follows.

System	$(\Delta\varphi)_{max}$eV	$N_{max} 10^{-14}$ см$^{-2}$	$p_0 \cdot 10^{18}$ cgs units	$p \cdot 10^{18}$ cgs units
CsCl—W	1,8	5	4	10
Cs—W	3,0	2,4	8	—
BaO—W	3,5	1,1	8	14 ($n=1$)
Ba—W	2,9	$\leqslant 4$	$\geqslant 9$	—

1) The question of Cs--W and Ba--W systems, i.e., of atomic films on the surface of a metal, has already been fairly well examined qualitatively in the literature;[18] here, the value of $\Delta\varphi$ is equal to

$$\Delta\varphi = (\varphi_0 - \varphi) = 4\pi a\sigma = 4\pi N\bar{p}, \qquad (3)$$

where σ is the average density of the positive surface charge produced by the double layer formed by a single system: adsorbed atoms--surface of the metal, with close electron interaction between them; p is the average dipole moment for one adsorbed atom. Unfortunately, however, these ideas have not yet been formulated into a theory that might lead to quantitative relations which would permit their direct experimental verification.

2) In contrast to the preceding case of atomic adsorption on the surface of a metal, the case of adsorption of molecules having a permanent dipole moment is still entirely unexplained, even along general lines, at the present time. In this case, the expression for the variation of the work function can probably be written in the following form:

$$\Delta\varphi = 4\pi(\beta pN + a\sigma) = 4\pi N\bar{p}, \qquad (4)$$

where the factor $\beta > 1$ characterizes the increase in the value of $\Delta\varphi$ due to the permanent dipole moment p; σ is the average density of the surface charge produced by additional electron interaction of the single system: adsorbed molecular film--surface of the metal; in general, β, p, and σ will depend on N. Unfortunately, however, before a theoretical examination of this new question, which we are undertaking at present, it is impossible to state anything conclusive. For the time being, we are limited to the following, purely qualitative remarks concerning the first and second members of Eq. (4) for the simpler case of a film with a very small degree of coverage, where we can disregard the interaction of the adsorbed molecules.

a) In a molecular clump, before deposition on the surface, all directions of the moments of the dipole molecules are equally probable and, therefore, a quite insignificant effect of a film of these molecules on the work function of the substrate was to be expected. However, the fact that not only in former cases of the molecules of BaO, SrO, and CaO[3] but in our case of CsCl molecules as well, we always obtain a noticeable decrease in the work function, clearly indicates, that, near the surface of the metal, there is a fairly strong, definitely oriented electric field. This follows, too, from the general nature of the surface field of force of the metal and its electrostatic component. This field E orients the molecules in a definite preferential manner, producing a situation that is somewhat similar to that described by the well-known Langevin theory. Moreover, for the case of infinitesimal surface concentrations, where interaction of the adsorbed dipoles can be neglected, direct application of the data of this theory to the question being examined here is possible; for example, for the ratio p_0/p (see the table), we can write

$$p_0/p = L\,(pE/kT), \qquad (5)$$

where $L(x)$ is the well-known Langevin function. Taking the necessary values for the CsCl--W and BaO--W systems from our Table, we obtain (for $T=300\,^\circ K$) the field intensities in the region of these dipoles: $E = 1.7 \times 10^6$ and 2.1×10^6 v/cm, respectively, i.e., approximately the same values characterizing the tungsten surface, etc. The generalization of a similar theory for the case of adsorbed films of dipole molecules of any concentration whatsoever and the basis for it will be pre-

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[18] R. Gurney, Phys. Rev. 47, 479 (1935). A. Ansel'm, Uch. Zap. Leningrad State University 38, 16 (1939). F. Vol'kenshtein, Zh. Fiz. Khim. 21, 1317 (1947). V. Bonch-Bruevich, Zh. Fiz. Khim. 25, 1033 (1951). L. Dobretsov. [e.g., see Ref. 1, L. Dobretsov. *Electron and ion emission*, GITTL, p. 136.].

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b) The question of the role played by the second member of Eq. (4), characterizing the additional double layer produced by electron interaction between the molecular film and the metal, must be decided analogously to the preceding case of the presence of an adsorbed atomic film on the metal.[18] However, in our case of the CsCl --W system, we experience additional difficulty in determining the sign of the quantity σ , i.e., the sign of the double layer obtained here. In fact, this sign depends on whether a surplus or an insufficiency of negative electron charge is produced in the adsorbed film; this, in turn, depends on whether the CsCl molecules are in stable states as negative and positive ions and on the electron level in these states with respect to the Fermi level in the metal. Actually, experimental investigation of a gaseous discharge in CsCl vapors[19] has already indicated the formation of the negative ions of these molecules and in the future their positive ions will probably also be discovered; however, the energies of the electron states here are still unknown. Therefore, this second question as to the role of additional surface charge also remains open for the time being.

Finally, let us point out that the small additional (irreversible) increase of $\Delta\varphi$ by ≈ 0.3 ev observed in the experiment during momentary heating of the film can probably be interpreted as an indication of the existence of a certain number of individual places on the surface of the metal where the state of the adsorbed molecules, based on factors a) and b) above, is different from the normal states. Both these states are separated from each other by a potential barrier, and it is possible to examine them within the framework of modern notions on activated adsorption. The possibility of a slight dissociation of the CsCl with the appearance in the film of a certain quantity of Cs atoms is not excluded here.

In this manner, then, using the CsCl--W system as a model, we have examined the details of the variation of the work function of a metal during the presence of an adsorbed layer of dipole molecules. The theoretical interpretation of this phenomenon is a matter for the future.

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[19] N. Ionov, Dokl. Akad. Nauk SSSR 59, 467 (1948). V. Dukel'skii, E. Zandberg and N. Ionov, Dokl. Akad. Nauk SSSR 68, 31 (1949).

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