

Home Search Collections Journals About Contact us My IOPscience

Photo-electric alloys of alkali metals

This content has been downloaded from IOPscience. Please scroll down to see the full text. 1943 Proc. Phys. Soc. 55 145 (http://iopscience.iop.org/0959-5309/55/2/307)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 134.193.117.53 This content was downloaded on 23/02/2015 at 14:13

Please note that terms and conditions apply.

Newton

seems to me true, not in the sense that nobody had ventured into these strange seas before him, making uncertain casts and returning with doubtful tales, but in the sense that he sailed alone. He never discussed his work with anybody: he was willing to use the work of others, as of Flamsteed, but not to take them into his confidence. It is doubtful if he ever took anybody into his confidence.

Newton was not a man of constant aim, like Rembrandt, like Beethoven, like Faraday. He did not throughout his life think physical and astronomical science supremely worth while. He probably had greater powers of concentration than any other man: he himself said: "If I have done the public any service, it is due to nothing but industry and patient thought", and that if he differed from other men it was in his capacity to pay attention to a problem. Again, when someone asked him how he had arrived at his discoveries, he replied : "By always thinking unto them". At another time: "I keep the subject constantly before me, and wait till the first dawnings open little by little into the full and clear light." Everything goes to show that he could bring his whole mind to bear on a subject for hours on end, when he was interested in it. He did not, however, think physical science of all-important interest for more than a few years together. After the writing of the Principia he could be brought from time to time to turn his mind to it, but the zest seems to have gone. He could not bear that men of learning should think either that he could not solve a problem if he cared to try it, or that he had ever been indebted to a contemporary for one of his discoveries, but science for itself no longer occupied his thoughts with the possession that the beloved has over the young lover. He is one of the strangest and most baffling personalities among the very great. We greet his achievement with envy, his memory with reverence, but we do not understand him.

PHOTO-ELECTRIC ALLOYS OF ALKALI METALS

BY ALFRED SOMMER, DR. PHIL., Cinema-Television, Ltd., London

MS. received 10 February 1941; in revised form 18 December 1942

ABSTRACT. The properties of the caesium-antimony alloy, first described by Görlich, have been investigated. It was found that this alloy has the stoichiometric formula $SbCs_{3}$, has the electric reistance of a semi-conductor and emits under favourable conditions about 1 photo-electron for 5 incident light-quanta at 4600 A. Alloys of similar structure were also investigated, and the effect of superficial oxidation was studied.

§1. INTRODUCTION

The photo-electric sensitivity of pure alkali metals is so small that very soon after the discovery of the external photo-electric effect, special sensitizing methods were developed to increase the sensitivity, these methods consisting of the introduction of other elements into the alkali layer. The first improvement consisted of sensitizing the alkali metal by a discharge

PHYS. SOC. LV, 2

in hydrogen. Later, a special layer was developed, which is produced by distilling caesium on to oxidized silver with a subsequent heating process; this layer consists of a complex mixture of silver, silver oxide, caesium and caesium This layer, hereinafter termed the Ag-O-Cs layer, has been used for oxide. many years for most practical purposes because of its high sensitivity to radiation from normal light sources. The caesium can be replaced in this layer by other alkali metals, in which case the sensitivity is considerably reduced. Owing to the complex nature of the Ag-O-Cs layer, the spectral sensitivity and the quantum yield vary from sample to sample, and it is difficult to carry out exact experiments to elucidate the photo-electric mechanism of the layer. Figure 1 shows the spectral sensitivity curve of an Ag-O-Cs cell on an equal energy scale. (I am indebted to the National Physical Laboratory for carrying out the measurements on which figures 1 and 2 are based.) Two deductions can be made from this curve: firstly, the quantum yield at the maximum, at 8400 A.,



is only of the order of 0.3 %. Secondly, the work function of the layer must be considerably below 1.5 volt because "infra-red" electrons of less than 1.5 volt velocity are able to leave the surface.

A new type of photo-electric layer containing an alkali metal was found by Görlich (1936) in the following way: he investigated alloys of caesium with other metals to obtain a layer which is uniform and sensitive from both sides (a useful property for transparent photo-electric layers in television tubes). Görlich found that alloys of Cs with metals like Bi and Sb fulfil this requirement. In a later publication Görlich (1937) emphasized that these *alloy layers* can only be used if they are very thin, a fact which he explains by the high resistance of the thicker layer, which prevents the supply of electrons to the surface layer. He obtained with a thick layer only about 10 % of the sensitivity of a very thin layer.

This effect and its explanation seemed to be improbable since a limitation of the photo-current caused by high resistance should make the sensitivity dependent on the illumination and on the voltage applied between cathode and anode. In our cells an effect of the high resistance was, in fact, observed, but only wnen the illumination was very strong, corresponding to photo-currents of In this case, deviations of the normal saturation curve occurred, about $50 \mu a$. but the effect was actually most apparent in very thin layers. This was to be expected, because the supply of electrons should be more affected by the longitudinal resistance of the layer (when deposited on glass) between the platinum contact and distant points of the layer than by the transverse resistance between the platinum and the surface. Hence a thicker layer, with lower longitudinal resistance, is likely to improve the supply of electrons. As to the sensitivity, we found that within the range of normal saturation the sensitivity of the layer at first rises with increasing thickness, to become eventually independent of the thickness. This was to be expected because of the incomplete light absorption in very thin layers. Görlich's result is probably due to the fact that in his thicker lavers the alloy did not have the optimum ratio of its components. The spectral sensitivity curve of a thick layer after superficial oxidation (see below) is drawn on an equal-energy scale in figure 2, and for comparison the curve for the Ag-O-Cs layer is redrawn on the same scale. A calculation shows that the quantum yield of the SbCs layer at the maximum, at 4600 A., has the surprisingly high value of 18 %, and, therefore, exceeds the quantum yield of the Ag-O-Cs layer by a factor of about 50, if one takes into consideration that a given amount of light energy at 4600 A. consists of fewer quanta than at 8400 A.

The SbCs layer appears to be more suitable for exact experiments than the Ag-O-Cs layer, because it consists of only two components and has a more uniform structure This can be concluded from the fact that layers of very similar sensitivity can easily be reproduced, contrary to the results obtained with Ag-O-Cs layers. Therefore we investigated the composition and some of the properties of this alloy in the hope of determining the conditions for its photo-electric emission and for the extraordinarily high quantum yield.

The following problems were selected for investigation :

(1) How does the optical appearance (absorption and reflection of light) change during the formation of the sensitive alloy? The pronounced maximum of the sensitivity curve between 4000 and 5000 A. may be caused by preferential absorption of light in this range of wave-lengths.

(2) What is the ratio of caesium to antimony in the alloy? The alloys of alkali metals with metals of the fifth column of the periodic system have been studied in detail by Zintl (1931, 33). He found for Na and Sb intermetallic compounds of the stoichiometric formulae Na₃Sb₃, Na₃Sb₇ and Na₃Sb. Compounds of Cs have probably not been investigated before, but it seemed probable that the stoichiometric composition of the photo-electric alloy corresponds to one of these formulae.

(3) How does the electric resistance of Sb change during the formation of the alloy? This experiment should disclose whether the alloy has metallic character or not, and might also indicate, by sudden variations of the resistance, if alloys of different composition are formed.

(4) How does superficial oxidation affect the total and the spectral sensitivity? With the normal Ag—O—Cs layer we found in some cases a marked improvement of the sensitivity on employing superficial oxidation. If this oxidation is not controlled very carefully, the sensitivity drops rapidly, after having passed through a maximum, because too many free Cs atoms, which are essential for the photo-electric effect, are oxidized. The initial effect of this formation of caesium oxide in the surface layer appears to be a lowering of the work function. The main evidence for this interpretation is the fact that the thermionic emission of the layer is greatly increased by the oxidation process. Therefore we can expect to obtain some information about the part played by the work function in the mechanism of the photo-electric effect of the SbCs layer by investigating the influence of oxygen on the electron emission.

(5) What are the properties of alloys in which Sb and Cs are replaced by metals of their respective groups? Görlich made alloys of Cs with other metals of the Sb group in 1936 and of Sb with other alkali metals in 1938, and has measured their spectral photo-electric sensitivity. In addition, we measured the stoichiometric composition and the resistance of some of these alloys in order to find a connection between these properties and the photo-electric sensitivity.

§2. EXPERIMENTAL METHODS

The SbCs layers were produced on the inner wall of a spherical glass bulb of 80 mm. diameter (figure 3). The electrical connection to the layer consists of one or, for resistance measurements, two platinum tags P on the inner wall of the glass bulb. The antimony is evaporated from a filament F in the centre of the bulb to produce a layer of uniform thickness. This filament is also used



as anode for photo-electric measurements. The bulb is sealed to the pump system at E. Caesium is introduced through a constriction from the side tube S. A window in the deposited antimony layer is obtained by fixing a small shield T near the filament.

To determine the ratio of Cs to Sb in the alloy, the following procedure is applied for quantitative experiments. A fragment of Sb of known weight is

fixed in the filament F and completely evaporated after the bulb has been evacuated and baked in the usual way. Thus not only is the total amount of Sb in the final layer known, but the thickness of the layer can also be calculated from the dimensions of the bulb. The thickness in most experiments was about 500 A. The amount of Cs in the alloy was determined in the following way: a glass capillary of bore about 1 mm., containing pure Cs, is weighed and put into an extension M of the side tube S before the whole system is evacuated. After the Sb layer has been deposited in the manner described above, the capillary is broken in two by a magnetically controlled iron ball and the whole of the Cs is distilled into S. The extension M is then sealed off and the two halves of the broken capillary are weighed so that the total amount (I) of Cs in the side tube S can be calculated as the difference of the weights of the capillary with and without Cs. Some Cs is then distilled from S on to the Sb laver in the bulb until the desired alloy is formed. Finally, the side tube S, containing the amount (II) of Cs that has not been used for the formation of the alloy, is sealed off and weighed. S is then opened, the Cs is removed and the side tube is weighed without Cs. The difference of the two weights gives the weight of Cs (II). The amount (III) of the Cs in the alloy layer is then calculated as the difference of the total amount (I) and the unused amount (II).

The longitudinal resistance of the layer can be measured between the two platinum contacts P, which are about 50 mm. from each other. The configuration of the deposit is such that the specific resistance cannot be directly deduced from the value of the resistance between the contacts, but the main point of interest is the ratio between the resistance of the pure Sb layer and the alloy layer. Furthermore, the specific resistance of the alloy layer can be calculated if one assumes that the known value of the specific resistance of Sb in bulk is the same as that of an evaporated layer. This assumption is most probably only correct to a limited degree, but we shall make use of it for the easier comparison of results obtained with different alloys.

The measurements of the total photo-electric emission were taken with an ordinary tungsten lamp. For measurements of spectral sensitivity, a red and a blue-green filter, for the wave-lengths below and above approximately 5700 A, were used in connection with a tungsten lamp. As a compensation for the lack of accuracy, this method had the advantage that a rough check on the change of spectral sensitivity was possible during the formation of the alloy and during the superficial oxidation.

§3. RESULTS

(a) Observations during the formation of the alloy layer

The distillation of the Cs on to the original Sb layer is accompanied by characteristic changes in the appearance of the layer. The first visible effect is that the Sb layer, which is practically opaque, becomes transparent and at the same time loses its metallic lustre. At this stage a very small photo-electric emission is first evident. If more Cs is introduced, the layer becomes more and more transparent, but the transparency is not uniform for all colours, since the layer now looks distinctly orange in transmitted light. The photo-electric emission does not rise appreciably during this colour change. After passing through a maximum of transparency, the layer grows optically denser again and the photo-electric emission rises rapidly until it reaches a maximum. At this stage the layer shows a beautiful ruby semi-transparency. Further distillation of Cs does not affect the appearance of the layer, while the photo-electric emission starts dropping. The whole process of forming the alloy is accelerated by heating the glass bulb. During the whole process the ratio of sensitivity to "red" and to "blue-green" is practically constant, the sensitivity to "red" being almost negligible.

The transparency of the layer to red light, i.e. the absorption of the blue and green light, corresponds to the shape of the sensitivity curve (figure 2). Although the spectral absorption curve has not been measured accurately, the qualitative observation indicates that the absence of sensitivity to red light is due to the fact that red light is not absorbed.

(b) Measurements of the Cs: Sb ratio

The experiments were carried out in the manner described above. The following are the actual figures of three experiments :---

	Experiment No.		
weight (in mg.) of	1	2	3
Sb evaporated	9.0	12.5	12.0
Glass capillary with Cs ,, ,, without Cs	202·5 158·0	216·5 160·0	234·5 173·5
Total amount of Cs (I)	44.5	56.5	61.0
Side tube + unused Cs ,, ,, without Cs (after correction for weight of air)	1400·5 1386·5	1676·5 1658·5	1347·5 1323·5
Unused Cs (II)	14.0	18.0	24.0
Used Cs $(III) = (I) - (II)$	30.2	38.5	37.0
Atomic ratio Cs : Sb = $\frac{Cs (III)}{Sb evaporated}$ × $\frac{atomic weight Sb}{atomic weight Cs}$	3.11:1	2.83 : 1	2.84:1

Assuming an accuracy of $\pm 10 \%$, these results suggest that the photo-electric alloy corresponds to the formula SbCs₃, and is, in chemical nomenclature, caesium antimonide. Since this formula corresponds to the formula of Zintl with the highest ratio of alkali metal to antimony, it is quite possible that alloys of smaller caesium-to-antimony ratio are formed temporarily during the introduction of Cs into the layer. There was no point, however, in making a quantitative measurement during an intermediate stage, because the properties of the layer vary continuously during the formation process (see experiments with BiCs alloys, *infra*). On the other hand, an attempt was made to produce an alloy with a higher Cs: Sb ratio than 3:1 in the following way. A cell, provided with a side tube containing excess Cs, was sealed off the pump system after the normal $SbCs_3$ layer had been formed. Then the Cs in the side tube was distilled on to the alloy layer, where it condensed as a metallic film, obviously without reacting with the alloy. Then the cell, together with the side tube, was heated to encourage a reaction, but without visible effect. Finally, the side tube was cooled while the cell was still at high temperature, with the result that the excess Cs condensed at once in the side tube. By weighing this amount of Cs in the usual way it was proved that no further Cs is absorbed by the alloy after $SbCs_3$ is formed.

(c) Resistance measurements

A typical result of a resistance measurement of the alloy layer (thickness of the original Sb layer about 300 A.) during the formation process is shown in the following table :---

Appearance of layer	Measured resistance (ohms)	Calculated * specific resistance (ohms/cm ³)
Metallic Sb layer	7 ·3 ×10	4·0×10 ^{−5}
Metallic lustre disappearing	2.5×10^{2}	1·4×10-4
Layer of maximum transparency	3·0×10*	1.6
Final SbCs ₃ layer	$3.0 imes10^6$	1.6

* Assuming 4.0×10^{-5} ohm/cm³ for the metallic Sb layer.

The table shows that the formation of the alloy $SbCs_3$ is accompanied by a rapid increase of resistance to about 10^5 times its initial value.

(d) Influence of superficial oxidation

The effect on the photo-electric emission of the SbCs₃ layer is similar to that achieved with Ag—O—Cs layers: the sensitivity rises to a maximum and then drops if the introduction of oxygen is continued. To obtain more detailed information about the influence of the oxidation on the spectral sensitivity, the oxidation process was carried out in steps, and the sensitivity to the three light sources, "white", "red" and "blue-green" (see above), was measured in each stage. The results of one experiment can be seen from the following table. The figures are given in % of maximum sensitivity to each light source.

Steps of	%	ivity	
oxidation	White	Red	Blue-green
0	49	3.5	59
1	55	4.0	64
2	61	5.0	70
3	65	8∙5	75
4	81	22.0	94
5	100	55.0	100
6	92	100.0	82
7	77	93.0	62
8	62	86.0	46
9	34	41·0	25
10	22	38.0	16

The first horizontal line of the table gives the values measured before the introduction of oxygen is started.

The table shows that

(1) The figures for "white" and for "blue-green" are of the same order during the whole sequence, and their maxima coincide. This was to be expected, because the absolute sensitivity to wave-lengths below 5700 A. represents the greatest part of the total sensitivity (see figure 2).

(2) The sensitivity to "red" rises by a factor of about 30 compared with the initial value, while the sensitivity to "blue-green" rises only by a factor of less than 2.

(3) The maximum for "blue-green" is passed before that for "red" is reached.

These results fit in very well with the assumption that the oxidation process lowers the work function. Lowering the work function must have a much greater effect on the "red" electrons, which have a very low velocity, than on "blue" electrons. With smaller work function, the sensitivity to red light will not only show a greater quantum yield, but will also be extended towards longer wave-lengths, since electrons with still smaller initial velocity will now be able to leave the surface. This explains the much greater improvement of sensitivity to "red" than to "blue-green" in the course of the oxidation. On the other hand, the SbCs₂ alloy, which is the actual photo-electric medium, will gradually be decomposed by oxidation (see below), and this unwanted effect will counteract the "positive" effect of reducing the work function. Therefore the sensitivity will drop as soon as the "negative" effect of the oxygen becomes greater than its "positive" effect. It is obvious that this turning point is reached earlier for "blue" electrons than for "red" electrons because the equilibrium of the two opposite effects will be reached earlier for the electrons of higher velocity, which are less affected by the "positive" effect of oxidation. This explains why the maxima for "red" and for "blue-green" do not coincide.

The amount of oxygen absorbed by the alloy layer is so small that an accurate measurement would be extremely difficult under the prevailing conditions. But the fact that the spectral-sensitivity curve after oxidation is still so fundamentally different from that of an Ag—O—Cs layer (see figures 1 and 2) indicates that only the very thin surface layer which determines the work function is affected by the oxidation, and not the actual photo-electric centres. The chemical reaction taking place after the introduction of oxygen can be expressed in the following way:

$$4$$
SbCs₃ $+3O_2 \rightarrow 4$ Sb $+6$ Cs₉O.

Superficial oxidation has an effect not only on the photo-electric emission, but also on the electric resistance and the thermionic emission of the alloy layer.

With continued oxidation the electric resistance drops rapidly; this can be explained by the reformation of metallic Sb according to the above-mentioned scheme of reaction.

The effect on the thermionic emission corresponds to that in the case of the Ag-O-Cs layer (see above); while the pure alloy layer has an immeasurably small thermionic emission at room temperature, and also at higher temperatures.

an appreciable thermionic emission sets in with continued oxidation, which can be explained by reduced work function in the same way as in the case of the Ag-O-Cs layer.

(e) Other alloys of the antimony-caesium type

We tried all metals of the fourth and fifth columns of the periodic system in combination with caesium, and found that no other alloy has a photo-electric sensitivity as high as that of $SbCs_3$. The same applies for alloys of Sb with Rb and K. The alloy of As with Cs requires further investigation, because so far difficulties due to the low sublimation temperature of As have not been overcome.

We did not investigate each of these alloys to the same extent as the SbCs alloy, because of their lower sensitivity, but some results may be summarized as follows. (The experimental methods were the same as for the investigation of the SbCs alloy.)

(i) Bi + Cs. The formation of $BiCs_3$ was definitely confirmed. During the distillation of Cs on to the initial Bi layer, a transparent layer is obtained which changes rather suddenly into a final opaque layer. Since this stage is better defined than the corresponding stage during the formation of $SbCs_3$, a quantitative measurement was made, showing that this very transparent alloy layer has probably the stoichiometric formula BiCs and, therefore, corresponds to the compound Na₂Bi₃ found by Zintl and mentioned above.

Apart from the much lower photo-electric sensitivity (about 5% of the sensitivity of the SbCs₃ layer for the light of an incandescent lamp), the BiCs₃ layer differs from SbCs₃ by its more metallic behaviour: the layer has a slight metallic lustre, it is completely opaque at a thickness at which the SbCs₃ layer is transparent, and, a more conclusive fact, it has a much lower electric resistance. During the formation of the alloy, the specific resistance rises from 1.19×10^{-4} ohm/cm³ (pure Bi metal) to a maximum of 10^{-2} (transparent stage) and drops again to 2×10^{-4} when BiCs₃ has been formed.

(ii) Sb + Rb and Sb + K. The formation of SbRb₃ and SbK₃ was established. The photo-electric sensitivity of the two alloys is still lower than that of BiCs₃. In both cases an intermediate transparent layer is obtained during the formation of the alloy, corresponding to the transparent stages during the formation of SbCs₃ and BiCs₃. The specific resistance rises with increasing transparency from 0.4×10^{-4} (pure Sb metal) to 10^2 (for Rb) and to 10 ohms/cm^3 (for K). The final layer of SbK₃ is slightly transparent to red light and has the specific resistance is 10^{-4} ohm/cm^3 . SbRb₃ is more opaque, and its specific resistance is 10^{-4} ohm/cm^3 . These results show that the alloys SbRb₃, SbK₃ and BiCs₃ are similar to each other, and different from SbCs₃, in having low resistance. It must be mentioned that the photo-electric sensitivity of the intermediate high-resistance stages of all investigated alloys is lower than that of the final layers. This is not surprising, because one cannot expect a high photo-electric emission if little or no light is absorbed, as is the case in these transparent high-resistance layers.

Alfred Sommer

§4. SUMMARY OF RESULTS

(1) A photo-electric antimony-caesium alloy has been obtained which has a maximum sensitivity at 4600 A., corresponding to a quantum yield of 18 %, and a very small sensitivity above 6500 A.

(2) This alloy shows no metallic reflection and is very transparent to red light, the latter fact explaining the low sensitivity to this part of the spectrum.

(3) The composition of the alloy of highest sensitivity corresponds to the stoichiometric formula $SbCs_3$.

(4) The specific resistance of the alloy is of the order of one ohm per cm³. This value is 10^5 times greater than that for metals and normal alloys. Hence the alloy belongs to the class of semi-conductors, in agreement with its non-metallic optical properties. As the term *alloy* usually implies metallic properties, it would probably be more correct to describe the substance SbCs₃ as an *intermetallic compound*.

(5) Superficial oxidation has three effects on the alloy. Firstly, the photoelectric sensitivity is increased, particularly to red light. Secondly, the thermionic emission is increased. Thirdly, the specific resistance is reduced. The first two effects indicate a lowered work function; the effect on the specific resistance can be explained by the formation of metallic antimony.

(6) Alloys of antimony with rubidium and potassium and of bismuth and arsenic with caesium have been produced. They all show photo-electric sensitivity, but of a much lower order than the antimony-caesium alloy. Alloys of the formulae SbRb₃, SbK₃ and BiCs₃ have been obtained. As compared with SbCs₃ they have more metallic character: in particular their specific resistance is similar to that of metallic conductors.

ACKNOWLEDGEMENT

Acknowledgement is made to Messrs. Cinema-Television, Ltd., for permission to publish this information

REFERENCES

Görlich, 1936. Z. Phys. 101, 335; 1937. Z. tech. Phys. 18, 460; 1038. Phil. Mag.* 25, 256.

ZINTL, 1933. Z. anorg. Chem. 211, 113; 1931. Z. phys. Chem.* A, 154, 1.

* Contain references to earlier work.