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The Photoelectric and Optical Properties of Sodium and Barium*

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Experimental spectral distribution curves have been obtained for sodium and barium using polarized and unpolarized radiation. The work function of sodium was determined as 2.28 ev and that of barium as 2.48 ev. The experimental data are compared with the theory of Mitchell. The theory fails satisfactorily to account for the absolute photoelectric yields and for the ratio of the photoelectric yields obtained with radiation polarized parallel and perpendicular to the plane of incidence.

THEORY

A GENERAL theory of the photoelectric effect in metals has been given by Mitchell.[1, 2, 3] This theory rests upon an observation by Tamm and Schubin[4] that the interaction of a light wave with a metal can be divided into two parts. Plausible reasoning leads to the conclusion that, within the range of wave-lengths ordinarily investigated, the interaction of a light wave with an electron moving in the periodic field of the lattice can make a negligible contribution to the photoelectric current. Upon this interaction does depend the reflection, refraction, and damping of the light wave. The photoelectric current results from an interaction between light wave and electron which is due to the surface field of the metal.

If the periodic field of the lattice is neglected, the reflection and refraction of the light wave may be introduced into the theory by means of Maxwell's equations and the experimental optical constants of the metal. Unfortunately, the calculations which are required for a complete comparison of this form of the theory with a set of experimental data are quite laborious. In this paper the experimental data will be compared with two forms of the theory which will be designated as approximations A and B.

Approximation A consists in neglecting the reflection and refraction of the light wave. A discontinuous potential jump at the surface of the metal is assumed. Myers[5] and Hill[6] have shown that the difference between calculations made with a square and an image field is chiefly due to the high reflection coefficient of the square barrier for slow electrons. By neglecting the reflection coefficient of the square barrier the calculations are not only greatly simplified but the agreement with experiment should be improved. The photoelectric yield is then proportional to the integral

$$\iiint \frac{1}{\nu^4}\frac{K_x^2}{[K_x^2+\mu\nu]^{\frac{1}{2}}}\frac{2}{8\pi^3} \times \frac{dK_x dK_y dK_z}{1+\exp\left\{\dfrac{h^2(K_x^2+K_y^2+K_z^2-\mu\bar{\nu})}{8\pi^2 mKT}\right\}}, \quad (1)$$

where the nomenclature is Mitchell's and the integral is taken over all electrons which, after absorption of a quantum, will have sufficient energy to escape. Except near the threshold the exponential is negligible compared with unity.

Near the threshold the variation of the Fermi distribution function cannot be neglected. If in this region the excitation probability is assumed independent of ν and proportional to K_x, then Eq. (1) goes over into DuBridge's[7] modification of Fowler's equation,

$$I=\alpha A T^2\varphi(x). \quad (2)$$

By means of the usual "Fowler plot" the thresh-

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[1] K. Mitchell, Proc. Roy. Soc. **A146**, 442 (1934).

[2] K. Mitchell, Proc. Camb. Phil. Soc. **31**, 416 (1935).

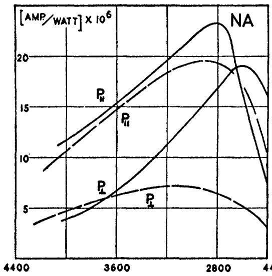
[3] K. Mitchell, Proc. Roy. Soc. **A153**, 513 (1936).

[4] I. Tamm and S. Schubin, Zeits. f. Physik **68**, 97 (1931).

[5] R. Myers, Phys. Rev. **49**, 938 (1936).

[6] A. G. Hill, Phys. Rev. **53**, 184 (1938).

[7] L. A. DuBridge, *New Theories of the Photoelectric Effect* (Hermann and Cie, Paris, 1935).



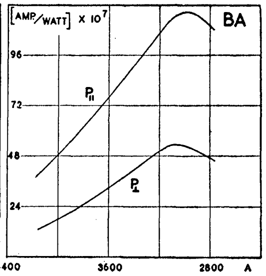


FIG. 1 (left). Calculated spectral distribution curves for sodium, electric vector parallel ($P_{\parallel}$), and perpendicular ($P_{\perp}$) to the plane of incidence. The difference between the solid and dashed curves shows the effect of neglecting the frequency variation of the optical constants.

FIG. 2 (right). Calculated spectral distribution curves for barium, electric vector parallel ($P_{\parallel}$), and perpendicular ($P_{\perp}$) to the plane of incidence.

old and the parameter α can be evaluated. DuBridge has interpreted α as the fraction of the number of electrons which come up to unit area of the surface in one second which absorb a quantum of energy when the light intensity is unity. By using the value of α so determined, the yields for frequencies far from the threshold (which have been calculated from (1) in arbitrary units) can be plotted to the same scale.

The theoretical curves shown in Figs. 4 and 8 were calculated in this manner. The constant potential inside the metal was fixed by the addition of the work function and the width of the Fermi band of electrons at 0°K. For sodium a band 3.24 ev wide and for barium one 3.28 ev wide were assumed.

The width of the Fermi band was determined by the number of "free" electrons per unit volume.

$$\xi_0 = \hbar^2[3\pi^2 n]^{\frac{2}{3}}/2m. \tag{3}$$

It was assumed that sodium possesses 1 "free" electron per atom and that barium possess 1.8 "free" electrons per atom.

This adjustment of theoretical and experimental curves to coincidence at the threshold where experiment and theory agree appears more logical than previous methods of comparison by adjustment of the yields at the maxima of the spectral distribution curves.

Approximation B is the form of the theory given by Mitchell in 1936.[3] The reflection and refraction of the light wave is taken account of by means of Maxwell's equations. This form of the theory allows the absolute photoelectric yield and its dependence upon the angle of incidence and state of polarization of the incident beam to be discussed.

To account for the photoelectric current excited by radiation whose electric vector vibrates in a plane parallel to the surface, Mitchell assumed that the surface is built up of small elements whose normals make an average angle ω with the normal to the geometrically plane surface. The elements are assumed small compared with the wave-length of the incident radiation but large compared with the wave-length of the photoelectrons. The angle ω must be evaluated from the ratio of the photoelectric yields for radiation polarized parallel and perpendicular to the plane of incidence.

Figure 1 presents the theoretical photoelectric yield curves for sodium for polarized radiation with the electric vector vibrating parallel and perpendicular to the plane of incidence. These curves were calculated from Eqs. 16 and 19 of Mitchell's 1936 paper.[3] The angle of incidence is taken as 60° and $\omega = 70°$. The positions of the maxima in these curves are necessarily wrong because of Mitchell's assumption that the width of the Fermi band is equal to the work function.

The solid curves were calculated by making use of the optical constants of sodium which have been published by Ives and Briggs.[8] The dashed curves were calculated by using the values of n_0 and K_0 for $\lambda = 5461$A and neglecting the variation of the optical constants with wave-length. The importance of a complete knowledge of the optical constants is obvious. It is to be noted that the frequency dependence of $P_{\parallel}$ is different from that of $P_{\perp}$. This is a possible explanation of the fact that no maxima occur in many of the $P_{\perp}$ curves which have been reported.

Similar curves for barium are shown in Fig. 2. The optical constants which were used were those reported in this paper.

EXPERIMENTAL

Photo-currents were measured with FP-54 tubes used in DuBridge-Brown circuits. The grid leaks were S.S. White and platinum-in-glass resistors. For the determination of the yields of sodium, using unpolarized radiation, the radia-

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[8] H. Ives and H. Briggs, J. Opt. Soc. Am. **27**, 181 (1937).

tion intensities were measured with a thermopile-galvanometer system having a sensitivity of 4×10^{-8} watt per cm deflection. For measurements with polarized light a small calibrated photo-cell was used to determine intensities. The surface in this cell was a thick matte layer of sodium on nickel. This cell was checked for linearity of response and independence of yield on azimuth of polarization.

The light sources were a 500-watt tungsten lamp and a low pressure d.c. mercury arc. The radiation was resolved with a Bausch and Lomb single quartz monochromator. Tests with filters established that the amount of scattered light was negligible.

Because of the small dispersion of quartz in the visible, an appreciable band of wave-lengths was transmitted by the monochromator. Thus, with the slits set at 0.05 mm a wave-length band almost 200A wide was passed at 5500A. The effect of this upon the precision of the threshold determinations was calculated as follows. With an assumed surface whose true yield was given by Fowler's theory the apparent yield was calculated by graphical integration. A wave-length band of 200A was taken. At the assumed threshold (5400A) the apparent yield was 17 percent too high and 200A from the threshold was 5 percent too high. The resulting error in the work function, determined by Fowler's method, was less than 0.01 ev.

The monochromator was mounted upon a heavy iron base which turned upon ball bearings to allow successive readings to be taken upon photo-cell and thermopile.

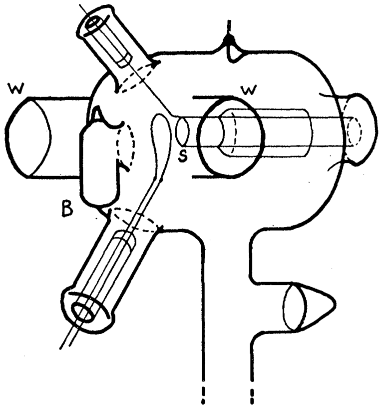

FIG. 3. Sodium photo-cell.

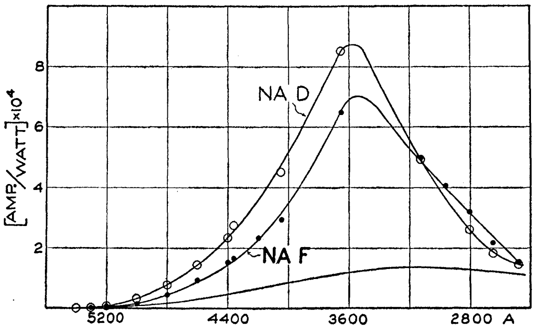

FIG. 4. Extreme variation in the shape of the spectral distribution curve for sodium, unpolarized radiation. The lower solid curve is calculated.

SODIUM

Figure 3 illustrates the photo-cell used for the measurements upon sodium surfaces with unpolarized radiation. The sodium was deposited upon the polished plane glass surface *S* by slow distillation from the reservoir *B*. Before the tube was sealed off from the pumps a heavy layer of sodium was deposited upon the inner walls of the tube. The skirt upon the re-entrant tube carrying *S* effectually insulated *S* from the rest of the tube. The quartz windows *W* fixed the angle of incidence at 60°.

The sodium was Baker's analyzed grade and was predistilled five times in glass. The pressure in the tube was measured with an ionization gauge and was about 2×10^{-8} mm Hg after sealing off from the pumps.

Five surfaces were formed with *S* held at temperatures between 25°C and 97°C during the distillation. None of the surfaces was sufficiently specular to allow the measurement of optical properties. Fowler curves, plotted for these surfaces, yielded thresholds between 2.28 ev and 2.29 ev. The values of α ranged between 3.3×10^{-32} and 5.0×10^{-32} cm^2-sec. per quantum. In plotting the Fowler curves the photoelectric yields were expressed in terms of electrons per quantum. The extreme variation in the shape of the spectral distribution curves is shown in Fig. 4. The Fowler curves for these surfaces are shown in Fig. 5.

These surfaces were fairly stable. A threshold shift to the red of about 20A was detectable 60 hours after the formation of one surface. The rest of the spectral distribution curve showed no change.

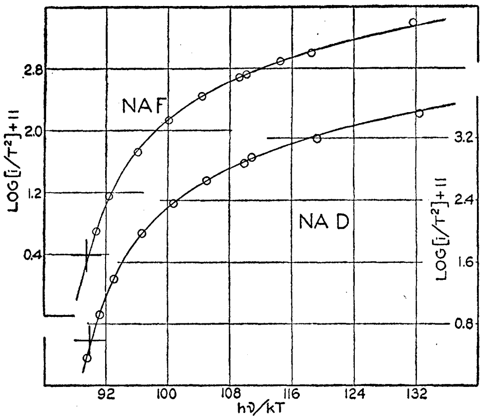

FIG. 5. Fowler plots for sodium surfaces for which the distribution curves are given in Fig. 4. For NaF $\varphi=2.29$ ev; $\alpha=3.3\times 10^{-32}$ cm²-sec./quantum; $T=298$°K. For NaD $\varphi=2.28$ ev; $\alpha=5.0\times 10^{-32}$ cm²-sec./quantum; $T=296$°K.

An attempt was made to prepare specular sodium surfaces by distilling the metal upon a polished glass plate which was cooled with liquid air during the distillation and kept cooled during the measurements. The tube used was similar to that illustrated in Fig. 6. The surfaces deposited in this way however were contaminated with gas and did not give a good fit to the Fowler curve. A typical spectral distribution curve for such a specular surface, taken with polarized radiation, is shown in Fig. 7. Table I gives the ratio of the photoelectric yields and of the energy absorbed, as calculated from the measured reflectivity of the surface.

BARIUM

The tube illustrated in Fig. 6 was used for the investigation of barium. The quartz windows fixed the angle of incidence at 60°. The barium was suspended above the tantalum ribbon *D* until the preliminary outgassing of this assembly had been completed. The barium was then lowered upon the ribbon which had a shallow *V* cross section. The shield *C* protected the polished, plane surface *S* during the melting and outgassing of the barium. The thick layer of barium, which deposited upon the inner walls of the tube during this operation, was used as anode. The pressure in the tube, after sealing off from the pumps, was 2×10^{-8} mm Hg.

TABLE I. *Sodium 7. Ratio of photoelectric yields and of energy absorbed.*

$\lambda(A)$	$P_{\parallel}/P_{\perp}$ $\omega=70°$ (CALC.)	$P_{\parallel}/P_{\perp}$ (EXP.)	$A_{\parallel}/A_{\perp}$
5200		2.2	1.5
4800		1.8	1.3
4400		1.7	1.3
4000	3.0	1.5	1.2
3600	2.3	1.5	1.1
3200	1.7	1.4	1.1
2800	1.4		
2400	0.5		

The data obtained from two surfaces in separate tubes are shown in Fig. 8. For the measurements upon Surface 2 a Glan-Thompson prism of 12 mm cross section was used to obtain polarized radiation.

Fowler plots, with the yields expressed in terms of electrons per quantum, indicated a threshold of 2.48 ev for each surface. The value of α for surface 1 was 2.3×10^{-32} cm²-sec. per quantum. Surface 2 gave values of $\alpha_{\parallel}=2.0\times 10^{-32}$ cm²-sec. per quantum and $\alpha_{\perp}=1.0\times 10^{-32}$ cm²-sec. per quantum. Fig. 9 is a Fowler plot for barium 1.

Cashman and Bassoe[9] recently reported a threshold of 2.49 ev for barium but their spectral distribution curve did not pass through a maximum. Dr. Cashman has informed the author, however, that barium surfaces more recently investigated by him have shown a maximum in the spectral distribution curve.

Table II compares the ratios of the photoelectric yields and of the energies absorbed by the surface. The energies absorbed were calculated from the measured optical constants of barium.

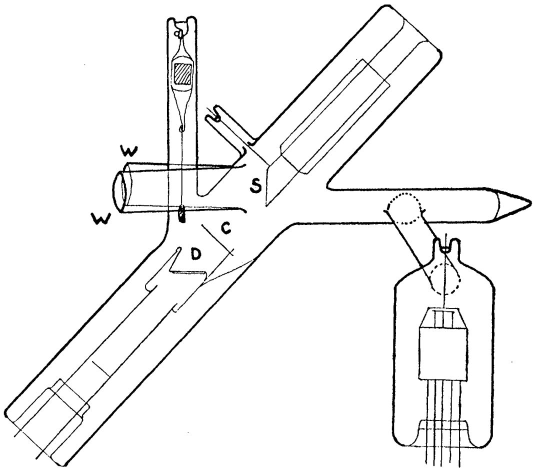

FIG. 6. Barium photo-cell.

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[9] R. Cashman and E. Bassoe, Phys. Rev. 55, 63 (1939).

TABLE II. *Barium 2. Ratio of photoelectric yields and of energy absorbed.*

$\lambda(A)$	$P_{\parallel}/P_{\perp}$ $\omega=70°$ (CALC.)	$P_{\parallel}/P_{\perp}$ (EXP.)	$A_{\parallel}/A_{\perp}$
5780			1.93
5460			1.87
4916		1.7	1.82
4358		2.1	1.74
4047	2.7	1.9	1.65
3650	2.3	2.0	
3341	2.2	2.0	
3130	2.1	2.0	

OPTICAL CONSTANTS OF BARIUM

The optical constants of barium were measured by the method of Drude.[10] A high pressure capillary mercury arc and the Bausch and Lomb monochromator, provided with Wratten filters, served as a light source. At 4916A, the arc was used to adjust the monochromator and then a tungsten lamp was substituted. The exit slit of the monochromator served as the source slit for a spectrometer having quartz optics. The polarizer and analyzer were Glan-Thompson prisms of 12 mm cross section cemented so as to transmit to 3000A. A Babinet-Soleil compensator was mounted before the analyzer.

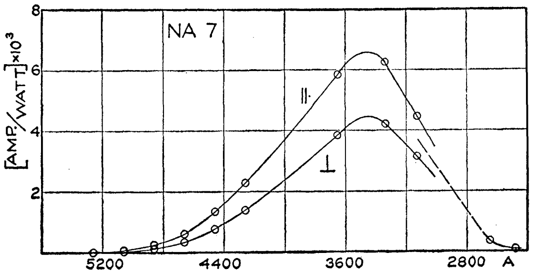

FIG. 7. Spectral distribution curves for sodium, electric vector parallel and perpendicular to the plane of incidence.

In the visible region of the spectrum, extinction was determined with the eye. In the ultraviolet, a sodium photo-cell was placed to intercept the beam emerging from the analyzer. Approximate settings of analyzer and compensator for minimum photo-current were first found. A curve of photo-current *versus* compensator setting was next taken. This accurately symmetrical curve could be folded upon itself to determine a better compensator setting for minimum photo-current. An improved analyzer setting was then determined in the same manner. One repetition of the procedure usually fixed compensator and analyzer positions satisfactorily. This method was rapid and more precise than the use of a fluorescent screen. The precision obtainable in the ultraviolet was as good as that obtained in the visible with the eye.

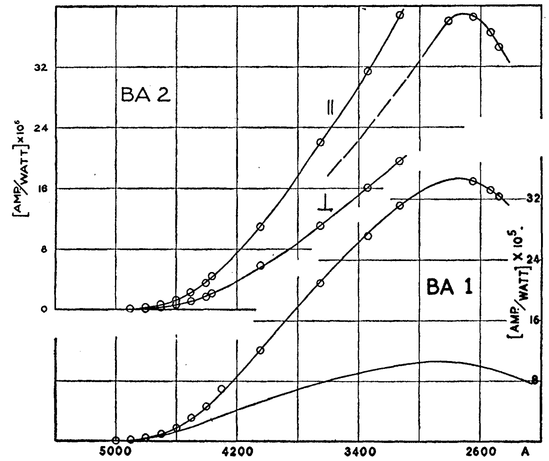

FIG. 8. Spectral distribution curves for two barium surfaces in separate tubes. The curves marked $\perp$ and $\parallel$ are for the radiation polarized with the electric vector $\perp$ and $\parallel$, respectively, to the plane of incidence. The distribution curve for Ba1 is for unpolarized radiation. The lower solid curve is calculated.

The most serious source of constant error was the residual strain in the quartz windows. A check showed that no rotation of the plane of polarization was caused by the windows. The net phase shift due to the windows was determined by measuring the phase shift produced by an aluminum mirror both inside and outside the tube. At 5461A the net phase shift of the

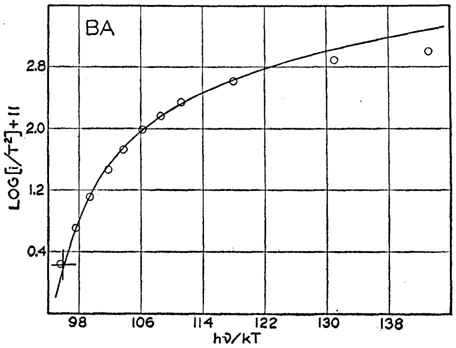

FIG. 9. Fowler plot for barium, electrons/quantum; $\varphi=2.48$ ev; $\alpha=2.3\times10^{-32}$ cm²-sec./quantum; $T=300°$K.

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[10] P. Drude, Wied. Ann. **64**, 159, (1898).

windows was 1°. The measured phase shifts have been corrected by using this result and the assumption that the phase shift due to the windows was inversely proportional to the wavelength. The dispersion of the birefringence can be safely neglected.

The results of the measurements upon barium 1 are shown in Fig. 10. Barium 2 was not a good optical surface but exhibited some "bloom." For the sake of comparison, however, the data from both surfaces are summarized in Table III. The nomenclature is that of König[11] and all calculations were made with his exact formulae. These results are in fair agreement with those of O'Bryan.[12] It is particularly interesting to note that two surfaces with very similar photoelectric properties show dissimilar optical properties.

CONCLUSION

It can be seen from the comparison of the theoretical and experimental curves of Figs. 4 and 8 that when the parameters, in the form of Mitchell's theory which we have called approximation A, are determined so as to fit the data near the threshold with a Fowler plot, the theory fails by a factor of about 4 to predict the correct yields at the maximum of the curve.

As Fig. 1 indicates, the optical constants of a metal can be of great importance in determining the form of the spectral distribution curve and the theory cannot neglect them.

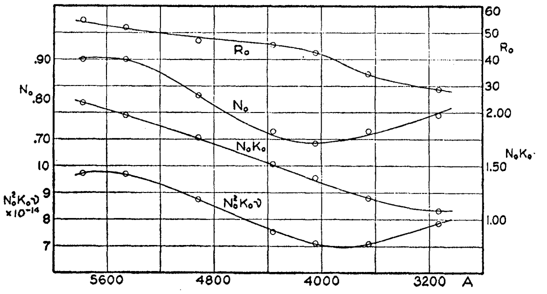

FIG. 10. Optical constants of barium.

TABLE III. *Optical constants of barium.*

	Barium 1				Barium 2		
$\lambda(A)$	n_0	k_0	$n_0^2k_0\nu$ $\times10^{-14}$	$R_0(\%)$	n_0	k_0	$R_0(\%)$
5780	0.90	2.32	9.77	54.8	0.81	1.74	38.3
5461	.90	2.19	9.71	52.0	.79	1.65	35.6
4916	.81	2.19	8.77	47.1	.74	1.59	32.8
4358	.72	2.12	7.55	45.4	.69	1.47	30.6
4047	.69	2.01	7.12	42.5	.73	1.25	23.6
3650	.72	1.66	7.10	34.7			
3130	.76	1.41	7.84	28.8			

The concept of surface roughness as an explanation of the photo-currents obtained when the electric vector vibrates in a plane parallel to the surface of the metal seems untenable. The large value of ω, which must be assumed in order to obtain small ratios, $P_{\parallel}/P_{\perp}$, is physically implausible. Furthermore, the frequency dependence of the calculated ratio $P_{\parallel}/P_{\perp}$ is completely wrong in the case of sodium. The calculated absolute yields of barium are about 50 times smaller than the experimental yields.

A simple explanation of the difference between the yields, $P_{\parallel}$ and $P_{\perp}$, would be that it is caused by the change in reflectivity of the surface with the variation of the azimuth of polarization. If this is so the ratio of the energies absorbed at a given frequency should be the same as the ratio $P_{\parallel}/P_{\perp}$. The data presented in Tables I and II do not justify this explanation.

Shiff and Thomas[13] have criticized Mitchell's method of taking account of the reflection and refraction of the light wave. Makinson[14] has applied to potassium the method of Shiff and Thomas, which does not assume a discontinuous change in the optical constants at the surface of the metal. The absolute yields which are obtained are larger than those given by Mitchell's theory and similar calculations for sodium would probably give better agreement with experiment. However, the difficulties faced by Mitchell's theory in explaining polarization phenomena are not removed.

The author is greatly indebted to Dr. L. A. DuBridge for advice and assistance; and to the Charles A. Coffin Foundation for the grant of a fellowship.

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[11] W. König, *Handbuch der Physik*, Vol. 20 (1928).

[12] H. O'Bryan, J. Opt. Soc. Am. **26**, 122 (1936).

[13] L. Shiff and L. Thomas, Phys. Rev. **47**, 860 (1935).

[14] R. Makinson, Proc. Roy. Soc. **A162**, 367 (1937).