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Optical Properties of the Alkali Metals

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The physical processes responsible for the unique optical properties of silver, in contrast to those of the alkali metals are briefly discussed from the standpoint of the zone theory of electron distribution in crystals. The results of experiments undertaken in the hope of finding a renewal of reflecting power in the remote ultraviolet in the case of the alkali metals, are recorded. Photographs of the spectra of the discharge of a condenser through a capillary tube after reflection from metal films condensed at liquid-air temperature showed no return of reflection in the region extending down to 500A.

The high transparency of comparatively thick films of the alkali metals in the ultraviolet region was first observed and studied by one of us in 1919.[1] In this investigation only potassium and sodium were investigated; the former showed high reflecting power from the red down to $\lambda = 3400$A, below which point the reflection fell off rapidly, and the metal became very transparent. Sodium, on the other hand, while exhibiting the high transparency in the ultraviolet below 3100A showed a reflecting power estimated at 50 percent between 2100A and 3000A, while in the visible spectrum it is of the order of 90 percent. In 1933[2] the behavior of the alkali metals was more thoroughly investigated and the region at which transparency commenced for all of these metals determined. Caesium showed high transmission beginning at wave-length 4400A, rubidium at 3600A, potassium at 3150A, sodium at 2100A, and lithium at a somewhat lower point, an uncertainty resulting from the presence of sodium as an impurity. In the region of transparency, which was investigated to wave-length 1850A, these metals have a Brewsterian angle and give plane polarized light by reflection. The transparency in the case of a potassium film was about 100,000 times as great in the ultraviolet as in the visible region; a film through which the sun's disk was barely visible transmitted 25 percent.

R. de L. Kronig[3] attempted to account for these results by his quantum theory of metallic dispersion, which is based on assumed quantum transitions of electrons from an energy level in one of the "zones" (formed by the widening of the atomic levels as the atoms approach one another) to a corresponding level in a zone of higher energy in the crystal lattice. While this treatment gives a qualitative picture of the narrow band of transparency of silver in the ultraviolet, it does not represent the behavior of the alkali metals. Zener[4] showed that good agreement with the observations of experiments resulted if the electrons were considered as free, and developed equations along the lines employed by Tonks and by Norton in their treatment of the action of the Kennelly-Heaviside layer on radio waves, in which case the dielectric constant is represented by $\epsilon = 1-(Ne^2)/(\pi m\nu^2)$ in which N is the number of electrons in unit volume (or atoms in the case of the alkali metals since only the valence electron is concerned). Zener then shows that there is a critical frequency ν_0 (or wave-length λ_0) which gives the dielectric constant the value 0. That is

$$(Ne^2)/(\pi m\nu_0^2) = 1 \quad \text{or} \quad \nu_0^2 = C/\lambda_0 = Ne^2/\pi m.$$

We then have total reflection when $\lambda > \lambda_0$ while for $\lambda < \lambda_0$ the proportion reflected is $R = (n-1)^2/(n+1)^2$ where $n = \sqrt{\epsilon}$.

The behavior of the alkali metals could thus be accounted for by free electrons in the crystal lattice; the energy states in the lower zone are incompletely filled. These electrons are considered as operating on radiant energy in the range of the visible spectrum in the same way that the electrons in the Heaviside layer operate on radio waves, reflecting them back to earth if

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[1] R. W. Wood, Phil. Mag. July (1919).

[2] R. W. Wood, Phys. Rev. **44**, 353 (1933).

[3] Kronig, Nature **132**, 601 (1932).

[4] Zener, Nature **132**, 968 (1932).

the electron concentration is sufficiently high in comparison to the wave-length. It is known for example that, in certain states of the ionosphere radio waves are sometimes reflected from a lower stratum which they subsequently are able to penetrate, only to be reflected from a stratum at a much greater elevation. The wave-length at which reflection resulting from free, or Zener, electrons will cease, will be greatest for caesium (large atoms and least dense packing of the valence electrons) and least for lithium (smallest atoms and densest packing, i.e., N has its smallest value in the case of caesium).

The object of the present investigation was to see whether an extension of the study of the optical properties into the region of the shortest possible wave-length would show evidences of quantum absorption such as is shown in the case of silver on the short wave-length side of its band of transparency around $\lambda = 3100$A.

A clearer picture of the problem can be gathered perhaps by comparing the optical properties of silver with those of the alkali metals.

In the case of silver we have zones somewhat as shown in Fig. 1. The reflection (nearly 100 percent) in the visible region, and 50 percent on the long wave-length side of the narrow band of transparency can be attributed to the electrons in the uppermost filled band of the lower zone b, which act in the manner of Zener's "free electrons." This gives the high reflection on the long wave-length side of the region of transparency (where ϵ becomes 0) which corresponds to the similar region shown by the alkalis, but extends only to a very limited distance, for at and beyond its edge on the short wave-length side, the light photons have energy enough to effect transitions from levels in zone b to *corresponding* bands in zone a as shown by arrows. This is termed inner photoelectric (or quantum) absorption, and the reflecting power (which is very nearly zero in the region of transparency, acquires a considerable value, which is determined by the usual equation for semi-transparent media,

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}.$$

It thus appears that the reflection on opposite sides of the band of transparency results from different physical processes.

In the case of the alkali metals the zones overlap, and form a continuum within which Zener's "free electrons" can operate, but in which quantum transitions can also occur. The quantum transitions are, however, of much smaller energy values than in the case of silver, and cause little or no absorption and reflection in the remoter ultraviolet. They do, however, introduce absorption on the long wave-length side of the point where $\epsilon = 0$ and consequently reduce the reflecting power as this point is approached from the visible region. Curves showing the reflection to be expected on Zener's treatment (free electrons only), and the same as modified by quantum absorption are shown in Fig. 2 for potassium.

It seemed possible however, that photons of sufficient energy might be able to effect quantum transitions for an electron in an inner closed shell,

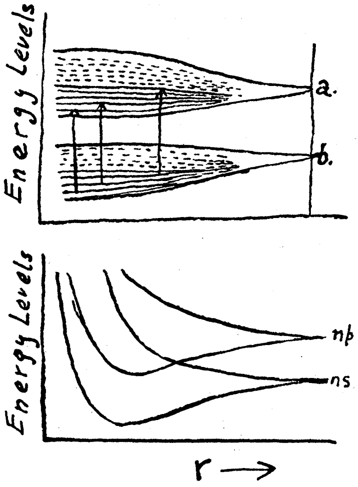

FIG. 1. Energy levels as a function of atomic distances. Upper curves for silver, lower curves for sodium.

and that such transitions would give rise to reflection as in the case of silver. In the case of caesium it seemed that such transitions could be brought about by light of wave-length not much shorter than 500A; this assumed value is based on the second ionization potential of caesium.

APPARATUS

The apparatus for the investigation was designed to operate as follows. The light from an

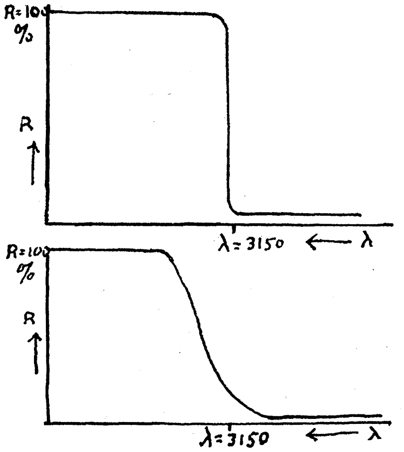

FIG. 2. Reflection coefficient. Upper curve for free electrons; lower shows modification by quantum absorption in potassium.

end-on capillary tube of Pyrex glass traversed by condenser discharges in helium fell on a hollow concave mirror which could be kept filled with liquid air. Below the mirror a small furnace was mounted from which the alkali metals were distilled onto the mirror, which then focused the light from the capillary on the slit of a small vacuum spectrograph. A diagram of the mirror and furnace chamber is shown in Fig. 3 (side view and not drawn to scale) and again in Fig. 4, in connection with the discharge tube (both viewed from above).

The hollow mirror was made by closing a fairly large Pyrex tube at the bottom, heating one side and pressing it in, until the flattened surface coincided with the axis of the tube. The flat surface was then ground concave and polished, with a radius of curvature of 13 cm and an area of 4 cm^2. The upper end was ground to a cone, and a thistle tube sealed in as shown. This construction was necessary to prevent the liquid air, (which was introduced through the thistle tube) from freezing the conical ground joint by which the mirror was rotated until the image of the capillary fell on the slit. The distance from the mirror to the ground joint was much longer than shown in the diagram.

The platinum furnace F was heated by an incandescent spiral of tungsten. The supply current came through wires sealed into the conical ground stopper G, which could be removed for charging or cleaning the furnace. The metals were evaporated from a shallow trough immediately above the spiral. The discharge tube, which was connected with the Y shaped furnace chamber by a ground joint is shown also in Fig. 4. (Side view immediately below the top view). It consisted of two large cylindrical tubes E_1 and E_2 containing the electrodes, joined by a short horizontal tube D with a sealed-in tube of smaller bore, into which the capillary discharge tube (surrounded by a glass sleeve), could be inserted by removing the window W. The insertion of a new capillary is necessary after every four or five hours of operation, as the bore is gradually enlarged by glass dust torn off from the surface by the heavy discharges. It is this dust, heated to a super-incandescence, which emits the continuum of short wave-lengths. Following Hopfield's technique we fitted the portion of the tube at H with another sealed-in tube into which a second capillary tube of 1 mm bore was inserted, to protect the mirror chamber and the attached spectrograph (where the lowest possible pressure was required) from the higher pressure necessary in the discharge tube to ensure its uniform operation. Helium, purified by passage through outgassed activated charcoal at liquid-air temperature, entered the discharge bulb E_1 through a long glass capillary thread; the rate of flow was about 100 cc per hour. In the capillary, L, which was 5 cm in length with a bore of one to three mm, brilliant flashes of light are produced about once a second by the dis-

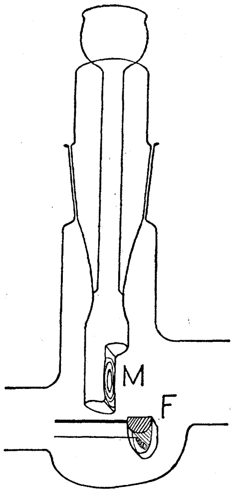

FIG. 3. Diagram of apparatus; side view.

charge of a condenser of 0.06 microfarad capacity charged to 50 kilovolts by a transformer and FP 84 thermionic rectifier. The impedance of the oscillatory circuit was made low by using heavy many stranded cable. The spark gap was between 5 inch brass spheres, one of which was swung to and fro by a constant speed motor. This gave better control of the exposures than with the irregular discharges which occurred with a fixed gap.

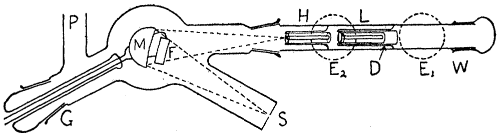

FIG. 4. Diagram of apparatus, as seen from above.

The light from the first capillary passed through the second, in part by multiple reflections, and fell upon the mirror. This second capillary was surrounded by a sheath of thin brass flared out at one end to a diameter equal to that of the tube connecting the two discharge bulbs. This blocked the passage of all light except that passing through the capillary, and facilitated the adjustment of the mirror to the position in which the image of the capillary was centered on the slit.

The spectrograph was equipped with a grating of 42 cm radius, 15,000 lines to the inch, etched on glass, and gave a nearly normal spectrum covering the wave-length range from 0 to 4100A on a 9 cm film. The film was Eastman process sensitized with one part Nujol in 30 parts benzene. Overlapping of the spectral orders was almost entirely eliminated by covering the fluorite region with a fluorite plate and the longer wave-length region with one of crystal quartz.

PREPARATION OF THE METALS

The metals, sodium and potassium were heated for an hour, with continual pumping in a Pyrex glass tube, one end of which had been drawn down to a thin walled "straw" about 3 mm in diameter and 50 cm in length. A plug of well-cleaned and heated steel wool had been previously packed into a constriction in the tube at the base of the tapering straw, and after outgassing the metal, the tube was sealed off from the pump, inverted and given a whip-like motion which projected the molten metal through the steel wool and down into the glass straw, in which it solidified, usually as short plugs with empty spaces between. In cases in which the tube filled solidly with metal, short bits were cut off as required and the open end sealed with a drop of molten Picein wax. The waxed end was cut off and rejected before using a second piece.

Lithium cannot be given this treatment, and was placed directly in the platinum trough of the furnace, after the surface was trimmed with a knife. Sodium and potassium were introduced by placing a short bit of the metal filled straw in the furnace, inserting the ground joint and starting the pump immediately.

Rubidium and caesium, sealed in short thin-walled tubes, were sent to us by Dr. H. E. Ives of the Bell Telephone Laboratories. Before attempting to introduce these tubes, the entire apparatus, including the spectrograph, was exhausted, and the "gate-valve" behind the slit closed. The rest of the apparatus was then filled with nitrogen, and a slow stream of the gas caused to flow out through the open joint, and past the furnace which was held just within the opening at *G*. The ends of the tube containing the metal were cut off as they were held (by gloved fingers) in the nitrogen stream issuing from *G*. This technique was imperative since caesium takes fire almost instantly on exposure to the air.

Photographs of the spectrum reflected from the glass mirror which were taken before any experiments with the metals were made showed that we were reaching a point a trifle short of 500 angstroms, but whether this limit was due to failure of the mirror to reflect or to the absence of shorter wave-lengths in the light, we did not determine.

PREPARATION OF THE METAL MIRRORS

The entire apparatus having been exhausted, the gate-valve to the spectroscope was closed, air (or nitrogen) admitted, and the metal placed in the furnace. Re-exhaustion was commenced immediately. The discharge tube was now operated for about an hour for outgassing. The helium was admitted after the vacuum had extinguished the discharge. The mirror was then turned into such a position that it faced away from the furnace and the glass walls in its neighborhood well heated with a small torch. The tube was then allowed to cool and the current turned on to the furnace; the temperature was raised very gradually at first until the metal boiled out of the tube from the pressure of the occluded hydrogen. Usually there was a considerable evolution of metal vapor when this occurred but none reached the concave face of the mirror. The current was now considerably reduced, and a clear spot produced on the wall of the tube by local heating for the purpose of observing the mirror, which was now filled with liquid air and turned to a position such that it faced the furnace. After the vacuum had reached the point at which a "leak-tester" showed only a feeble fluorescence of the wall of the tube, the temperature was raised until evaporation of the metal commenced. The thickness of the film could be judged by its transmission of visible light.

If the evaporation was too rapid the mirror appeared grey or even black, probably because its surface was heated too rapidly for the heat to diffuse through the glass to the liquid air, or perhaps by too rapid a rise of pressure. Slow evaporation for about two hours invariably produced excellent mirrors.

The discharge was now started and the mirror turned until the image of the capillary appeared on the slit.

It will be readily understood that the assembling of the tubes and the spectroscope, so that this could be accomplished by simple rotation on a fixed axis, was a labor of some magnitude, as it involved local heating and slight bending of the glass on several occasions.

The exposure times for the spectrograms varied from 30 minutes to an hour or more.

RESULTS

Taken as a whole the apparatus functioned very perfectly. The chief difficulty was with the source of the light; the ratio of the intensity of the continuum to that of the line spectrum was very variable. With a capillary of large bore the line spectrum predominated, and if we started with a small bore a progressive enlargement was always present owing to the stripping of the surface by the discharge.

Misleading results occur if the metal film is too thin, as in this case transmission in the ultraviolet occurs, and we have reflection from the glass.

The wave-length scale was determined approximately from the grating constant and the measured distance from the grating to the film, and checked by comparator measurements on several lines. Only a few lines due to helium were present; most of the others were ascribed to nitrogen, oxygen, hydrogen, carbon silicon, and boron.

The "central image" was reduced in intensity by a small strip of red Cellophane mounted in front of the plate, and appeared in the spectrograms as a sharp narrow line, on which accurate settings could be made.

With long exposures traces of tarnish appeared on the mirrors especially in the case of caesium, and it was usually found expedient to apply a second coat either from the furnace, or by driving off some of the deposit from the surrounding wall of the tube. A number of the spectrograms are reproduced in Fig. 5. The upper and lower, *a* and *i*, show the reflection spectrum from the glass mirror; the former, one of the first photographs taken, (with a discharge tube of 1 mm bore) was badly fogged in the short wave-length region but shows the continuum, with superposed lines, down to 500A, while the latter made with a discharge capillary of 3 mm bore, shows only the lines, but nothing beyond 500.

Spectrum *b* was made with a sodium mirror which was opaque to visible light, but sufficiently thin to permit the reflection from the glass to extend the spectrum to 1000A.

The next five spectrograms, *c* to *g*, show the reflection from all of the alkali metals in the order of their atomic numbers.

Spectrum *h*, taken with a thin film of rubidium shows strong reflection from the glass; the sharp breaks indicate the regions covered by the quartz and fluorite plates used for suppressing the second order spectrum of the shorter wave-lengths. Taken as a whole the spectra do not give a very satisfactory impression of a progressive shift of the limit of reflection. It must be remembered, however, that there is no sharply defined limit; the reflecting power decreases, in the case of

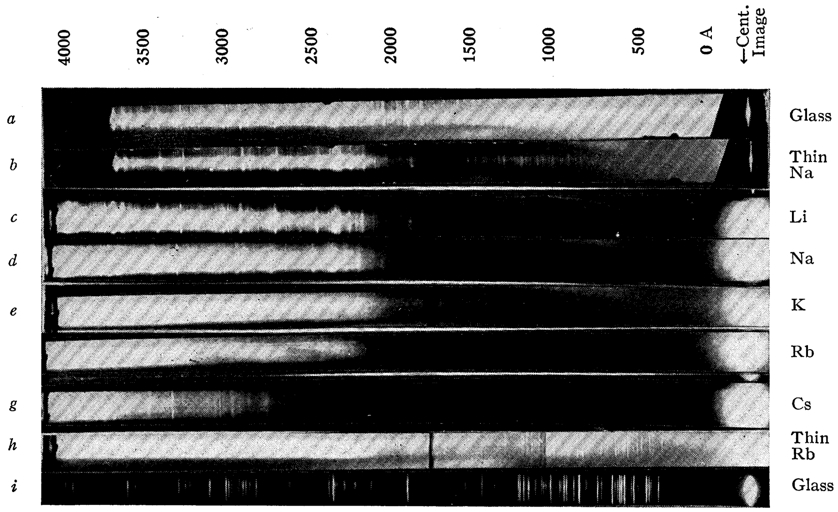

FIG. 5. Reflection spectra from various mirrors.

rubidium, from 60 percent to 10 percent in a range of 800A according to Ives.[5] Our spectrum *f* shows reflection down to 2300A, though Ives gives a value of about 1 percent at this point. The film in this case was evidently partially transparent and considerable reflection from the glass is evident. The oblique shadows are interference minima similar to those reproduced in the earlier paper.

From an inspection of all of our plates, and consideration of the reflection from the glass and the absorption of the gelatine and the oil film, we assigned the following values as the limits of reflection:

Li	Na	K	Rb	Cs
1550A	2100A	3150A	3400A	3800A

The limit cannot, however, be sharply defined as shown by the curves obtained by Ives, published in recent numbers of the *Journal of the Optical Society of America*, and the spectra reproduced would be very misleading in the absence of other data. They show, however, the complete absence (less than 1 percent) of reflection in the region of shorter wave-lengths as far down as 500A which was the limit of the spectrum of our discharge tube. To reach shorter wave-lengths it would have been necessary to employ a "capacity" many times greater than the one at our disposal. This would have given a higher temperature, and a consequent extension of the spectrum with a greatly reduced time of exposure. We made an attempt to secure this result with a vacuum spark, but the products of the discharge ruined the mirrors by corrosion in a few minutes.

An investigation is planned in which the simultaneous reflection and transmission spectra of a film will be photographed in coincidence from which the true absorption at various points of the spectrum can be computed.

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[5] Herbert E. Ives, J. Opt. Soc. Am. **27**, 397 (1937).

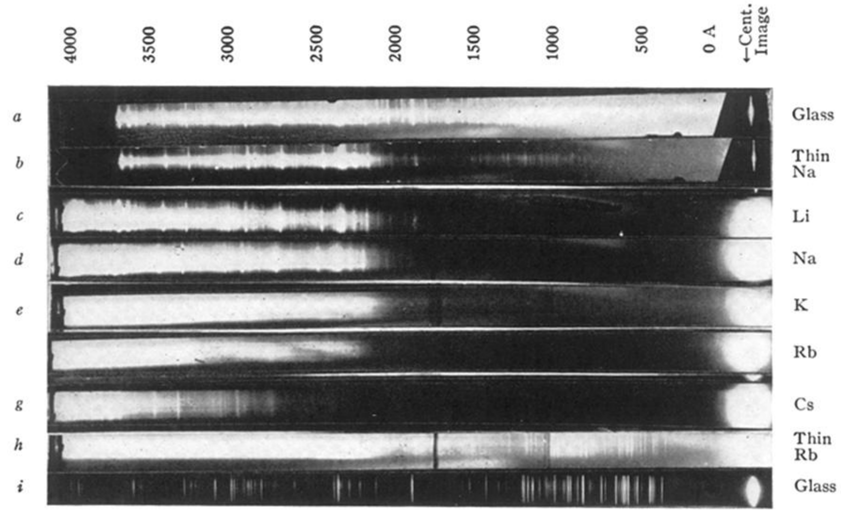

FIG. 5. Reflection spectra from various mirrors.