

For instance,

$$P^0 + P_2^1 + P_{22}^2 + P_3^1 + P_{32}^2 + P_4^1 + P_5^1 = 1,$$

when n is 5 and $N \geq 5$.

The values of $N!$, etc., in the expression for P^0 may be obtained by using Stirling's formula. If n is small, however, it is easy to compute P^0 directly with the aid of either logarithms or an electrical computing machine.

Table II gives some numerical results on probabilities for one value of N and three values of n .

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The Photoconductivity of Sodium Chloride in the Far Ultraviolet

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Measurements have been made on the wave-length dependence of the photoconductivity of an uncolored sodium chloride crystal in the far ultraviolet region of 900 to 1350 angstroms in order to test the theories of Peierls, Frenkel, and Mott regarding the existence of discrete energy levels, called exciton levels, lying just below the conduction bands. A region was found between 1300 and 1350 angstroms in which there was large absorption but very small if any photoconductivity or external photoelectric effect indicating the existence of exciton states. At wave-lengths shorter than 1300 angstroms both the photoconductivity and the photoelectric effect began to set in and these showed a doublet structure. The photoconductivity rises abruptly at the second absorption peak in the absorption spectrum and shows structure which locates energy levels above the ground state. The experiments of Podubnij on the iodides are a contradiction to this experiment inasmuch as the alkali halides should reasonably be expected to behave similarly.

INTRODUCTION

PEIERLS,¹ Frenkel,² and Mott³ have introduced the concept of non-photoconductive absorption in crystalline insulators because of the possible existence of discrete energy levels lying just below the conduction bands. The withdrawal of an electron by light of quantum energy corresponding to the distance AB , Fig. 1, leaves a hole in the filled band below A . This electron, termed an "exciton" by Frenkel, is then thought to be in the electric field of its positive hole, giving rise to discrete energy levels. Absorption of light of quantum energy corresponding to the distance AE would be a photoconductive absorption. A test for the existence of these exciton states would be to compare the dependence of photoconduct-

tivity and absorption on wave-length for an alkali halide crystal. Experimental data on the photoconductivity of pure alkali halides are very meager. To the author's knowledge the only previous work is by Podubnij⁴ in which potassium and sodium iodide were illuminated over a wave-length range of 2500 to 1900 angstroms. The data showed photoconductive currents which depend in the same way on wave-length as does the absorption, and Podubnij concluded that all the absorbed energy is used to produce photoconductivity. There is no evidence that any care was taken to separate the primary photoconductive currents from secondary currents which Gudden and Pohl⁵ have shown must be done in order to obtain interpretable results.

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¹ R. Peierls, *Ann. d. Physik* **13**, 905 (1932).

² J. Frenkel, *Physik. Zeits. Sowjetunion* **9**, 158 (1936).

³ N. F. Mott, *Trans. Faraday Soc.* **34**, 500 (1938).

⁴ Podubnij, *J. Exper. and Theo. Phys.* **8**, 410 (1939).

⁵ Hughes and DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1931), p. 291.

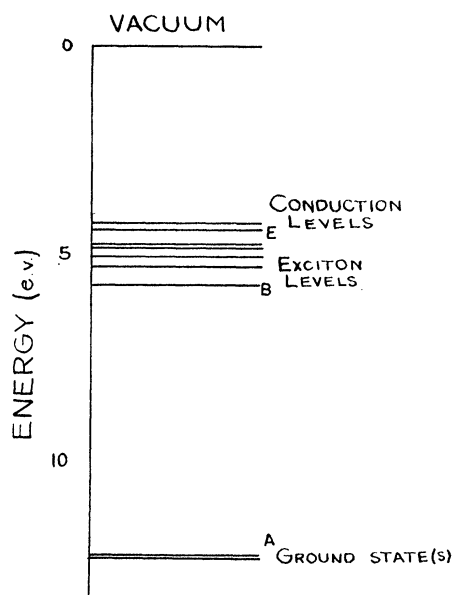


FIG. 1. Energy level scheme.

In view of the meager information about the photoconductivity of pure alkali halides, in addition to the desirability of obtaining evidence to confirm the existence of the exciton states introduced by Peierls, Frenkel, and Mott, it was considered worth while to attempt measurements of the photoconductivity of an easily produced and easily handled salt such as sodium chloride.

APPARATUS AND EXPERIMENTAL PROCEDURE

Illumination of the crystal was accomplished by mounting the crystal, as shown in Fig. 2, in a

vacuum ultraviolet normal incidence spectrograph. The grating could be rotated to give various wave-lengths on the crystal. The source of illumination was a capillary air discharge tube. An electrically controlled shutter was placed at *F* between the exit slit and the grating so that the crystal could be illuminated for short fixed periods of time.

In order to measure relative intensities of the spectral lines used, a windowless silver cathode photoelectric cell was placed at *E* on the side of the crystal holder away from the grating. The crystal could be moved into or out of the beam from outside the vacuum.

The electric circuit for measuring the quantity of charge released by light flashes and for measurements of currents in the photoelectric cell was the Barth type electrometer tube circuit whose sensitivity was 310,000 millimeters per volt drop across the input resistor.

Thin single crystals of sodium chloride were produced by cleaving artificial crystals of high purity.⁶ In order to decrease the possibility of surface conduction being measured as volume conductivity, the electrodes were behind the crystal and the crystal was mounted between them and the exit slit of the spectrograph. The technique developed by Gudden and Pohl⁷ for elimination of secondary effects of polarization and decrease of resistance owing to release of electrons in the crystal was followed. This consisted

⁶ Harshaw Chemical Company, Cleveland, Ohio.
⁷ Hughes and DuBridge, reference 5, p. 289.

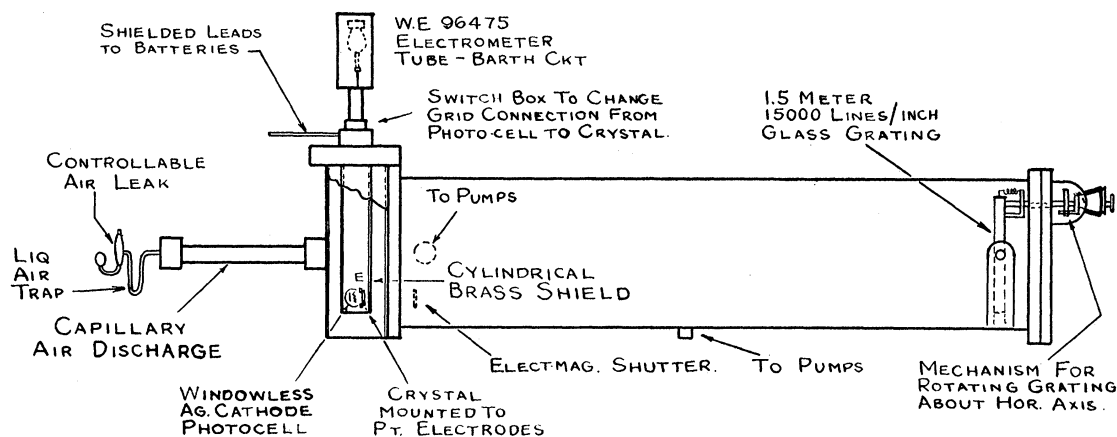


FIG. 2. Schematic diagram of apparatus.

in measuring all crystal photo-effects ballistically with low light intensity flashes and with a fairly low applied electrical field intensity in the crystal. The procedure was to set a spectral line on the slits by observing the photo-cell currents with the crystal out of the beam. After the intensity was observed to be steady within ten or fifteen percent, and it was usually much steadier than this, the shutter was closed; the crystal slid into position; and the electrometer tube grid connected to the crystal. The shutter was then opened for a fixed period of about one second by a timing device. The ballistic reading thus obtained was found to be made up of both external photoelectric currents as well as photoconductivity currents. These were separated in the following manner: The reading just described was made with a retarding potential, small compared to the potential drop across the crystal, between the

effect of the crystal i_e , plus the photoconductivity i_c . To obtain measurement of the photoelectric effect alone, a small potential was applied across the crystal in a direction opposite to the large potential in the above measurement. This small potential was to insure that photoconductivity would not contribute appreciably to the current. A large accelerating potential was next applied, and a ballistic reading was made as before. This is the current i_e . Saturation of the current thus measured with accelerating voltage indicated that most of the photoelectrons were being measured. No measurable deflections were obtained at any wave-length if the crystal were removed from the crystal holder and normal operating conditions established.

Sources of error in this experiment are the following: (1) Unsteadiness of the light source. The light source gave two sources of unsteadiness: one owing to the nature of the method of excitation of the discharge; the other to non-uniform rate of leak of air into the tube. The discharge was remarkably steady, however, and the photoelectric cell showed that over a period of half an hour the average intensity taken over the period of the galvanometer system never varied by more than 25 percent and was usually 10 percent or less. (2) Non-monochromatism of the light flashed on the crystal. This was owing to three causes: first was the necessity of a broad slit width of approximately 0.5 mm in order to furnish enough light to get substantial galvanometer deflections. The second was the scattering of light into the slit. This was of course minimized in the customary ways by baffles and black walls. The third cause was the presence of overlapping orders of the spectrum. It is thought that the second-order intensity is small compared to the first-order intensity. Some evidence of this is that the photo-cell showed less than one-third as much current for the line 1085A in the second order as it did in the first order. (3) Unsteadiness of the electrometer tube. The proximity of a discharge tube to the electrometer tube brought about magnetic and electrical pick-up. These were so minimized that during the final runs reported here the tube was steady enough that readings could be made to plus or minus half-centimeter deflection. This was in general never greater than ten percent of the deflection.

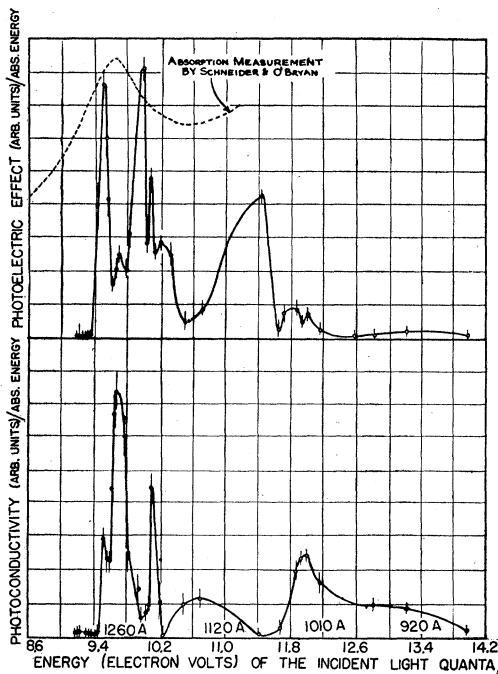


FIG. 3. Plot of photoconductivity current and photoelectric effect current in arbitrary units per unit absorbed energy as a function of the energy in electron volts of the incident light quanta.

brass shield, Fig. 2, and the crystal electrodes. The value of this potential was adjusted so as to be sure that all photoelectrons ejected from the crystal were collected by the positive crystal electrode. The reading i_a is the photoelectric

RESULTS AND DISCUSSION

Overlapping data taken on separate days are plotted in Figs. 3 and 4. The photoconductivity current i_c was obtained from the data by the relation

$$i_a = i_e + i_c.$$

Assuming that the yield of the photoelectric cell, i.e., the number of electrons released per unit incident energy, is a slowly varying function over the spectral region studied, one can take the photoelectric cell reading i_p to be proportional to the intensity of the light and compare intensities at different wave-lengths. This assumption was made and the yields in arbitrary electrical units per unit absorbed light energy were calculated, the crystal photoelectric effect yield being i_e/i_p , and the photoconductivity yield being i_c/i_p . It is noticed in Figs. 3 and 4 that there is a region of large absorption in which there is no measurable photoconductivity or photoelectric effect (even though the photo-cell showed considerable light intensity in this region), but that these both set in sharply and almost at the same wave-length. These facts are in agreement with the exciton theory; the absorbed energy in the region in which we have neither photoconductivity nor external photoelectric effect is used in the formation of excitons. Curves for both the photoconductivity and photoelectric effect show doublet structure. Since the ground state of chlorine is a doublet of separation 0.11 electron volt, the first four peaks in the photoconductivity curve can be accounted for by assuming two narrow unfilled energy bands at 9.53 ± 0.02 and 10.06 ± 0.02 electron volts above the higher of the doublet ground states. The other peaks and region of continuum are explained by locating a band beginning at about 10.5 electron volts and another at about 11.6 electron volts above the higher of the ground state levels. Since the data were taken

at larger energy intervals in the shorter wave-length regions, location of the latter two levels is approximate and there may be other levels as well. In comparing the two curves of photoelectric effect *versus* energy of the incident light quanta

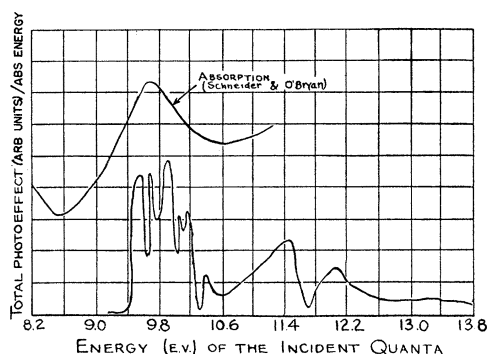


FIG. 4. The total photoelectric effect in arbitrary units per unit absorbed light energy as a function of the energy of the incident light quantum.

and photoconductivity *versus* the energy of the incident light quanta, it is noticed that peaks in the former curve occur where troughs of the latter curve occur, and vice versa. This would be expected if one realizes that any electron, given energy equal to or more than a certain minimum amount, can be ejected from the crystal as a photoelectron and is so ejected unless the value of the energy given is the correct amount to place the electron in a photoconductivity band. In that case the electron is a photoconductivity electron which moves through the crystal in the general direction of the field and the photoelectric current is small for the corresponding wave-length.

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