

AN INTERPRETATION OF THE SELECTIVE PHOTO-ELECTRIC EFFECT FROM TWO-COMPONENT CATHODES

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ABSTRACT

Evidence is produced to support the view that photoelectrically selective, two component cathodic surfaces are crystalline in nature. Then, assuming that Fowler's equation for the energy of electrons selectively transmitted through a single potential valley [$W = (n^2 h^2 / 8 m d^2)$] is equally valid for the energy of electrons selectively transmitted through the periodic sequence of valleys characteristic of the potential field within a crystal, and that all of the energy of photoelectrons is acquired from the incident light quanta, the wave-lengths of light to which such a surface should respond selectively can be computed. Such computations have been made with d equal to the internuclear distance between electro-positive ions in the lattice structure of alkali metal hydride, oxide and sulphide crystals. The hydride crystals belong to the sodium chloride type and the oxide and sulphide crystals are supposedly of the calcium-fluoride type. The correlation between these computed values and the positions of the observed selective maxima is exceptionally good. Moreover, the fact that the alkali metal hydrides exhibit but one selective maximum and the oxides two or three maxima is in keeping with the geometry of their respective crystalline types.

ONE of the most significant characteristics of the photoelectric emission from two-component cathode surfaces, such as those of the alkali metal hydrides and oxides, is the selective response to light of specific frequencies. This results in the appearance of definitely located maxima in the spectral response curves for these compounds. To avoid the necessity of repeated reference to other publications, I have assembled a group of typical curves and present them in Fig. 1.

A number of ideas have been advanced to account for a selective response to light, but heretofore no theory has adequately explained why: (1) A single specifically located maximum is always observed in the spectral response curve of any given alkali metal hydride surface; (2) One, two or three definitely located maxima may appear in the spectral response curve of an alkali metal oxide cathode, depending presumably upon the relative proportions of metal and oxygen, and the technique involved in the preparation of the compound; (3) The wave-length of the light to which a two-component surface responds selectively is a direct function of the size of the components.

In this paper I propose an interpretation of the composition of two-component cathode surfaces, and an explanation of the selective photoelectric emission therefrom which accounts for all the above observations with striking precision.

PREPARATION OF TWO-COMPONENT SELECTIVE PHOTOELECTRIC SURFACES

The preparation of light sensitive alkali metal hydride photoelectric cells,^{1,2} as is quite generally known, consists in ionizing hydrogen by means of an electrical brush discharge, on a coating of freshly distilled metal. Possibly

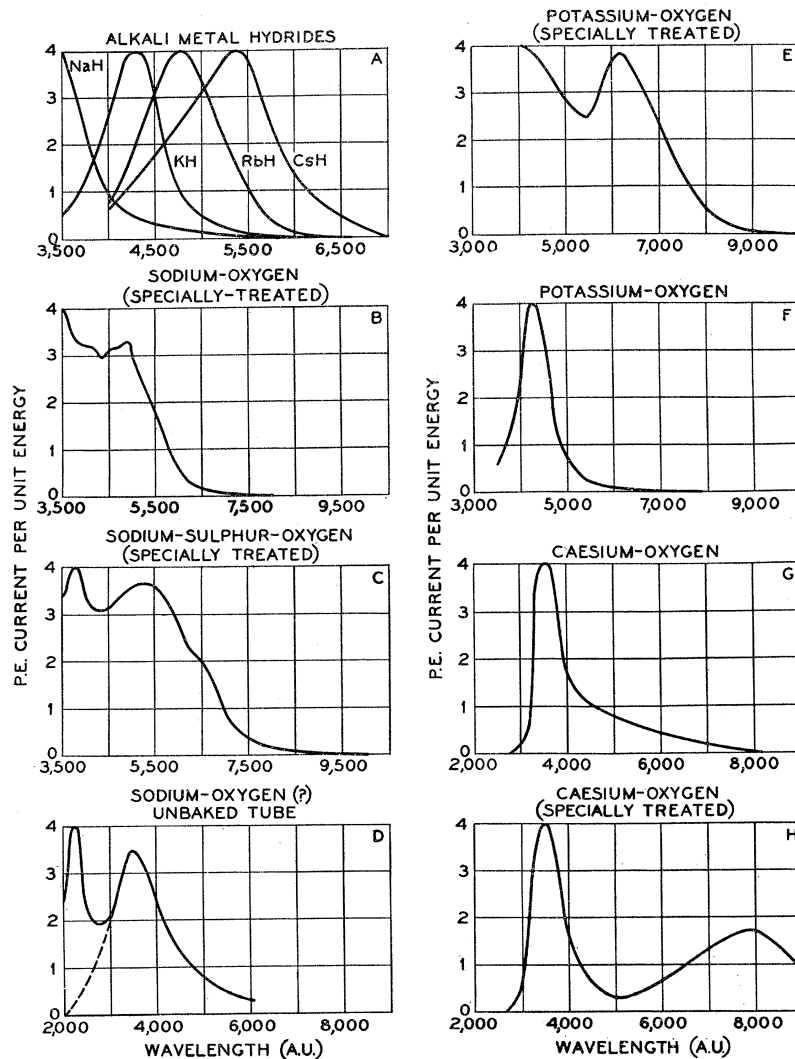


Fig. 1. Groups of typical spectral response curves for various gas-treated alkali metal photoelectric cells.

better results are obtained when the metal is made the cathode during the discharge, but this is not absolutely essential. Typical spectral response characteristics of such cells for visible light are shown in Fig. 1A.

¹ H. E. Ives, *Bell System Tech. J.* 5, 320 (1926).

² E. F. Seiler, *Astrophys. J.* 52, 3, 129 (1920).

The method of preparing selectively emitting cathodes of the alkali metals by the use of oxygen has been the subject of considerable experimentation in recent years. The mere introduction of small amounts of this gas onto an alkali metal surface is sufficient to greatly enhance the photoelectric sensitivity,³ but in these cases the pronounced selective maxima in the spectral response curves appear, in general, at practically the same wave-lengths as those for the pure metals or the hydrides, as illustrated for the cases of sodium and potassium by the curves in Fig. 1D and 1F. However, if after oxidizing the surface of a sodium cathode, a limited area is heated to create a vapor of sodium and oxygen, a coating is formed on the cool portions of the cathode which is very much more sensitive to light and exhibits a quite different spectral response characteristic, with a new selective maximum at longer wave-lengths (Fig. 1B). Moreover, if on a silver plate which has been oxidized under control, caesium in the proper proportions is deposited and the whole sub-

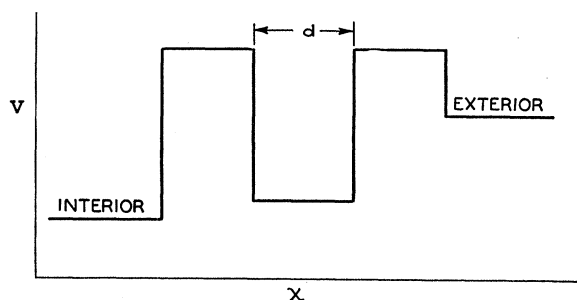


Fig. 2. Conventional representation of the work done by an electron in passing through a surface consisting of alternate layers of electropositive and electronegative elements, as Ag-O-Cs-O-Cs.

jected to a heat treatment which includes as a final step, heating to a temperature just under that at which caesium monoxide volatilizes (250°C),⁴ a cathode strikingly sensitive to red and near infrared light is obtained (Fig. 1H).⁵ By means of a similar process, red sensitive potassium-oxide photoelectric cells can also be made (Fig. 1E).⁶ Obviously, the processes described above produce a complex surface structure, physically favorable to the emission of electrons by light. The nature of this structure and an explanation of these pronounced maxima are the subjects of this discussion.

CAMPBELL-FOWLER THEORY

Campbell,⁷ in an attempt to account for the selective response of caesium-oxide cells to red light, suggested that the surfaces of their cathodes consist of alternate layers of oxygen and caesium. The structure he mentioned as most

³ A. R. Olpin, *Phys. Rev.* **36**, 251 (1930).

⁴ J. W. Mellor—"A Comprehensive Treatise on Inorganic and Theoretical Chemistry." Vol. II p. 486. Longmans, Green and Co., Ltd., London (1927).

⁵ L. R. Koller, *Phys. Rev.* **36**, 1639 (1930).

⁶ N. R. Campbell, *Phil. Mag.* **6**, 633 (1928).

⁷ N. R. Campbell, p. 10 "A Discussion on Photoelectric Cells and their Application"—The Physical and Optical Societies, London (1930).

likely was Ag-O-Cs-O-Cs. The potential energy of an electron moving through such a sequence of atomic or molecular layers was conventionally represented by a diagram similar to the one in Fig. 2, wherein the abscissa is the distance normal to the surface and the ordinate, the potential energy of an electron moving in this direction. Fowler⁸ then showed, by means of the wave mechanics, that, to a first approximation, the transmission of electrons through such a surface structure will be greatest provided the waves associated with their motion are of such length that they will form stationary waves in the potential valley.

If the width of the valley is d , the condition for standing waves to form, obviously, is that

$$\lambda = \frac{2d}{n} \quad (n = \text{an integer}). \quad (1)$$

But since the wave-length associated with a moving electron is

$$\lambda = h/mv, \quad (2)$$

according to Campbell and Fowler's theory, the speed of electrons most readily transmitted should be

$$v = \frac{nh}{2md}. \quad (3)$$

Consequently, the kinetic energy of such electrons will be

$$w = \frac{1}{2}mv^2 = \frac{n^2h^2}{8md^2}, \quad (4)$$

which is the expression Fowler obtained from a rigorous solution of Schrodinger's wave equation.

If all the energy possessed by the electron is acquired from the incident light quanta, then

$$w = \frac{1}{2}mv^2 = h\nu = \frac{n^2h^2}{8md^2} \quad (5)$$

and

$$\nu = \frac{n^2h}{8md^2}. \quad (6)$$

A hasty computation of this energy value when d is of atomic or molecular dimensions indicates that if it is to correspond to that of a quantum of visible or near infrared light, n must be unity. Eq. (6) is thus a simple relationship between the frequency of light ν for which maximum emission should occur and the width of the potential valley d responsible for this selectivity. Replacing ν by c/λ and simplifying, we get

$$d = 0.0551(\lambda_{\max})^{1/2} \quad (7)$$

or

$$\lambda_{\max} = 330 \cdot d^2, \quad (8)$$

where both λ_{\max} and d are expressed in Angstrom units.

⁸ R. H. Fowler, Roy. Soc. Lond. Proc. **A128**, 123 (1930).

More recently Frenkel,⁹ while adhering to Fowler's idea of selective transmission, announced that a "selective transparency must exist for any type of surface field involving a transition of the potential energy from one (constant) level inside the metal to another constant level outside it irrespective of the presence or absence of local maxima or minima".

NATURE OF COMPOUNDS ON TWO-COMPONENT CATHODE SURFACES

On account of the simplicity of the relationships expressed by Eq. (8), it would be easy to check Fowler's theory, were it possible to determine the proper value of d to use. Physically, the conventional distribution of potential showing a valley as diagrammed in Fig. 2 does not exist. Even though we concede the actual presence of alternate layers of electropositive and electronegative atoms or ions on the cathode surface, as postulated by Campbell, the potential energy of an electron passing through such a configuration must more nearly resemble that represented by the diagram in Fig. 3. Here

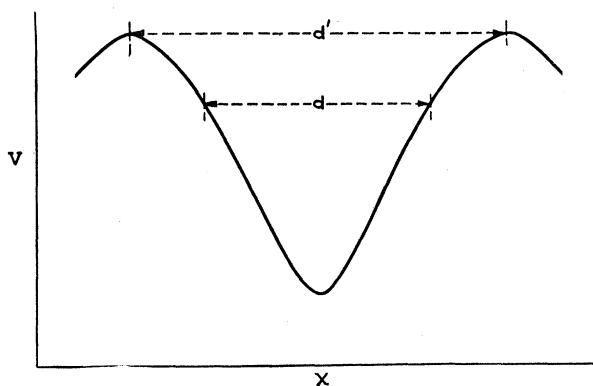


Fig. 3. Potential energy of an electron passing through a structure consisting of a layer of electropositive ions sandwiched between layers of electronegative ions.

the width of the valley is a function of its depth, and consequently it is not easy to obtain a quantitative correlation between λ_{max} and d . We can, however, insert the observed values of λ_{max} in Eq. (7) and see whether or not the values of d called for, are of the order of magnitude of atomic dimensions. Actually, they are found to lie between 3 and 5 Angstroms, which suggests a very rough correlation with the atomic diameters of the alkali metals.

The values of d obtained by Eq. (7) when the observed values of λ_{max} for alkali metal surfaces sensitized with hydrogen are used, have been tabulated in Table I, and those obtained when the observed values of λ_{max} for alkali metal surfaces sensitized with oxygen are used are listed in Table II.

It will be noted that the values in the first table are very nearly equal to the sum of the diameters of the positive metal and negative hydrogen ions multiplied by $\frac{1}{2}(2)^{1/2}$, and those in the latter table are approximately equal to the sum of the diameters of the positive metal and negative oxygen ions multiplied by either $\frac{1}{3}(3)^{1/2}$, $\frac{1}{2}(2)^{1/2}$, or $\frac{1}{3}(6)^{1/2}$.

⁹ J. Frenkel, Phys. Rev. **38**, 309 (1931).

TABLE I.

Cathode material	λ_{\max} (observed)	$d=0.0551(\lambda_{\max})^{1/2}$	d' = sum of diameters of positive metal and negative H ions ¹⁰	$\frac{d}{d'}$
LiH	2800A	2.92A	4.10A	0.712
NaH	3300	3.17	4.50	.704
KH	4350	3.63	5.20	.698
RbH	4800	3.82	5.52	.692
CsH	5400	4.05	5.84	.694
				$[\frac{1}{2}(2)^{1/2}=0.707]$

TABLE II.

Cathode material	λ_{\max} (observed)	$d=0.0551(\lambda_{\max})^{1/2}$	d' = sum of diameters of positive metal and negative O ions ¹⁰	$\frac{d}{d'}$
Sodium oxide	2270A	2.62A	4.60A	0.570
"	3500	3.26	4.60	.709
"	4700	3.78	4.60	.822
Potassium oxide	3130	3.08	5.30	.582
"	4260	3.57	5.30	.674
"	6200	4.34	5.30	.819
Caesium oxide	3500	3.26	5.94	.549
"	5500	4.09	5.94	.689
"	8000	4.93	5.94	.830

$$[\frac{1}{3}(3)^{1/2}=0.578; \frac{1}{2}(2)^{1/2}=0.707; \frac{1}{3}(6)^{1/2}=0.818]$$

Obviously, these factors suggest a definite configuration or alignment of molecules on the surface in some form of cubical arrangement, which, in turn, suggests the presence of a crystalline formation on the gas-treated alkali metal cathodes of photoelectric cells, and the existence of selective maxima because of selective transmission of electrons through the periodic fields of potential characteristic of such structures. The nature and dimensions of the respective crystalline forms will be considered in greater detail in succeeding paragraphs.

An interpretation of the cathode surface as a crystalline arrangement of the component ions impresses us as a very reasonable picture, for the amount of material used in forming some of the best photoelectric cells indicates that the surface coatings of the cathode might be as thick as 1,000 atom diameters. Certainly, they are sufficiently thick to be plainly visible and they contribute a definite coloration to the surface. Now, the fact that it is the ratio of alkali metal to oxygen (approx. 3 to 1) and not the total amount of each that determines the selective characteristic of a surface,¹¹ together with the fact that the final heat treatment previously described is of such a nature that the molecules deposited on the cathode will be thermally agitated but not evaporated, suggest strongly the likelihood of a crystalline formation. At the same time

¹⁰ See Table of Ionic Radii, V. M. Goldschmidt, Far. Soc. Trans. 25, 6, 253 (1929).

¹¹ This is based on an unpublished report by Dr. C. H. Prescott of the Bell Telephone Laboratories after considerable experimentation. A recent paper by N. R. Campbell [Phil. Mag. 12, 75, 173 (1931)] further substantiates this ratio.

any excess free alkali metal, having a lower boiling point than the salt, will deposit on the top surface of the crystal and greatly reduce the work function.

A crystalline surface structure will exhibit a periodic succession of potential valleys instead of a single potential valley as postulated by Campbell and Fowler. Just how this condition will affect the validity of Eqs. (4) to (8) has not yet been investigated. However, I shall proceed to point out a striking correlation between observed positions of selective maxima and those computed by means of Eq. (8) when values of d associated with the period of the potential field in a crystal are used.

ALKALI METAL HYDRIDES

All of the alkali metal hydrides are known to crystallize with the sodium chloride structure.¹² The arrangement of ions in a unit cell of this type is diagrammatically shown in Fig. 4.

The most likely path for an electron to follow in passing through such a crystal is one normal to the 110 plane and quite close to the positive metal

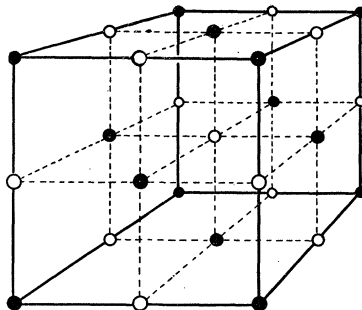


Fig. 4. Arrangement of ions in alkali metal hydride crystals (NaCl structure).
The circles represent the metal and the dots the hydrogen ions.

ions. In any other direction through the crystal, an electron will encounter more powerful retarding potentials because of the presence of negative hydrogen ions along its path. The nature of the potential field normal to the 110 plane, that is, the work an electron must do in passing through a hydride crystal in this direction, has been computed by Mr. L. A. MacColl of these laboratories on the basis of certain simple assumptions as to the nature of the potential fields of atoms and ions. His results are illustrated by the curve in Fig. 5. The potential is periodic and the period is $\frac{1}{2}(2)^{1/2}$ ($=0.707$) times the sum of the diameters of the positive alkali metal and negative hydrogen ions. As illustrated in Table I, this is very close to the value of d , which when used in Eq. (8) gives values of λ_{\max} in striking agreement with those observed. The fact that small deviations from the value 0.707 are noted for the hydrides of the more electropositive metals is likely due to the fact that Goldschmidt's values for ionic radii may not be altogether proper, since, as Bode¹² points out, the hydrogen ion is probably greatly deformed in the alkali metal hydrides, as indicated by the large refractive indices.

¹² H. Bode, *Zeits. f. phys. Chem. (B)* **6**, 251 (1930).

ALKALI METAL OXIDES

Whenever small amounts of oxygen or air come in contact with a clean alkali metal surface in an evacuated tube, the photoelectric sensitivity is greatly enhanced and a selective response to light of certain specific wavelengths produced.¹³ In such cases a chemical reaction almost invariably occurs and it is usually of sufficient intensity that the heat of reaction might conceivably create a vapor pressure of the metal, so that a thin metallic film will deposit on the surface. Presumably, the compound formed by the chemical reaction and deposited underneath the metallic film is either the monoxide or peroxide of the metal. Similar compounds might be obtained by heating to high temperatures an oxidized silver or copper plate in the presence of the more reactive alkali metals, like caesium.

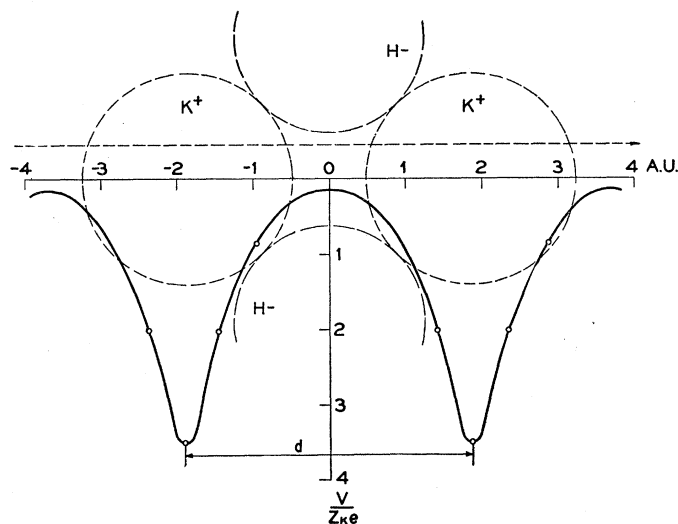


Fig. 5. The potential energy of an electron moving through a potassium-hydride crystal in a direction normal to the 110 plane, and at a distance from the nuclei of the potassium ions indicated by the dotted line with the arrowhead, can be represented by a periodic sequence of hills and valleys like the one shown here.

The selective transmission of electrons through surfaces coated with oxide films will be dependent upon the arrangement of ions in the individual molecules to a large extent. Adopting Slater's conclusions¹⁴ that the valence bonds of the oxygen atom are mutually perpendicular, the diagrams in Fig. 6 representing caesium monoxide and sodium and caesium peroxide have been prepared. Obviously, an electron passing through such a surface structure will encounter a periodic field of potential and the period in the case of the monoxide will be $\frac{1}{2}(2)^{1/2}$ times the sum of the diameters of the metal and oxygen ions. In the case of the peroxide, the period is equal to the diameter of the larger ion in the molecule. More specifically, it is the diameter of the alkali

¹³ A. R. Olpin, reference 3.

¹⁴ J. C. Slater, Phys. Rev. **37**, 481 (1931).

metal ion in all cases excepting those of sodium and lithium cells; in the latter cases it must be the diameter of the negative oxygen ion.

These dimensions correlate closely with the value of d demanded by Eq. (8). The chief discrepancy comes in the case of the monoxide of the heavier metals, and this may result from the fact that the angle between the valence bonds in alkali metal monoxides is slightly greater than 90° . As a matter of fact Pauling¹⁵ said it should be between 90° and $109^\circ 28'$ but closer to the former value. Actually 95° will give the proper value of d to correlate the calculated and observed positions of the selective maxima. Or, this slight discrepancy may result from a number of other causes, such for example, as ionic deformation or selective light absorption. It is not the fact that there are slight discrepancies that is surprising, but rather the fact that they are so few and small.

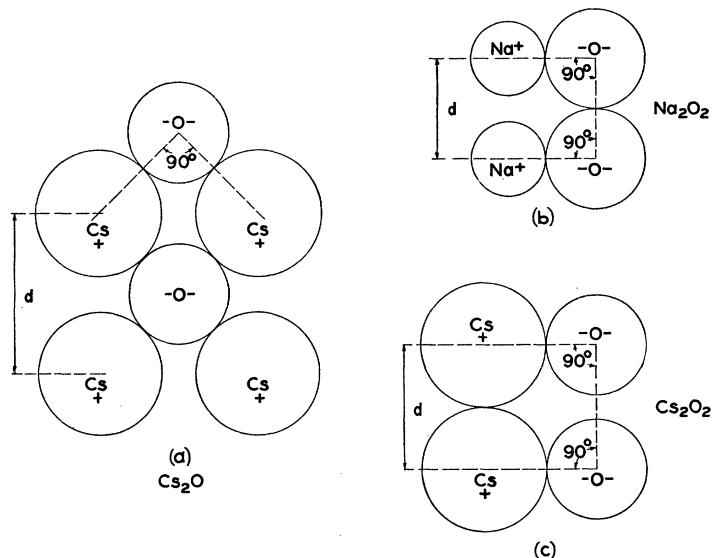


Fig. 6. Diagrams of molecular configurations illustrating distance of closest approach of component positive ions. (a) caesium monoxide, (b) sodium peroxide, and (c) caesium peroxide.

Whenever, as described previously, a cathode coated with an alkali metal oxide is heated under control in such a way that the surface molecules are agitated but not evaporated, and then the surface cooled rather quickly, the characteristic spectral response of the surface changes decidedly. Where there was a spectral maximum previously, there now appears a minimum, and new maxima appear at other wave-lengths. Presumably this is due to a rearrangement of the ions or molecules on the surface into a crystalline structure.

The crystalline structure of the oxides of the alkali metals of large radii

¹⁵ L. Pauling, *J. A. C. S.* **53**, 1356 (1931).

¹⁶ Bijvoet and Karssen, *Recueil des Travaux Chimiques des Pays—Bas* **43**, 680 (1924).

¹⁷ Claassen, *Recueil des Travaux Chimiques des Pays—Bas* **44**, 790 (1925).

has not been reported, but I have assumed that the monoxides have structures identical with those of Li_2O ¹⁶ and Na_2S .¹⁷ In Fig. 7 the arrangement of ions in such a crystal is diagrammatically illustrated. Because of the nature of electrostatic forces within such a crystal, an electron transmitted through it will tend to follow a path close to the nuclei of the positive metal ions and normal to the 100 or 110 planes. The work it must do at various points along either of these paths can be represented by curves similar to the one in Fig. 5, which means that the electron encounters a periodic field of potential within the crystal. In the direction normal to the 100 plane the period is $\frac{1}{3}(3)^{1/2}$ times the sum of the diameters of the positive metal and negative oxygen ions, and in the direction normal to the 110 plane, the period is $\frac{1}{3}(6)^{1/2}$ times this sum. These are the values which must be used for d to satisfy Eq. (8) when the observed positions of the selective maxima are used, as shown in Table II.

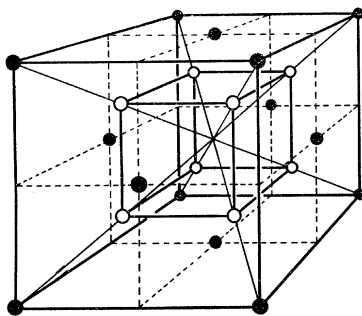


Fig. 7. Arrangement of ions in alkali metal monoxide crystals (CaF_2 structure). The circles represent the metal and the dots the oxygen ions.

ALKALI METAL SULPHIDES AND OTHER COMPOUNDS

In the light of the foregoing discussion, it is natural to expect that the wave-lengths of light to which an alkali metal sulphide responds selectively should be longer than for the corresponding oxide. Similarly, the selective maximum might be expected to appear at longer wave-lengths for selenides than for sulphides, and at still longer wave-lengths for tellurides as compared with selenides. Actually this condition has been qualitatively observed in the cases of potassium-oxides, sulphides, selenides and tellurides,¹⁸ and to some extent in the case of corresponding sodium compounds.¹⁹ Also, I have recently obtained a good set of curves showing that the position of the selective maximum for the potassium halides is a function of the size of the halogen ion.

Since, in the preparation of the potassium sulphide photoelectric cells referred to in the preceding paragraph, no attempt is made to produce a crystalline arrangement of the surface ions, the separation of the positive ions undoubtedly is that determined by their positions in separate sulphide molecules; and the determination of this value will be similar to that used for the noncrystalline oxides. If the angle between the valence bonds in alkali metal

¹⁸ W. Kluge, *Zeits. f. Physik* **67**, 497 (1931).

¹⁹ A. R. Olpin, reference 3.

sulphides be taken as 90° and the surface coating be similar to that illustrated in Fig. 6 (a), the period of the resulting periodic field of potential is almost exactly the value of d called for by Eq. (8) in the light of experimental data.

When a sulphur-treated sodium photoelectric cell is subjected to treatment similar to that which supposedly forms a crystalline oxide surface, the selective maximum in the spectral response curve always appears at longer wave-lengths than is the case without the sulphur. Moreover, a small hump or irregularity is frequently observed in the spectral response curve at $\lambda 6500$, where a maximum should appear for crystalline sodium sulphide, if it crystallizes with the calcium-fluoride structure (see Fig. 1C).

TABLE III.

Cathode material	Sum of diameters of metal and gas ions	d ($=\frac{1}{2}(2)^{1/2}d'$)	λ_{\max} ($=330.d^2$)	λ_{\max} (observed)	Observer						
LiH	4.10A	2.9A	2770	2800	Pohl and Pringsheim ²⁰						
NaH	4.50	3.18	3340	{ 3400	{ Pohl and Pringsheim ²⁰						
KH	5.20	3.68	4470	{ 3300	{ Olpin and Briggs ²¹						
RbH	5.52	3.9	5020	4350	Pohl and Pringsheim ²⁰						
CsH	5.84	4.13	5630	4800	Pohl and Pringsheim ²⁰						
Na ₂ O	4.60	3.25	3480	5400	Seiler ²²						
K ₂ O Cs ₂ O	5.30 5.94	3.75 4.20	4640 5820	4000-4600 5400	Olpin ²³ Richardson and Compton ²⁴						
						non-crystalline					
Na ₂ O ₂		d (=diameter of O ion) 2.64	2300	2270	Richardson and Compton ²⁴						
Cs ₂ O ₂		d (=diameter of metal ion) 3.30	3590	3500	Koller ²⁶						
Na ₂ O K ₂ O Co ₂ O	4.60 5.30 5.94	d ($=\frac{1}{3}(3)^{1/2}d'$)	2.65 3.06 3.43	2320 3090 3880	2270 3130 3500	Richardson and Compton ²⁴ Wiedmann ²⁷ Koller ²⁶					
							crystalline				
								Na ₂ S K ₂ S Cs ₂ S	4.60 5.30 5.94	d ($=\frac{1}{3}(6)^{1/2}d'$)	3.76 4.33 4.85
non-crystalline											
	Na ₂ S K ₂ S	5.44 6.14	d ($=\frac{1}{2}(2)^{1/2}d'$)	3.84 4.34	4860 6200	4900 6000-6200	Olpin ²³ Olpin ²³				
								non-crystalline			
Na ₂ S ₂ K ₂ S ₂									3.48 3.48	4000 4000	3800 4100
	Na ₂ S (Crystalline)	5.44	d ($=\frac{1}{3}(6)^{1/2}d'$)	4.44	6500	6500	Olpin ²³				

²⁰ R. Pohl and P. Pringsheim, "Die Liechtelektrischen Erscheinungen" Sammlung Viewig, Berlin (1914).

²¹ A. R. Olpin and H. B. Briggs, unpublished.

²² E. F. Seiler, reference 2.

²³ A. R. Olpin, reference 3.

²⁴ O. W. Richardson and K. T. Compton, Phil. Mag. **26**, 549 (1913).

²⁵ W. Kluge, reference 18.

²⁶ L. R. Koller, reference 5.

²⁷ G. Wiedmann and W. Hallwachs, Verh. d. D. phys. Ges. **16**, 107 (1914).

²⁸ V. K. Zworykin and E. D. Wilson, "Photocells and Their Application," p. 57.—John Wiley and Sons, N. Y. (1930).

²⁹ J. W. Ballard, J. O. S. A. **20**, 11, 618 (1930).

It appears, then, that the secret of making selective cathodes in photoelectric cells is that of forming a surface structure in which there is a periodic field of potential. If the selective response is desired at long wave-lengths, a large period is required; if at short wave-lengths, a small period. Of course, the surface work function is the limiting factor, however, for it is important that electrons transmitted or conducted through the periodic potential field can be emitted from the surface. In order to keep the work function as low as possible, a monoatomic film of electropositive metal is deposited on the surface.

In Table III are listed the values of d computed from the postulated surface structures described above, and the positions of the selective maxima given by Eq. (8) when these values are used. Opposite these computed values of λ_{max} are recorded the observed values and the observer.

THE LINDEMANN FORMULA

In 1911 F. A. Lindemann³⁰ derived the following expression for the natural period of a vibrating system composed of two interpenetrating spheres of radius r and continuously distributed charge $\pm ne$ and $\pm e$ respectively:

$$\nu = \frac{1}{2\pi} \left(\frac{ne^2}{mr^3} \right)^{1/2} \quad (9)$$

This frequency, which is also the frequency of an electron revolving around a central body of charge $+ne$, was identified with that of the selective photoelectric maximum. Putting n equal to unity, the valence of the normal alkali metal atom, and r equal to the radius of each monovalent alkali metal atom in turn, values of ν are obtained in striking agreement with the observed frequencies for the metals and their hydrides.

More recently I pointed out³¹ that if the several maxima, characteristic of oxide cells, result from the formation of different compounds, then all that is necessary to obtain values of ν by the Lindemann formula equivalent to the observed selective maximum is to assign to n the valence of the metal in those compounds. In this way the ultraviolet peaks in the response curves were ascribed to the peroxides (as Na_2O_2) of valence 2 and the maxima at long wave-lengths were ascribed to suboxides of valence 1/2 (as Na_4O). Although it is inconsistent with modern theory to think of a nuclear charge equal to $\frac{1}{2}e$ it was suggested that the force exerted on an electron by surrounding atoms might give that net effect.

By the Lindemann formula

$$\nu = \frac{1}{2\pi} \left(\frac{ne^2}{mr^3} \right)^{1/2}$$

and by the Fowler equation,

$$\nu = \frac{h}{8md^2} \quad (10)$$

³⁰ F. A. Lindemann, *Verh. d. D. phys. Ges.* **13**, 482 (1911); *ibid.* **13**, 1107 (1911).

³¹ A. R. Olpin, reference 3.

Equating these two expressions for the natural frequency of electronic systems,

$$\frac{1}{2\pi}(ne^2/mr^3)^{1/2} = \frac{h}{8md^2}, \quad (11)$$

or, simplifying,

$$d^2n^{1/2} = kr^{3/2} \quad (k = \text{const.}) \quad (12)$$

Now for any given metal atom r is constant, so that

$$d^2n^{1/2} = \text{a constant} \quad (13)$$

and d^2 varies inversely as $n^{1/2}$ or the square root of the valency.

As a specific case of this, take the case of the oxides of potassium. Eq. (13) becomes

$$d^2n^{1/2} = 9.12A^2, \quad (14)$$

when the radius of the potassium atom for coordination number 12 is used. By substituting the values of d computed from the structure of the surface compounds as described above [i.e. the sum of the diameters of the positive potassium and negative oxygen ions multiplied by $\frac{1}{3}(3)^{1/2}$, $\frac{1}{2}(2)^{1/2}$, and $\frac{1}{3}(6)^{1/2}$ respectively], the following values of n are obtained: $n = 1.98$; $n = 0.88$; $n = 0.49$.

Similar values are found for the other alkali metals. These compare favorably with the values 2, 1 and 0.5 used as the valence of the alkali metal as mentioned above, and account for the generally close correlation between the experimentally observed positions of the selective maxima and those computed by either the Lindemann formula or the wave mechanics.

SUMMARY AND CONCLUSIONS

A theory of the selective photoelectric effect for gas-treated alkali metal cells is presented, based on the calculations of wave mechanics, the main features of which are: (1) A two-component cathodic surface structure within which there is a periodic field of potential; (2) Selective transmission of electrons through this field provided their energy bears a definite, fixed relation to its period; (3) Emission of electrons arriving at the surface provided the surface work function is sufficiently low.

A periodic field of potential is shown to be typical of that within a crystal, and a microcrystalline surface structure is postulated for all red-sensitive photoelectric cathodes.

Data are presented correlating the positions of selective maxima in observed photoelectric response curve for the alkali metal hydrides with the sodium chloride arrangement of ions, and the alkali metal oxides and sulphides with the calcium fluoride structure.

The single selective maximum observed in the spectral response of each hydride cell, and the several maxima characteristic of oxides and sulphides are shown to be the natural consequences of these structures.

A correlation between data heretofore obtained by the modified Lindemann formula and those obtained by the wave mechanics is explained.