

LCM

**RB-44**

**MULTI-ALKALI PHOTOCATHODES**

DR JCN LES  
 JAS EFS JWD CD  
**RECEIVED**  
 APR 30 1956  
 G. R. TUBE ENGINEERING  
 NOTE FILE DISCUSS  
 ANS RETURN LOG

---

DR JCN LES  
 JAS EFS JWD CD  
**RECEIVED**  
 APR 10 1956  
 G. R. TUBE ENGINEERING  
 NOTE FILE DISCUSS  
 ANS RETURN LOG

ANS RETURN LOG  
 NOTE FILE DISCUSS  
 G. R. TUBE ENGINEERING  
 APR 10 1956  
**RECEIVED**  
 JAS EFS JWD CD  
 DR JCN LES



RADIO CORPORATION OF AMERICA  
 RCA LABORATORIES  
 INDUSTRY SERVICE LABORATORY

**RADIO CORPORATION OF AMERICA****RCA LABORATORIES****INDUSTRY SERVICE LABORATORY****RB-44****Multi-Alkali Photocathodes**

This report is the property of the Radio Corporation of America and is loaned for confidential use with the understanding that it will not be published in any manner, in whole or in part. The statements and data included herein are based upon information and measurements which we believe accurate and reliable. No responsibility is assumed for the application or interpretation of such statements or data or for any infringement of patent or other rights of third parties which may result from the use of circuits, systems and processes described or referred to herein or in any previous reports or bulletins or in any written or oral discussions supplementary thereto.



## Multi-Alkali Photocathodes

Many improvements in multiplier phototubes for scintillation counting are desirable. High secondary emission factors, high speed, low dark currents at room temperature, stability at high voltages, large output current, etc. may be particularly wanted, depending on the specific application. However, there is one parameter in which an improvement is advantageous for all purposes, i.e., the sensitivity of the photocathode.

In this bulletin some new cathodes will be described which have been developed during the last two years. Before reporting on this work, the problem of photoemission will be discussed in a general way, followed by a survey of the cathodes that have been developed in the past.

### General Considerations

In the ideal case, every photon incident on a photocathode should release one electron, i.e., the theoretical limit of photoemission is represented by a quantum efficiency of 10 percent. This efficiency is never reached, for a number of reasons which are diagrammatically shown in Fig. 1.\*

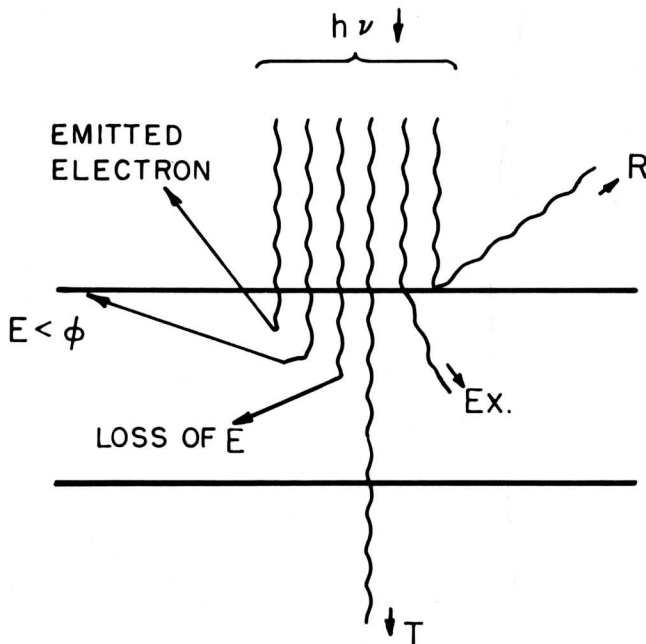


Fig. 1 - Diagram representing the reasons for not obtaining 100 percent efficiency in photoemission.

\* Confining all consideration to the visible part of the spectrum, including the near infrared and ultraviolet.

The light incident on a cathode can be reflected (R), transmitted (T) or absorbed. In the first two cases the light energy obviously cannot be converted into electronic energy. Even for the absorbed photons the chance of conversion into electrons is not too good as is indicated qualitatively in the figure. Some photons will raise electrons into excited states without freeing them completely. Other photons will produce free electrons, but there are again several reasons why these electrons are not all emitted into the vacuum. First, the electrons may lose energy to the crystal lattice, i.e., create phonons; second, they may lose energy by inelastic collisions with other electrons, i.e., electron scattering (this will apply almost with certainty to all electrons released in a direction away from the vacuum surface); third, the electrons may reach the cathode-vacuum interface without sufficient energy to overcome the surface barrier, i.e., when the work function of the cathode material is too high.

It is easy to see from the above discussion that high quantum efficiency can only be expected from materials with a very critical combination of properties. Some qualitative statements about the required properties can be made. First, pure metals are poor photoemitters because a large fraction of the incident light is reflected. Furthermore, the large number of free electrons in a metal will cause great losses due to electron scattering. On the other hand, in materials which are insulators at room temperature, most of the incident light is usually lost by transmission and it is also difficult to replace any electrons lost by photoemission.

This leaves the materials in the semiconductor group and the photocathodes of highest quantum efficiency have,

in fact, been found to be semiconductors. Using the conventional band model of a semiconductor (Fig. 2) in the simplest form, we have the filled valence band (F) separated by a forbidden gap ( $E_i$ ) from the conduction band (C). In order to produce an emitted photoelectron, the absorbed light energy must be sufficient not only to raise an electron from band (F) to band (C), but to impart to it the energy to reach the vacuum level (V). We will not discuss here the more complicated case of impurity semiconductors where additional levels appear between the valence and conduction bands.

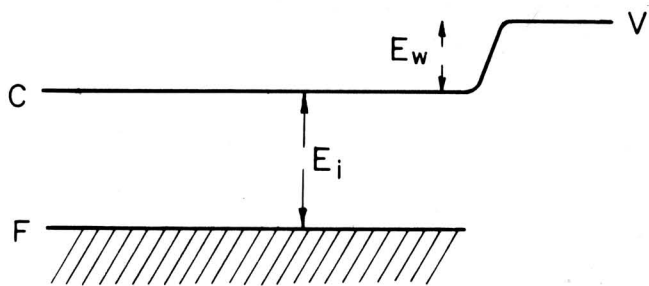


Fig. 2 - Conventional band model of a semiconductor.

In the visible range from 4000 to 8000 Å, we deal with photons having energies from 1.5 to 3 volts; hence, for photoemission to occur, the sum of  $E_i$  and  $E_w$  in Fig. 2 must be less than 3 eV at 4000 Å and less than 1.5 eV at 8000 Å. In other words, we have to use a material combining a small intrinsic gap with a low value  $E_w$  of the electron affinity.\*\* It is well known that the alkali metals Li, Na, K, Rb and Cs are the elements with lowest work function and that the work function decreases in the sequence from Li to Cs. This explains why the cathodes of high quantum efficiency which have been used in the past all contained Cs combined with other materials in such a way that a more or less semiconducting material was formed. Whereas the use of Cs is a well established practice, the additional elements required to produce suitable semiconductors for use as photocathodes have been found predominantly by trial and error methods.

### The Ag-O-Cs, Sb-Cs and Bi-Ag-O-Cs Photocathodes

In the past, three types of photocathodes have found wide application because of high quantum efficiency and/or desirable color response. These are represented by

\*\* We must be careful to distinguish between the electron affinity  $E_w$  and the work function  $\phi$ . The work function is the distance from the Fermi level to the vacuum level and determines the thermionic emission. Since in semiconductors the Fermi level is always between F and C (Fig. 2),  $\phi$  is always larger than  $E_w$ .

the formulae Ag-O-Cs, Sb-Cs and Bi-Ag-O-Cs. The most important properties of all cathodes under discussion are summarized in Table I which shows the chemical composition, wavelength of maximum sensitivity, peak quantum efficiency and threshold wavelength. From the Table, together with Fig. 3 showing spectral response curves of the three above-named cathodes, the following facts can be derived. The Ag-O-Cs cathode (Curve I) has a low quantum efficiency of only 0.5 percent at the maximum; on the other hand, it is the only cathode with infrared response. As a result, it is mostly used for applications where detection of infrared radiation is essential. The low work function of the Ag-O-Cs cathode, which is responsible for the long threshold wavelength, carries with it the disadvantage of high thermionic emission at room temperature. Hence, without cooling, the cathode is not useful where extremely low signals are concerned because the noise component of the thermionic emission has an adverse effect on the signal-to-noise ratio.

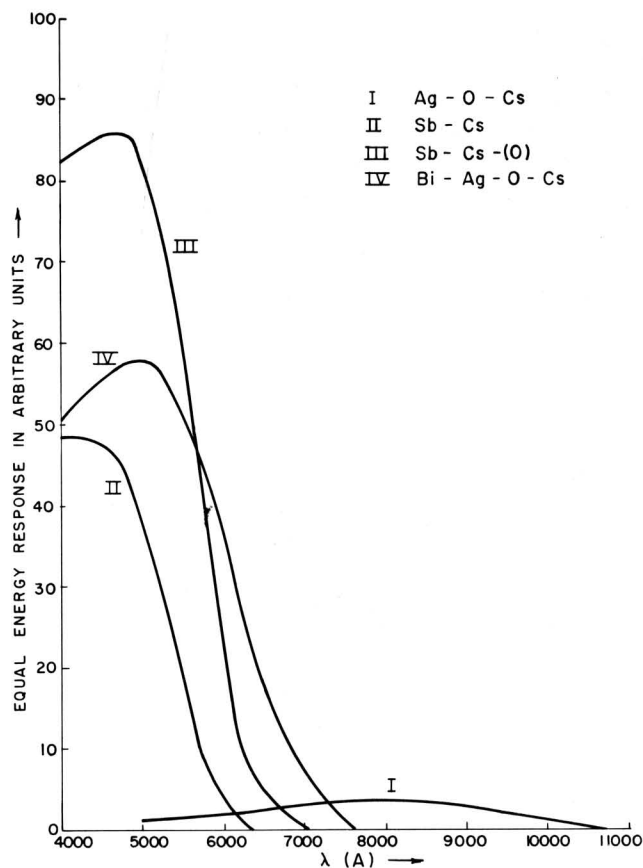


Fig. 3 - Spectral response curves for Ag-O-Cs, Sb-Cs, and Bi-Ag-O-Cs photocathodes.

The Sb-Cs cathode (Curve II) has a much shorter threshold wavelength but a higher quantum efficiency than the Ag-O-Cs cathode. The sensitivity can be further increased (Curve III) by introducing minute amounts of oxygen into the cathode, either by depositing it on an oxide or by exposing the surface to oxygen. This oxygen treat-



TABLE I

| Material   | $\lambda$ (Peak) | Q.E. (Peak)<br>in visible<br>range | $\lambda_0$<br>(1% of peak) | Maximum<br>$\mu\text{a/lumen}$ |
|------------|------------------|------------------------------------|-----------------------------|--------------------------------|
| Ag-O-Cs    | 8500             | 0.5%                               | 14,000                      | 50                             |
| Sb-Cs      | 4500             | 10%                                | 6,500                       | 25                             |
| Sb-Cs-(O)  | 4800             | 20%                                | 7,000                       | 90                             |
| Bi-Ag-O-Cs | 4800             | 10%                                | 7,500                       | 90                             |
| Sb-Na      | $\ll 4000$       |                                    |                             | $< 0.1$                        |
| Sb-K       | $\ll 4000$       |                                    |                             | 5                              |
| Sb-K-Na    | $< 4000$         | 10%                                | 6,200                       | 60                             |
| Sb-K-Na-Cs | $< 4000$         | 20%                                | 8,500                       | 200                            |

ment seems to reduce the work function of the cathode and the quantum efficiency is increased from about 10 percent to 20 percent in the 4000 Å range. This is remarkably high considering the many facts which contribute to a reduction in efficiency, as shown in Fig. 1. The Sb-Cs cathode has been particularly useful for scintillation counters because it combines very high sensitivity in the relevant spectral range with relatively low thermionic emission at room temperature.

The mechanism of photoelectric emission from the Ag-O-Cs cathode is still very little understood, but we have at least an approximate model for the mechanism of the Sb-Cs cathode which we shall discuss later on.

The third cathode in Fig. 3 is the Bi-Ag-O-Cs layer whose spectral response curve is shown in Curve IV. The values for quantum efficiency and threshold wavelength of this cathode, as well as for thermionic emission at room temperature, lie between those of the Sb-Cs and the Ag-O-Cs cathode, though in every respect closer to the first than to the second. This cathode was developed principally for applications where approximately panchromatic response is essential and is generally used in television pickup tubes such as the image orthicon. As can be seen from the composition formula, this cathode is more complex than the Ag-O-Cs and Sb-Cs cathodes in that it has four components instead of two or three. It is, therefore, not surprising that practically nothing is known about its mechanism.

Referring to the special application of photocathodes for scintillation counting, the Sb-Cs-(O) cathode is satisfactory, but further improvements, at least theoretically, are possible in two directions. First, the quantum efficiency is still a factor of five below the theoretical maximum; second, an increase in the work function would further reduce the thermionic emission at room temperature. With the second aim in mind, Schaetti and his co-

workers in Switzerland have replaced the Cs in the Sb-Cs cathode by other alkali metals which, as mentioned above, have higher work functions than Cs. They found that with an Sb-Li cathode the thermionic emission, in comparison with the Sb-Cs cathode, is lower while the quantum efficiency at 4000 Å is not appreciably reduced.

### Multi-Alkali Cathodes

We tried to repeat Schaetti's experiments with what was believed to be pure Li and Sb and obtained surprisingly high sensitivities. However, some peculiarities in the activation process led us to determine the chemical composition of the photocathodes. To our surprise, we discovered that the cathodes, apart from Sb, contained K and Na, but no Li. The explanation for this result was found in the fact that even the purest commercially available Li metal and Li salts contain traces of Na and K. During the activation process, the alkali metal is distilled onto an Sb base and since only a minute amount of metal is needed and K and Na have a much higher vapor pressure than Li, the Sb layer is apparently saturated with K and Na before Li starts to evaporate.

This new cathode can be represented by the formula Sb-K-Na and is distinguished by quite unexpected properties. By careful control of the relative amounts of K and Na, sensitivities can be obtained (Curve IV in Fig. 4) exceeding those of unoxidized Sb-Cs cathodes. This contradicts the only empirical rule that applied to all earlier cathodes, namely, that the sensitivity is always improved by replacing one alkali metal by another in the sequence from Li to Cs. Curves I, II and III show that this rule applies in the series Sb-Na, Sb-K, Sb-Cs; therefore, the

high sensitivity of the Sb-K-Na cathode must be due to the use of a mixture of alkali metals.

After this "multi-alkali" effect was established, the next step was to investigate other mixtures in combination with Sb. The best combination found hitherto is that represented by the formula Sb-K-Na-Cs. From Table I and Fig. 4, Curve V, it is apparent that this cathode is distinguished by very high quantum efficiency at 4000 Å combined with a higher overall sensitivity in the visible spectrum than has been found in any other type of cathode.

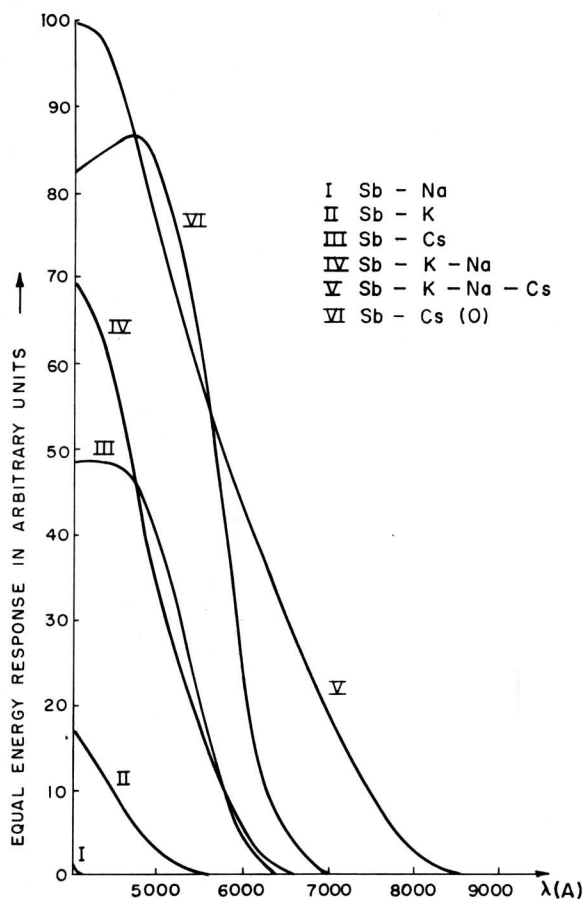


Fig. 4 - Spectral response curves for Sb-Na, Sb-K, Sb-Cs, Sb-K-Na, and Sb-K-Na-Cs photocathodes.

As regards application in scintillation counters, both the Sb-K-Na cathode and the Sb-K-Na-Cs cathode look promising for different reasons. The Sb-K-Na-Cs has, on the average, higher quantum efficiency in the relevant wavelength range and therefore gives better energy resolution and all the other advantages of improved cathode sensitivity. It was feared that the high red response might be associated with high thermionic emission at room temperature but preliminary experiments indicate that the thermionic emission is of the same order as in the Sb-Cs cathode. This came as a surprise because, in the past, thermionic emission and long wave threshold were always found to change together. A possible explanation for this unexpected result will be referred to below.

The Sb-K-Na cathode appears to be similar to the Sb-Cs cathode in sensitivity, but the absence of Cs should have two advantages. First, it can be expected that the thermionic emission at room temperature is reduced; second, in Sb-Cs multiplier phototubes the use of high overall potentials, which are desirable for high speed, is limited by breakdown above a certain voltage. This breakdown is usually attributed to cold emission from electrodes and/or to ionization processes. By eliminating Cs, which has a lower work function and a higher vapor pressure than Na and K, higher voltages can be used before cold emission or ionization limits the performance. It must be mentioned that work on the Sb-K-Na and Sb-K-Na-Cs cathodes is still in the early stages and that the cathodes are not yet used in commercially available tubes.

### Semiconductor Model of Multi-Alkali Cathodes

In the last section of this bulletin it is intended to suggest a qualitative model to provide a unified picture of photoemission from antimony alkali cathodes. These cathodes lend themselves more to speculation than the Ag-O-Cs and Bi-Ag-O-Cs cathodes because they are simpler in chemical composition and the comparison of single- and multi-alkali cathodes provides additional information. The following parameters have been studied to gain a better understanding of the antimony-alkali cathodes.

#### Chemical composition.

It has been known for many years that the composition of the Sb-Cs cathode corresponds to the stoichiometric formula  $SbCs_3$ . The same applies to the other single-alkali cathodes such as  $SbK_3$  and  $SbNa_3$ . In the Sb-K-Na cathode, the ratio of Sb to alkali metal is again 1:3 and indications are that in the most sensitive cathodes the ratio of Na to K is 2:1, i.e., the cathode approaches the formula  $SbNa_2K$ . On addition of Cs to this cathode, only a very small amount of Cs seems to be incorporated and it is believed that only the surface is affected and not the bulk of the cathode.

#### Light absorption.

Each one of the single- and multi-alkali cathodes has a characteristic light absorption, with the exception of the Sb-K-Na-Cs cathode whose light absorption is identical with that of the Sb-K-Na cathode (this is one of the reasons why only a surface effect of the Cs is presumed). The magnitude of the absorption (absorption coefficient) is of the order expected from an intrinsic semiconductor, i.e., many orders greater than that of an impurity semiconductor. The long wavelength threshold of the absorption gives an indication of the forbidden gap ( $E_g$  in Fig. 2)

and thus we can arrive at approximate  $E_i$  values for various cathodes.

#### *Photoconductivity.*

In several antimony-alkali cathodes photoconductivity has been detected. The long wave threshold of the photoconductivity can be used to determine  $E_i$  and some preliminary results agree quite well with those obtained from light absorption measurements.

#### *Color response of photoemission.*

The long wave threshold of photoemission which represents the sum ( $E_i + E_w$ ) is for all measured cathodes at shorter wavelengths than that for light absorption and photoconductivity. The difference ( $E_i + E_w$ ) -  $E_i$  provides approximate values for  $E_w$ .

#### *Thermionic emission.*

Further information about  $E_w$  could be obtained from thermionic emission measurements. As mentioned above, final data for the antimony alkali cathodes are not yet available, but one fact seems to be established, i.e., the relatively low thermionic emission from the Sb-K-Na-Cs cathode where much higher values had been expected from the high red response of photoemission.

On the basis of the results described above, some relative values for the intrinsic gap ( $E_i$  in Fig. 2) and the electron affinity ( $E_w$ ) as the difference ( $E_i + E_w$ ) -  $E_i$  can be postulated. The following statements seem to be consistent with experimental results and among each other.

1. The light absorption measurements indicate a higher  $E_i$  for Sb-Cs than for Sb-K and Sb-Na, while the  $E_i$  for Sb-K-Na is of the same order as, or somewhat lower than, that of Sb-K and Sb-Na.

2. On the other hand,  $E_w$  decreases from Sb-Na through Sb-K to Sb-Cs with the values for Sb-K-Na and Sb-K-Na-Cs lying between those for Sb-K and Sb-Cs. In the Sb-K-Na cathode, we have the interesting case where  $E_i$  seems to be smaller than in Sb-Cs by about the same amount by which the corresponding  $E_w$  value exceeds that for Sb-Cs. The result is an approximately identical ( $E_i + E_w$ ) value which agrees with the similar photoemission response curves for both cathodes as shown in Fig. 4. It is hoped that additional information concerning  $E_w$  will be obtained from thermionic emission measurements.

3. The light absorption of Sb-K-Na-Cs is the same as that of Sb-K-Na, hence they both have the same  $E_i$ . The much larger red response of the three-alkali cathode is therefore explained by a lowering of  $E_w$  due to a Cs surface layer. The outstanding sensitivity of the Sb-K-Na-Cs layer, particularly to red light, seems to be qualitatively explained by the assumption that the low  $E_i$  of the Sb-K-Na is combined with the low  $E_w$  caused by the presence of Cs in the surface. Comparing Sb-Cs and Sb-K-Na-Cs, we come to the conclusion that the small  $E_i$  of the latter is the main reason for its higher red response while the  $E_w$ , though smaller than for Sb-K-Na, is still larger than for Sb-Cs. This interpretation agrees qualitatively with the above-mentioned finding that the thermionic emission of Sb-K-Na-Cs is of a smaller order than had been expected from its red response, considering the high thermionic emission of other red sensitive cathodes.

The above suggested band models are obviously only tentative and over-simplified suggestions which have to be supplemented by more quantitative measurements. If they should prove correct in principle, the interpretation of the multi-alkali effect would be that K and Na in combination with Sb cause a lower intrinsic gap than Cs, while the presence of Cs in the surface layer tends to reduce the electron affinity.

*A. H. Sommer.*

---

A. H. Sommer